PHOTOCATALYTIC OXIDATION

OF

BIORECALCITRANT COMPOUND AND ITS OPTIMIZATION

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Submitted
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DECLARATION CUM CERTIFICATE

I hereby declare that the work embodied in thesis entitled, "**Photocatalytic Oxidation of Biorecalcitrant Compound and its Optimization**", is an original piece of work and was conducted in the Department of Biotechnology and Environmental Sciences, Thapar University, Patiala. 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

The presence of highly biorecalcitrant organic contaminants in the environment due to industrial sector is of prime 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), a group of chemical reactions characterized by the "in situ" production of OH radicals under mild experimental conditions, have shown to rapidly degrade many different biorecalcitrant compounds. 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, Acrylonitrile (ACN), which has been listed third in the priority pollutants list of EPA, was chosen as the model compound. ACN is an important industrial raw material frequently used in the manufacture of acrylic and modacrylic fibres, resins and rubber and as a chemical intermediate. The photocatalytic degradation of ACN (50 mg/L) was carried out in slurry mode in the specially designed photoreactor equipped with UV tubes at constant temperature. The rate of degradation has been examined in terms of change in the absorbance at λ_{max} of 204 nm. The effect of varying various photocatalytic process parameters such as catalyst dose, pH, UV intensity, area to volume ratio, oxidant concentration, light source (UV/solar) and mixed catalyst has been investigated. 78.9% and 71.1% degradation efficiency was achieved in 30 min under UV light employing ZnO and TiO_2 under optimized conditions (1.5 g/L ZnO; pH 8.0; 5mM/L H_2O_2 and 1.5 g/L TiO_2; pH 4.0; 5mM/L NaOCl), respectively. The results demonstrated that ZnO exhibited better photocatalytic activity as compared to TiO_2 for the degradation of ACN. Experiments were also conducted in solar light under optimized conditions which showed 82% and 78.4% degradation efficiency after 30 min with ZnO and TiO_2, respectively. The results depicted that heterogeneous photocatalysis could be used as an efficient and eco-friendly technique for the complete degradation of biorecalcitrant organic compounds. 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 ACN with ZnO (50 mg/L). The variables examined in this study included ZnO dose, pH and H_2O_2 concentration. The significant variables and optimum conditions were identified (ZnO dose 1.48 g/L, pH 7.0 and H_2O_2 concentration of 4.22 mM/L) from statistical analysis of the experimental results using response surface methodology (RSM). 89.6% degradation efficiency was achieved under these conditions which was in agreement with the predicted value. The results depicted that heterogenous photocatalysis employing solar light can be efficiently and cost effectively used for the degradation of ACN.

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CHAPTER 1

INTRODUCTION

1.0 Background

Nowadays, 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 are xenobiotic chemicals of natural or anthropogenic origin which are accumulated in the environment and biota, due to their highly refractory chemical structures and physico-chemical properties. Structurally they are polycyclic conjugated compounds (polycyclic aromatic hydrocarbons) or they have a high number of halogen atoms, especially chlorine or bromine, pesticides, polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), brominated flame retardants, etc. Because most POPs are semi-volatile they suffer long range transportation and can be found anywhere, even in distant regions where they have never been produced or released. 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)*. Many of these compounds are biologically active possessing mutagenic or carcinogenic or even endocrine disruption properties. Although several of them have natural sources, the fast industrial development since the late nineteenth century led to an enormous increase either in the quantity or in the diversity of the persistent organic pollutants from anthropogenic origin present in the environment. Conjugation of their above mentioned characteristics determines that these compounds represent a high risk to public and environmental health.

Several of those substances have already been classified as prioritary substances for environmental monitoring. Dibenzodioxins, dibenzofurans, polychlorinated biphenyls and organochlorinated 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)*. The Stockholm Convention regulates this matter worldwide. This Convention presents a list of POPs (originally 12 substances: aldrin, dieldrin, endrin, chlordane, PCDDs, PCDFs, BHC, DDT, heptachlor, mirex, PCBs, toxaphene). Nowadays there are other under consideration: HCH, chlordecone, hexabromobiphenyl, hexa and heptabromobiphenyl ether, pentachlorobenzene tetra and pentabromodiphenyl ether e perfluorooctanosulfonic acid and its salts) whose production, use and trading are banned or

severely restricted *(UNEP, 2005; SCPOP, 2005; Oliveira et. al., 2008)*. There are many other synthetic substances that have been identified as priority pollutants for environmental monitoring by the United States Environmental Protection Agency (USEPA) based on their probable or confirmed carcinogenic, mutagenic, teratogenic or acute toxicity characteristics. POPs can be further classified as volatile organic compounds, agricultural fertilizers and chlorinated residues resulting from disinfection processes at water public supply systems. Many of those substances can either be found in the air (as in the case of the volatile organic compounds) or in surface/ groundwater and they reach the reception media through domestic or industrial wastewater systems or due to drain-off from agriculture. EPA classifies Acrylonitrile (ACN) as a priority pollutant, a toxic air as well as water pollutant, and a volatile organic compound. ACN is a colorless, flammable liquid with a garlic type odour and is considered to be extremely hazardous. It is reasonably anticipated to be a human carcinogen based on sufficient evidence of carcinogenicity in experimental animals. It may enter into environment accidentally, during its storage and transport but the highest potential for exposure is at the work place where acrylonitrile is dealt with. It is found in the wastewater mainly because of industrial activities. There are also several substances (i.e. dyes, pharmaceuticals, etc.) which have been especially synthesized to be resistant to degradation and conventional wastewater treatment processes are inefficient in their treatment *(Eckenfelder, 2000)*. Although these substances are not classified as prioritary pollutants, their negative impact on aquatic life and the changes of physical-chemical characteristics of the water bodies even when present in low concentrations make the control of their concentration very important.

Since the use and discharge of bioactive organic substances in the different environmental segments is not easy to eliminate and appears extremely difficult to control, it is essential to develop new powerful, clean and safe environmental remediation technologies for their treatment especially for the biorecalcitrant organic pollutants. One of the most promising technologies available uses hydroxyl radical, a highly reactive chemical species that can attack and destroy organic molecules and is denominated as advanced oxidation processes *(Eckenfelder, 2000; Metcalf & Eddy, 2003)*.

1.1 Advanced Oxidation Processes

Advanced oxidation processes (AOPs) is the common name for several chemical oxidation methods used to remediate substances that are highly resistant to the biological degradation. Although oxidation can be complete, frequently a partial oxidation is sufficient to decrease the toxicity of the biorecalcitrant compound enabling their final treatment by conventional biological treatment. The complete oxidation leads to mineralization and yields CO_2, H_2O and inorganic ions. The partial oxidation can be enough to decrease toxicity enabling biological degradation, but is essential to verify if the intermediary products formed are not more toxic than the parent compound under treatment. AOPs can remediate all different types of organic pollutants in liquid, gaseous or solid media, that is why they are used for the remediation of contaminated waters, liquid or gaseous effluents and also for the treatment of different hazardous wastes namely on contaminated soils *(Legrini et. al., 1993; Blake et. al., 2001).*

1.1.1 Theory of advanced oxidation

Although different advanced oxidation processes use several different reaction systems, all of them have the same chemical characteristic: i.e., the production and use of hydroxyl radicals (OH•). Hydroxyl radicals are highly reactive species 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. Table 1.1 shows oxidation potential of the hydroxyl radical and compares it with other common oxidants used in the chemical oxidation *(Fox et. al., 1993).*

Table 1.1 Oxidation potential of most common oxidizing agents

Oxidizing agent	Oxidation potential ,Volt
Flourine	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

Hydroxyl radical is the most powerful oxidant after fluorine; it is able to initiate several oxidation reactions leading to complete mineralization of the original organic substances and their subsequent degradation products. Hydroxyl radical reacts with all classes of organics mainly by hydrogen abstraction:

$$OH\bullet + RH \rightarrow R\bullet + H_2O \quad (1)$$

Hydrogen abstraction produces organic radicals which are able to react with molecular oxygen and originating peroxyl radicals.

$$R\bullet + O_2 \rightarrow R\,O\bullet_2 \rightarrow \quad (2)$$

Electrophilic additions may also occur *(Legrini et. al., 1993)*

$$OH\bullet + PhX \rightarrow HOPhX\bullet \quad (3)$$

Electron transfer reactions,

$$OH\bullet + RX \rightarrow RX\bullet^{+} + OH^{-} \quad (4)$$

and reactions between hydroxyl radicals,

$$2\ OH\bullet \rightarrow H_2O_2 \quad (5)$$

Hydroxyl radical is characterized by a non-selective attack; this is an extremely useful characteristic for an oxidant to be used for environmental remediation and all reactions occur at normal temperature and pressure. AOPs advantageously promote complete degradation of pollutants being remediated while classical treatments usually only transfer target pollutants to another phase, leading to the production of secondary residues (slugs) that require further treatment or deposition. Therefore, the advanced oxidation process is a good method for environmental decontamination *(Linsebigler et. al., 1995).*

AOPs versatility is also favoured by the existence of various pathways to produce hydroxyl radicals, which enables a high adaptability 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. AOPs are categorized as Homogeneous and Heterogeneous, latter being more efficient in the degradation of POPs.

1.2 Homogeneous Photocatalysis

Treatment of contaminated waters by the application of homogeneous photocatalysis (single-phase system) dates back to the early 1970s. The first applications involved the use of UV/ozone and UV/H_2O_2. The use of UV light for photodegradation of pollutants can be classified into two principal areas:

- **Photo-oxidation**- Light-driven oxidative processes principally initiated by hydroxyl radicals.
- **Direct photocatalysis**- Light-driven processes where degradation proceeds following direct excitation of the pollutant by UV light.

Photooxidation concerns the use of UV light plus an oxidant to generate radicals. The hydroxyl radicals then attack the organic pollutants to initiate oxidation. Three major oxidants used are hydrogen peroxide, ozone and Photo-Fenton reaction.

1.3 Heterogeneous Photocatalysis

Photocatalysis is the combination of photochemistry and catalysis, a process where light and catalysis are simultaneously used to promote or accelerate a chemical reaction. So, photocatalysis can be defined as "catalysis driven acceleration of a light induced reaction". Direct light absorption is one of the biggest advantages of photocatalysis as compared to thermally activated catalytic processes.

Nowadays, photocatalysis appears as an excellent tool for final treatment of samples containing persistent organic pollutants (POPs) as compared to classical treatments *(Doll et. al., 2005; Hincapié et. al., 2005)*. In the near future, it may turn into one of the most used technologies for POPs remediation.

1.3.1 Mechanism of Photocatalysis

When Ultraviolet (UV) radiations from sunlight or illuminated light source (fluorescent lamps) are absorbed by photocatalyst, it will produce pairs of electrons and holes. The electron of the valence band of titanium dioxide gets excited when illuminated by UV light. The excess energy of this excited electron promotes the electron to the conduction band of titanium dioxide therefore creating the negative-electron (e^-) and positive-hole (h^+) pair. This stage is known as the '**photo-excitation'** state of the semiconductor. The energy difference between the valence band and the conduction band is known as the '**Band Gap'**. Wavelength of the light necessary for photo-excitation is: 1240 (Planck's constant, *h)* / 3.2 eV (band gap energy) = 388 m.

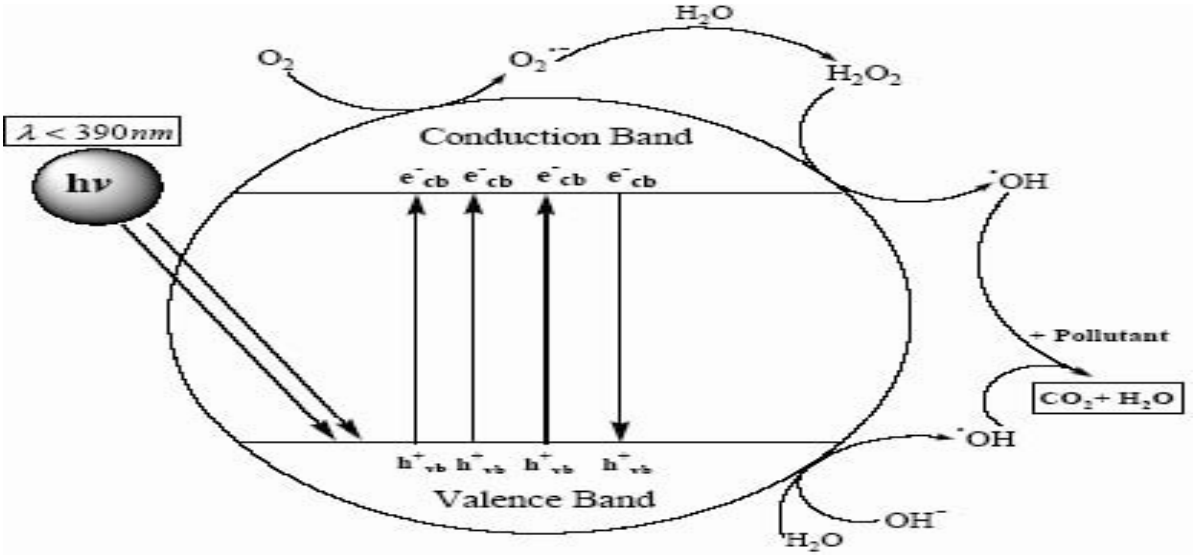


Fig 1.1 Mechanism of Photocatalysis

The positive-hole of Titanium dioxide breaks apart the water molecule which leads to the formation of hydrogen gas and hydroxyl radical. The negative-electron reacts with oxygen molecule to form super oxide anion. This cycle continues till light is available. It is a process in which the initial absorption of photons by a semiconductor, leads to the formation of electrons and holes. The band structure of the electronic energy levels of the semiconductor consists of the highest occupied band, called the valence band and the lowest unoccupied band called the conduction band separated by band gap energy (Ebg). The band gap energy falls in the UV-Visible region of the electromagnetic spectrum. Hence activation of the semiconductor surface (SC) with UV or Visible radiation results in the promotion of the valence band electron to the conduction band, generating electron(e^-) / hole (h^+) pairs.

$$SC \longrightarrow e^- + h^+ \quad (1)$$

In aerated aqueous suspensions of the semiconductor in contact with organic substances, the photogenarated e^-/h^+ pairs initiate a series of redox reactions via a number of mechanisms which include:

1) Oxidation of adsorbed water molecules and hydroxyl ions by photo generated holes to give hydroxyl radicals

$$h^+ + OH^- \longrightarrow OH \quad (2)$$

$$h^+ + H_2O \longrightarrow OH^\bullet + H^+ \quad (3)$$

2) Reduction of dissolved oxygen by the photo generated electrons to produce super oxide anions radicals, which in turn, can lead to generation of H_2O_2 through a series of redox reactions

$$O_2 + e^- \longrightarrow O_2^- \quad (4)$$

$$O_2^- + H^+ \longrightarrow HO_2^\bullet \quad (5)$$

$$HO_2^\bullet + HO_2^\bullet \longrightarrow H_2O_2 + O_2 \quad (6)$$

$$^\bullet O_2^- + HO_2^\bullet \longrightarrow HO_2^- + O_2 \quad (7)$$

$$HO_2^- + H^+ \longrightarrow H_2O_2 \quad (8)$$

The photo generated hydrogen peroxide undergoes further decomposition to yield hydroxyl radicals

$$H_2O_2 + O_2^{\cdot -} \longrightarrow >OH^\cdot + OH^{\cdot -} + O_2 \quad (9)$$

$$H_2O_2 + e^- \longrightarrow >OH^\cdot + OH^- \quad (10)$$

3) Direct participation of the holes and electrons in oxidation / reduction reactions.

4) Formation of singlet oxygen, which can participate in oxidation reaction.

The primary oxidants, viz., hydroxyl radicals, super oxide anion radicals and H_2O_2 are strong, non selective oxidants, capable of initiating a series of oxidative degradation reaction of adsorbed organic molecules. Oxidation of organic compounds proceeds through a number of free radical reactions, producing a large number of intermediates, which in turn, undergo oxidative cleavage, ultimately resulting in the formation of carbon dioxide, water and inorganic ions.

1.3.2 Photocatalysts

A wide range of semiconductors may be used for photocatalysis, such as TiO_2, ZnO, MgO, WO_3, Fe_2O_3, CdS. The ideal photocatalyst should possess the following properties:

- photoactivity
- biological and chemical inertness
- stability towards photocorrosion
- suitability towards visible or near UV light,
- low cost
- lack of toxicity

TiO_2 is known to have excellent pigmentary properties, high ultraviolet absorption and high stability which allow it to be used in different applications, such as electroceramics, glass and in the photocatalytic degradation of contaminants in water and air. It has been used in the form of a suspension, or a thin film in water treatment and correspondingly termed as suspended or immobilized mode. Titanium dioxide has different crystalline forms. The most common forms are anatase and rutile. The third crystalline form is brookite, which is uncommon and unstable. Anatase is the most stable form by 8-12 KJ mol^{-1} and can be converted to rutile by heating to temperatures ~ 700 ºC. The density of rutile is greater (4.26 g/ml) than anatase (3.9 g/ml). In the photocatalysis applications, it is known that, anatase is having better photocatalytic activity than rutile.

Degussa P25, is commercially available, consists of two forms of TiO_2 (closely approximating to 25% rutile, 75% anatase) and has been used in many studies of photocatalytic degradation. Studies employing P25, have been widely reported because of its chemical stability,

ready availability, reproducibility, and activity as a catalyst for oxidation processes. It has also been suggested as a standard for such studies.

ZnO is a semiconductor with wide band gap (3.3 eV), large exciton bindig energy (60 MeV), abundant in nature, natural n-type conductivity and is environmental friendly. ZnO offer low cost, mild reaction conditions, high photochemical reactivity, while affording the use of sunlight. ZnO can absorb UV light with the wavelength equal to or less than 385 nm. The other photocatalysts like CdS is an important n- type semiconductor with band gap of 2.42 eV. It has abroad application prospects in the photocatalytic degradation due to its small particle diameter, large surface area, small band gap and response to visible light.

1.4 Applications of Photocatalysis

Since 1972, when Fujishima and Honda discovered the photocatalytic splitting of water using TiO_2 electrodes; research on the heterogeneous photocatalysis started growing rapidly *(Linsebigler. et. al., 1995)*. The research work focused on energy storage, and in recent years applications have been directed towards environmental clean-up. Later, other applications of this technique have been implemented in many fields such as, drinking water treatment, industrial, and health applications.

1.4.1 Removing trace metals

Trace metals such as mercury (Hg), chromium (Cr), lead (Pb) and others metals are considered to be highly health hazardous. Thus, removing these toxic metals is essentially important for human health and water quality. The environmental applications of heterogeneous photocatalysis include removing heavy metals such as mercury (Hg), chromium (Cr), lead (Pb), cadmium (Cd), arsenic (As), nickel (Ni), copper (Cu) etc. *(Blake et. al., 2001; Ollis et. al., 1991)*. The photoreducing ability of photocatalysis has been used to recover expensive metals from industrial effluent, such as gold, platinum and silver *(Ollis et. al., 1991)*.

1.4.2 Destruction of organics

Photocatalysis has been used for the destruction of organic compounds such as alcohols, carboxylic acids, phenolic derivatives, or chlorinated aromatics, into harmless products e.g., carbon dioxide, water, and simple mineral acids *(Bhatkhande et. al., 2001)*. Water contaminated by oil can be treated efficiently by photocatalytic reaction *(Joanna et. al., 2001)*. Herbicides and

pesticides that may contaminate water such as 2,4,5-trichlorophenoxyacetic acid, 2,4,5-trichlorophenol, s-triazine herbicides and DDT can be also mineralized.

1.4.3 Removing inorganic compounds

In addition to organic compounds, wide ranges of inorganic compounds are sensitive to photochemical transformation on the catalyst surfaces. Inorganic species such as bromate, or chlorate *(Mills et. al., 1996)*, azide, halide ions, nitric oxide, palladium and rhodium species, and sulfur species can be decomposed *(Michael et. al., 1995)*. Metal salts such as $AgNO_3$, HgCl and organometalic compound (e.g CH_3HgCl) can be removed from water, as well as cyanide, thiocyanate, ammonia, nitrates and nitrites.

1.4.4 Water disinfections

Photocatalysis can also be used to destroy bacteria and viruses. *Streptococcus mutans, Streptococcus natuss, Streptococcus cricetus, Escherichia coli, scaccharomyces cerevisisas, Lactobacillus acidophilus,* poliovirus 1 were destructed effectively using heterogeneous photocatalysis *(Mills et. al., 1997)*. The increasing incidence of algal blooms in fresh water supplies and the consequent possibility of cyanobacterial microcystin contamination of potable water *Microcystin toxins* is also degraded on immobilized Titanium dioxide catalyst *(Shephard et. al., 2002)*. Photodisinfection sensitized by TiO_2 had some effect on the degradation of *Chlorella vulgaris* (Green algae), which has a thick cell wall.

1.4.5 Seawater treatment

Humic substances (HS) were decomposed in highly saline water (artificial seawater) and natural seawater using different photocatalytic materials *(Al-Rasheed et. al., 2003)*. The decomposition rate of HS in seawater was slow compared with pure water media. No toxic by-products were detected during the decomposition.

1.5 Response surface methodology

Response surface methodology is a collection of statistical and mathematical methods that are useful for the modelling and analyzing engineering problems. In this technique, the main objective is to optimize the response surface that is influenced by various process parameters.

Response surface methodology also quantifies the relationship between the controllable input parameters and the obtained response surfaces.

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:

$$y = f(x_1, x_2, \ldots x_k) \quad (1)$$

The goal is to optimize the response variable *y*. 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. Usually a second-order model is utilized in response surface methodology.

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k} \beta_{ij} x_i x_j + € \quad (2)$$

where € is a random error. The β coefficients, which should be determined in the second-order model, are obtained by the least square method. In general (2) can be written in matrix form.

$$\mathbf{Y = bX + E} \quad (3)$$

where **Y** is defined to be a matrix of measured values, **X** to be a matrix of independent variables. The matrixes **b** and **E** consist of coefficients and errors, respectively. The solution of (3) can be obtained by the matrix approach.

$$\mathbf{b= (X^TX)^{-1}X^TY} \quad (4)$$

where $\mathbf{X^T}$ is the transpose of the matrix **X** and $\mathbf{(X^TX)^{-1}}$ is the inverse of the matrix $\mathbf{X^TX}$.

The mathematical models were evaluated for each response by means of multiple linear regression analysis. As said previous, modelling 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 achieved 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.

1.6 Acrylonitrile

Acrylonitrile is a colorless to pale yellow liquid with an unpleasant odor that is considered to be an important industrial chemical. It is soluble in water and most common organic solvents such as acetone, benzene, carbon tetrachloride, ethyl acetate, and toluene. It is produced commercially by the process of propylene ammoxidation, in which propylene, ammonia and air are reacted in a fluidized bed in the presence of a catalyst. It is used in the

production of acrylic and modacrylic fibers, resins and rubbers, and as a chemical intermediate. It is also used in fumigants. It has been listed third in the EPA list of 129 priority pollutants. It may reasonably be anticipated to be a carcinogen, according to the Sixth Annual Report on Carcinogens, published by the National Toxicology Program of the U.S. Department of Health and Human Services. It is also classified by the U.S. Environmental Protection Agency as a carcinogen in the national Toxic Release Inventory (TRI). It is a flammable liquid, and its vapors can easily form explosive mixtures in air, so it must be stored in tightly closed containers in a cool, well-ventilated area, away from heat, sparks, flames, strong oxidizers (especially bromine), strong bases, copper, copper alloys, ammonia, and amines.

1.6.1 Routes of environmental exposure

Acrylonitrile apparently does not occur naturally. Sources of release of acrylonitrile to the environment include fugitive emissions from facility producing and using the chemical in the manufacture of acrylic and modacrylic fibers, ABS and SAN resins, adiponitrile, acrylamide, and other resins and chemicals. Small amounts of acrylonitrile have been detected in cigarette smoke and auto exhaust. It may also be released from polyacrylic fibers and plastics. During the production of acrylonitrile, the following wastes are produced: gaseous wastes; liquid wastes (wastewater column bottoms, acetonitrile column bottoms, heavy ends, crude acetonitrile, hydrogen cyanide); and solid wastes (catalyst fines and organic polymers). Three types of on-site disposal methods have been described: (a) flare; (b) thermal incineration; and (c) deep-well pond and deep-well injection. Acrylonitrile may be released accidentally into the environment. Acrylonitrile is also present in effluent discharged from chemical and latex manufacturing plants.

Effect of release to water

Acrylonitrile is lighter than water so it will initially form a light surface sheen if spilled into water. Due to its moderately high solubility, it gets quickly dissolved into the water column. Acrylonitrile is considered moderately toxic to aquatic organisms, freshwater and marine fish. Acrylonitrile will not persist in receiving waters for more than a few weeks. In addition to volatilizing, it slowly biodegrades in both fresh and salt water. Biodegradation products include ammonia and carbon dioxide. Acrylonitrile can also hydrolyze slowly in water. Hydrolysis products include acrylamide and acrylic acid.

Effect of release to air

Acrylonitrile is highly volatile, so volatilizes quickly from spill surfaces, soils and water into the atmosphere creating potential inhalation concerns in the immediate spill area. Vapors are heavier than air so they accumulate in low spots and in confined areas creating exposure, fire and explosion hazard. Vapors are very irritating to the eyes and can cause toxic and lethal effects via inhalation or skin absorption.

Health effects

The primary routes of potential human exposure to acrylonitrile are inhalation and dermal contact; it can also expose humans through ingestion or skin absorption. Exposure can cause asphyxia, eye irritation, headaches, sneezing, nausea, vomiting, weakness, lightheadedness, skin vesiculation, and scaling dermatitis. The primary organs affected by acrylonitrile are the central nervous system, peripheral nervous system, skin, and eyes.

1.7 Objectives of the present study

The study was undertaken with the following objectives:

- Photocatalytic degradation of the model compound Acrylonitrile (ACN), a persistent non-biodegradable pollutant.
- Investigation of the effect of operating parameters such as catalyst dose, pH, UV intensity, area to volume ratio of the reaction vessel, concentration of oxidants (hydrogen peroxide & sodium hypochlorite), light source (UV/solar) and mixed catalyst on the degradation efficiency of ACN.
- Optimization of the photocatalytic process parameters by applying Box Behnken design using response surface methodology (RSM).

CHAPTER 2

REVIEW OF LITERATURE

2.0 Overview

As recalcitrant organic pollutants continue to increase 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. Ultimately, research activities centered on advanced oxidation processes (AOPs) for the destruction of synthetic organic species resistant to conventional treatment methods. AOPs rely on in situ generation of highly reactive radical species, mainly HO^{*} by using solar, chemical or other forms of energy *(Kudo et. al., 2003; Bahnemann, 2004)*. 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 *(Guillard et. al., 1999)*. Heterogeneous photocatalysis involves the acceleration of photoreaction in presence of semiconductor photocatalyst. Response surface methodology is a widely used technique for modelling 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 biorecalcitrant organic pollutants and optimization of the process parameters by Response surface methodology.

2.1 Photocatalytic treatment of persistent organic pollutants (POPs)

2.1.1 Textile Dyes

Balcioglu et al., 2001 carried out the treatment of two commercial reactive dyes, the azo dye Reactive Black 5 and the copper phythaocyanine dye Reactive Blue 21 by Titanium dioxide mediated photocatalytic (TiO_2/UV), dark and UV light assisted Fenton (Fe_2^{+}/H_2O_2) and Fenton-like (Fe^{3+}/H_2O_2) processes in acidic medium. It was found that both the heterogeneous and homogeneous AOPs were capable of completely decolourizing the azo dye Reactive Black 5 after the treatment of 2 h.

Titanium dioxide (TiO_2) was used as a photocatalyst for the detoxification of water containing methyl orange (MO), which was used as a model compound. Solar radiation was used as an irradiation source. It was found that there was no degradation for the MO in the dark and in the presence of TiO_2. Also no degradation was observed for MO when the solution was placed under solar radiation but without TiO_2 (*Al-Qaradawi et. al., 2002).*

Sakhtivel et. al., 2003 investigated the photocatalytic activity of commercial ZnO powder and compared with that of Degussa P25 TiO_2 using acid brown 14 as the model pollutant. Solar light was used for the photocatalytic experiments and it was found that the highest values of photodegradation were observed for ZnO.

Liu et. al., 2006 investigated the photocatalytic decomposition of a synthetic dye, C. I. Acid Yellow 17 using TiO_2 photocatalyst. The factors affecting the dye wastewater treatment in terms of dye removal ratio, color removal ratio, and mineralization ratio: pH value of the solution, initial concentration of the dye wastewater, flow rate of the wastewater inflow and light intensity were studied. It was found that the COD level of original wastewater lowered down significantly while the BOD/COD ratio was elevated significantly in the 9 h of reaction time, which indicated that some non-biodegradable organic materials were also removed in the C. I. Acid Yellow 17 decomposition process.

Swaminathan et. al., 2006 evaluated the decolourisation of an azo dye Reactive Yellow 14 (RY14) by three advanced oxidation processes viz., solar/TiO_2, solar/H_2O_2 and solar/H_2O_2/Fe^{+2} (photo-Fenton). The results showed that all the three processes could be effectively used for the decolourisation. The photodecolourisation efficiencies with solar irradiation were comparable to UV irradiation.

A comparative study between the sonolytic, photocatalytic and sonophotocatalytic oxidation processes of aqueous solutions of malachite green was carried out in the presence of carbon tetrachloride, using Titanium dioxide as a photocatalyst. Enhanced rates of sonolytic degradation of malachite green in the presence of CCl_4 were demonstrated rather than of sonolysis and photocatalysis in the presence of CCl_4 does not improve the degradation rate of malachite green in comparison with the one obtained using only sonolysis *(Bejarano-P. et. al., 2007*).

The decolourisation of Vat Green 01 textile dyestuff and real textile wastewater was investigated using UV radiation in the presence of H_2O_2 as function of pH, hydrogen peroxide

concentration and dye concentration. The results showed that the degradation increased as the initial H_2O_2 concentration increased up to a certain point at which hydrogen peroxide inhibited the wastewater photolytic degradation *(Silvia et. al., 2007).*

Karaoğlu et .al., 2010 made an attempt to investigate the photocatalytic degradation of Reactive Red 195 (RR195) in aqueous suspensions by using ultraviolet (UV), sodium hypochlorite (NaOCl) and TiO_2/Sep nanoparticles together. The influence of pH, catalyst amount, oxidant and initial dye concentration was investigated in all the experiments. It was found that the maximum colour and chemical oxygen demand (COD) removal were 99.9% and 78% respectively, at a dye concentration of 250 mg /L, NaOCl dosage of 50.37 mM, 0.1 g/L weight of TiO_2/Sep and pH of 5.45 in 3 h.

2.1.2 Phenolic compounds

Devipriya et. al., 2010 made an attempt to study the photocatalytic degradation of chemical pollutants in water using semiconductor oxide catalysts, Zinc oxide (ZnO) and Titanium dioxide (TiO_2) and phenol as the substrate. Influence of various parameters such as characteristics of the catalyst, irradiation time, substrate and catalyst concentrations, pH etc. was studied and optimum conditions for the complete degradation of phenol in water were identified. TiO_2 was found to be far superior to ZnO in terms of activity and durability. Mixing ZnO with TiO_2 does not affect its activity significantly.

Dixit et. al., 2010 studied the photochemical oxidation of phenol and chlorophenol aqueous solutions in a batch recycle photochemical reactor using ultraviolet 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.

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.

Dhir et. al., 2012 carried out the comparative study on TiO_2 and ZnO facilitated photocatalytic degradation of 4-chlorocatechol (4-CC) typically found in bleach mill effluents (BME). Of the two catalysts screened, ZnO was observed to be a better catalyst over TiO_2. The maximum degradation of 99.2 and 91.6% was obtained with 1.5 g/L ZnO, at pH 8, after 2 h

irradiation and with 2.5 g/L TiO_2, at free pH (6.5), 0.04M NaOCl concentration after 6 h irradiation, respectively. It was also found that the addition of sodium hypochlorite (0.04 M) enhanced considerably treatment efficiency (91.6%) in case of TiO_2. Solar light was also found to be efficient in the degradation of 4-CC when compared to UV.

2.1.3 Pesticides

Dionysiou et. al., 2000 carried out the hydrogen peroxide assisted photocatalytic degradation of the pesticide precursor 4-chlorobenzoic acid (4-CBA) in water using different TiO_2 powders and near-UV radiation and it was found that the addition of hydrogen peroxide up to 248 mg/l resulted in an increase of the reaction rates with a corresponding increase in photonic efficiency by ≈ 20%. Above this concentration, hydrogen peroxide either did not enhance or caused a significant inhibition of the mineralization rates.

Bhatkhande et. al., 2004 examined the photocatalytic degradation of chlorobenzene using solar and artificial UV radiations. The effect of pH the range of 3-10 and the presence of different anions at a concentration of 0.1 mol/dm^3 on the degradation of chlorobenzene was studied for both cases. Chlorobenzene was found to be a strongly adsorbing and hence rapidly degrading species when subjected to photocatalysis. Both pH and the presence of anions affect adsorption and the degradation but the overall effect was negligible (<5%).

Yu et. al., 2007 investigated the photocatalytic degradation of organochlorine pesticides including α-, β-, γ-hexachlorobenzene (BHC), dicofol and cypermethrin on nano-TiO_2 coated films under UV irradiation in the air. The photocatalytic conditions, including the amount of TiO_2, irradiation time and the intensity of light were optimized. The pesticides were most effectively degraded with in 20 min under the condition of 2.24 mg/cm^2 on TiO_2 film and a 400W UV irradiation of high-pressure mercury lamp with a wavelength of 365 nm.

2.1.4 Herbicides

Vulliet et. al., 2002 have investigated the degradation of two sulfonylurea (Sus) herbicides, cinosulfuron and triasulfuron in aqueous solutions containing TiO_2 suspensions as photocatalyst and the calculated quantum efficiencies (φ) of both Sus have been found similar (0.73%).

Chu et. al., 2004 studied the direct photolysis and the photocatalytic degradation of dicamba in TiO_2 suspensions with and without the use of hydrogen peroxide using two different

monochromatic UV irradiations (300 and 350 nm). Photolysis reactions were slow but the corresponding photocatalysis rates were increased by about 3 and 5 times in the presence of TiO_2 at 300 and 350 nm of UV, respectively. The results of H_2O_2-assisted photocatalysis experiments showed that a low H_2O_2 dosage in photocatalysis using UV 300 nm would enhance the decay rate of dicamba by 2.4 times, but an overdose of H_2O_2 will retard the rate because of the expenditure of hydroxyl radicals.

2.1.5 Other persistent organic pollutants (POPs)

Minero et. al., 1997 studied the decomposition of some components in crude oil (dodecane and toluene) in the seawater media. They found that no chlorinated compounds have been detected during the irradiation and complete decomposition was achieved after few hours of irradiation.

Wang et. al., 2000 investigated the use of UV light of 365 nm and Titanium dioxide in aqueous suspension to study the photocatalytic reaction of o-methylbenzoic acid under the influence of pH values, anion additives and the varieties of titanium dioxide. The experimental results demonstrated that under the condition of 5 g/l TiO_2, pH 3 and light intensity of 2.45 mW/cm^2, 0.1 mM of o-methylbenzoic acid could be completely decomposed in 2 h.

Kim et. al., 2002 investigated the photocatalytic degradation of volatile organic compounds including gas-phase trichloroethylene (TCE), acetone, methanol and toluene over illuminated TiO_2 was closely examined in a batch photoreactor as a function of water vapor, molecular oxygen and reaction temperature. The results showed that oxygen is an essential component in photocatalytic reactions by trapping photogenerated electrons on the semiconductor surface and by decreasing the recombination of electrons and holes.

Kunz et. al., 2002 made an attempt to study the hydrogen peroxide-assisted photochemical degradation of ethylenediaminetetraacetic acid (EDTA). The results demonstrated that the mineralization ratios higher than 90% were observed at reaction times of 6 min by working at optimized experimental conditions (pH of 2 and H_2O_2:EDTA molar ratio of 10), using a microwave-activated photochemical reactor and monitoring the EDTA degradation by total organic carbon analysis.

Matsuzawa et. al., 2002 studied the photocatalytic oxidation of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6DMDBT) in acetonitrile using Titanium Dioxide (TiO_2) A 200 W Hg–Xe lamp was used as a light source, and the catalytic performances of four

commercially available TiO_2 photocatalysts (PC-1, PC-2, PC-3 and P25) were compared. The results demonstrated that of the photocatalysts used, P25 showed the highest rate of photooxidation.

Another study conducted on the decomposition of seawater-soluble crude-oil fractions found that it can be decomposed under illumination of nanoparticles of TiO_2 using artificial light *(Ziolli et. al., 2002).*

The effect of hydrogen peroxide and pH was investigated in UV/TiO_2 and UV/TiO_2/H_2O_2 systems on 2-Chloroaniline (2-ClA) under monochromatic UV light at 300 nm. The experimental results showed that the pH was a sensitive parameter to the rate of degradation. Low reaction rate at acidic pH and at high pH, rate enhancement was observed at UV/TiO_2 system because of the increase generation of HO*. However, the introduction of H_2O_2 slowed down the decay rate at such alkaline medium *(Chu et. al., 2007).*

2.2 Photocatalytic degradation of Acrylonitrile

Krichevskaya et. al., 2009 studied the photocatalytic oxidation of acrylonitrile on titanium dioxide in the gaseous phase. Acrylonitrile readily undergoes photocatalytic degradation in a gas–solid system by using TiO_2 Degussa P25. The acrylonitrile photocatalytic oxidation volatile products, visible in the infrared spectra, included nitrogen dioxide, nitrous oxide, carbon dioxide, water, hydrogen cyanide and carbon monoxide. Longer contact time resulted in deeper oxidation of acrylonitrile with decreasing hydrogen cyanide and increasing nitrogen dioxide content.

The gaseous products of photocatalytic oxidation of acrylonitrile on sulphated P25 in concentrations from 10 to 100 mg/L at 60 to 130^0C were CO_2, HCN and HNCO. This photocatalyst showed disproportionally improved performance at higher temperature and longer retention times. The temperature-programmed oxidation after Photocatalytic oxidation disclosed possible reaction routes *(Joks et. al., 2011).*

Zhang et. al., 2011 studied the pretreatment of acrylonitrile manufacturing wastewater by Fenton process. The effects of dose of H_2O_2, pH value and ratio of Fe^{2+}/H_2O_2 on removal efficiency of TOC and COD_{Cr} were researched. Experimental results showed that highest TOC and COD_{Cr} removal efficiency were acquired at pH 3.0, with 5.54 g/L H_2O_2 and Fe^{2+}/H_2O_2 ratio about 0.1.

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

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.

Kansal et. al., 2007 carried out the photocatalytic degradation of 2,4,6-trichlorophenol (2,4,6-TCP) in a batch reactor under UV light in aqueous solution for 5 h using titania P-25 as a photocatalyst and sodium hypochlorite as an oxidant. The optimal values of operational parameters leading to 2,4,6-TCP abatement were obtained by using response surface methodology. The percent degradation and COD reduction of 2,4,6-TCP was found to increase with increase in the catalyst dose up to the dose of 1.1 g/L, pH in the range of 4– 4.5, and oxidant concentration of 9.95×10^{-6}M.

Betianu et. al., 2008 applied the response surface methodology for the investigation of photodegradation of 20 mg/L Orange II in aqueous solutions and for optimization of color removal efficiency .The input variables considered for experimental design were solution initial pH, oxidizing agent (H_2O_2) initial concentration and UV-A irradiation time. A 100% color removal efficiency was obtained in experiments under the optimum conditions established in the region of experimentation (pH = 6.9, $[H_2O_2]_0$= 183 mg/L and t = 32 min).

The acrylonitrile removal from wastewater using an agri-based adsorbent-sugarcane bagasse fly ash (BFA) and powdered activated carbon (PAC) was investigated. The effect of such parameters as adsorbent dose (w), temperature (T) and time of contact (t) on the sorption of acrylonitrile was studied using response surface methodology (RSM) based on Box–Behnken surface statistical design at an initial acrylonitrile concentration, C_0 = 100 mg/L as a fixed input parameter. The results of RSM indicated that the proposed models predict the responses adequately within the limits of input parameters being used. The optimum conditions obtained were: adsorbent dose = 25 g/L, temperature = 30 and contact time = 20 min in case of ACN removal by PAC *(Kumar et. al., 2008 a,b).*

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.

Kumar et. al., 2009 performed statistical Box–Behnken design of experiments to evaluate the effects of individual operating variables and their interactions on the acrylonitrile (ACN) removal of C_0 =100 mg/L as fixed input parameter. The variables examined in this study included activated carbon-granular (AC) dosage, *w*, temperature, *T*, and time of contact, *t*. The significant variables and optimum conditions were identified (w=4 g/L, T=30^0C, and t=120 min with ACN uptake of 23.97 mg/g of AC) from statistical analysis of the experimental results using response surface methodology (RSM).

Ray et. al., 2009 applied a four factor three level Box-Benkhen design (BBD) to describe 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 min^{-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.

Zhang et. al., 2010 applied the experimental design methodology for modelling and optimizing the operational parameters on photocatalytic degradation of chloramphenicol (CAP) using TiO_2 as photocatalyst. The interaction effects and optimal parameters were obtained by using Design Expert software. The optimal values of the operation parameters under the related constraint conditions were found at pH 6.4, TiO_2 concentration of 0.94 g/L and CAP initial concentration of 19.97 mg/L, respectively. The degradation rate of CAP approached 85.97% under optimal conditions. It was found that pH and TiO_2 concentration had a significant influence on the degradation rate of CAP.

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.

Jafarzadeh. et. al., 2011 applied the Response surface methodology (RSM) using D-optimal design to optimize the photocatalytic degradation of phenol by new composite nano-catalyst (TiO_2/Perlite) and studied the effect of seven factors (initial pH, initial phenol concentration, reaction temperature, UV irradiation time, UV light intensity, catalyst calcination 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^oC; UV irradiation time 6.5 h; UV light intensity 250W; catalyst calcination temperature 600^oC; and TiO_2/ perlite dosage 6 g/L.

Narayana et. al., 2011 conducted experiments to study the efficiency of carbon prepared from waste prawn shells for the removal of crystal violet (CV) and investigated the effect of various process parameters such as temperature, initial pH, contact time, adsorbent dosage and initial dye concentration of the solution. Response surface Methodology was used to optimize the process parameters. ANOVA analysis was also studied to know the interaction effect of dye and adsorbent. It was found that 92% of removal of CV dye from solution was obtained at optimized conditions (temperature of 200^0C, pH of 12, contact time of 90 min, adsorbent dose of 0.41 g and initial dye concentration of 53 mg/L).

Tantriratna et. al., 2011 applied the Box-Behnken design to evaluate the optimal conditions for UV-photocatalytic degradation of paraquat over titanium dioxide on rice husk silica (TiO_2/RH-SiO_2) catalyst which is affected by four independent variables, namely initial paraquat concentration, pH of solution, titanium dioxide content (%TiO_2) and catalyst loading. The highest paraquat removal efficiency of 90.04 % was obtained at 10 mg/L initial paraquat concentration, 5.91 pH, 30 wt % TiO_2 and 2.0 g/L catalyst loading.

Sahoo et. al., 2012 studied the photocatalytic degradation of methyl blue (MYB) using Ag^+ doped TiO_2 under UV irradiation in which the catalytic dose, initial concentration of dye and pH of the reaction mixture were found to influence the degradation process the most. Using the three factors, three levels Box–Behnken design of experiment technique 15 sets of experiments were designed considering the effective ranges of the influential parameters. Design Expert software version 8.0.6.1 was used to optimize the effects of the experimental parameters

on the responses. The optimum values of the parameters were found to be dose of Ag^{+} doped TiO_2 0.99 g/L, initial concentration of MYB 57.68 mg/L and pH of reaction mixture 7.76.

Vaez et. al., 2012 applied the experimental design methodology to model and optimize the operational parameters of the photocatalytic degradation of Acid Red 73 using immobilized TiO_2 nanoparticles. Four experimental parameters were chosen as independent variables: pH, initial dye concentration, H_2O_2 concentration, and anion concentration. 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.

Zhou et. al., 2012 applied Central composite design method of response surface methodology (RSM) to investigate the optimum value of the selected factors for naphthalene degradation enhanced naphthalene degradation by TiO_2/Fe_3O_4-SiO_2 (TFS) photocatalyst. The experimental results showed that irradiation time, pH, and TFS photocatalyst loading had significant influence on naphthalene degradation and the maximum degradation rate of 97.39% was predicted when the operational parameters were irradiation time 97.1min, pH 2.1, and catalyst loading 0.962 g/L, respectively.

CHAPTER 3

MATERIALS AND METHODS

This chapter describes the materials and methods used during the study, including the chemicals, glasswares, instruments and procedures used to treat the compound with the UV/ZnO and UV/TiO_2 catalysis. The compilation of the varying photocatalytic conditions like pH, ZnO and TiO_2 dosages and oxidant dose for the degradation of acrylonitrile with constant concentration (50 mg/L) make up the experimental matrix.

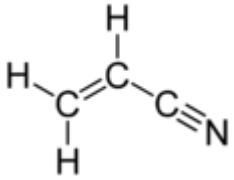
3.1 Materials

3.1.1 Acrylonitrile (ACN)

Acrylonitrile (ACN) having CAS number 107-13-1 was purchased from Sigma Aldrich (USA). Acrylonitrile solution was used without further purification. 50 mg/L of acrylonitrile solution was prepared by dissolving 62.5 µL of the model compound in double distilled water and make the solution quantity to 1 L.

Table 3.1 Physico-chemical properties of Acrylonitrile

Common Name	Acrylonitrile [C_3H_3N]
Physical state	Clear, colorless to slightly yellow liquid
Odour	Pungent garlic type odour that most individuals cannot smell below concentrations of 13-20 mg/L
Boiling point	77.3 °C (171.1°F)
Melting point	83.5 °C (-118.3°F)
Density (at 20°C)	806 kg/m^3
Molecular weight	53.1

Solubility (20°C)	7.35 wt % ACN in water 3.1 wt % water in ACN
Evaporation Rate	4.54 (butyl acetate = 1.0)
Flash Point	32°F (0°C)
Flammability limits	3 - 17%
Vapor Pressure	100mm Hg at 23°C
Structure	

3.1.2 Photocatalysts

The photocatalytic materials TiO_2 and ZnO were used. 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.

3.1.3 Chemicals

Hydrogen peroxide and Sodium hypochlorite (4% available Cl_2, BDH Merck) were used as an oxidant. All the experiments were performed with double distilled water. Different normality of 0.1 N HCl and 0.1 NaOH were used for adjustment of pH of the ACN solution.

3.2 Instruments and Equipments

3.2.1 Photoreactor

Photocatalytic treatment of Acrylonitrile was performed in batch experiments. For photocatalytic treatment, UV reactor was used which is rectangular having dimensions of 4.5 X 3 X 3.5 and was made up of 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. 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 during the experimentation in order to solve the problem of mixing and keeping photocatalyst in suspension. Photocatalytic degradation was carried out in reaction vessels in the UV reactor. Glass bowls were used for the photocatalytic reactions having a capacity of 1 L. The experiments were conducted in batch mode. Reaction vessel with magnetic stirrer is shown in Fig. 3.2.

Fig. 3.2 Reaction vessel with magnetic stirrer

3.2.3 Air sparger

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

3.2.4 Filtration

After photocatalytic treatment by UV photoreactor, the solution was filtered through syringe filters having millipore filters of 0.45 µm pore size as shown in Fig 3.3.

Fig 3.3 0.45 µm pore size syringe filters

3.2.5 pH meter

A digital desktop, pH Meter (CP 901) from Century Instrument Company was used to monitor the pH of the solution and the pH was adjusted with the help of NaOH (0.1 N) and HCl (0.1 N). Freshly prepared buffer solutions (of pH 4 and 9) were used to calibrate the instrument from time to time throughout the research.

Fig 3.4 pH meter

3.2.6 Spectrophotometer

The spectrum was taken with UV-Vis Spectrophotometer (Hitachi V-500 UV/VIS (Japan) double-beam spectrophotometer). The degradation studies were conducted by measuring absorbance in UV-Vis spectrophotometer, having a wavelength range from 190-1100nm 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. Spectrophotometer is having both Tungsten and Deuterium lamp at operating temperature of 0-40^{o}C.

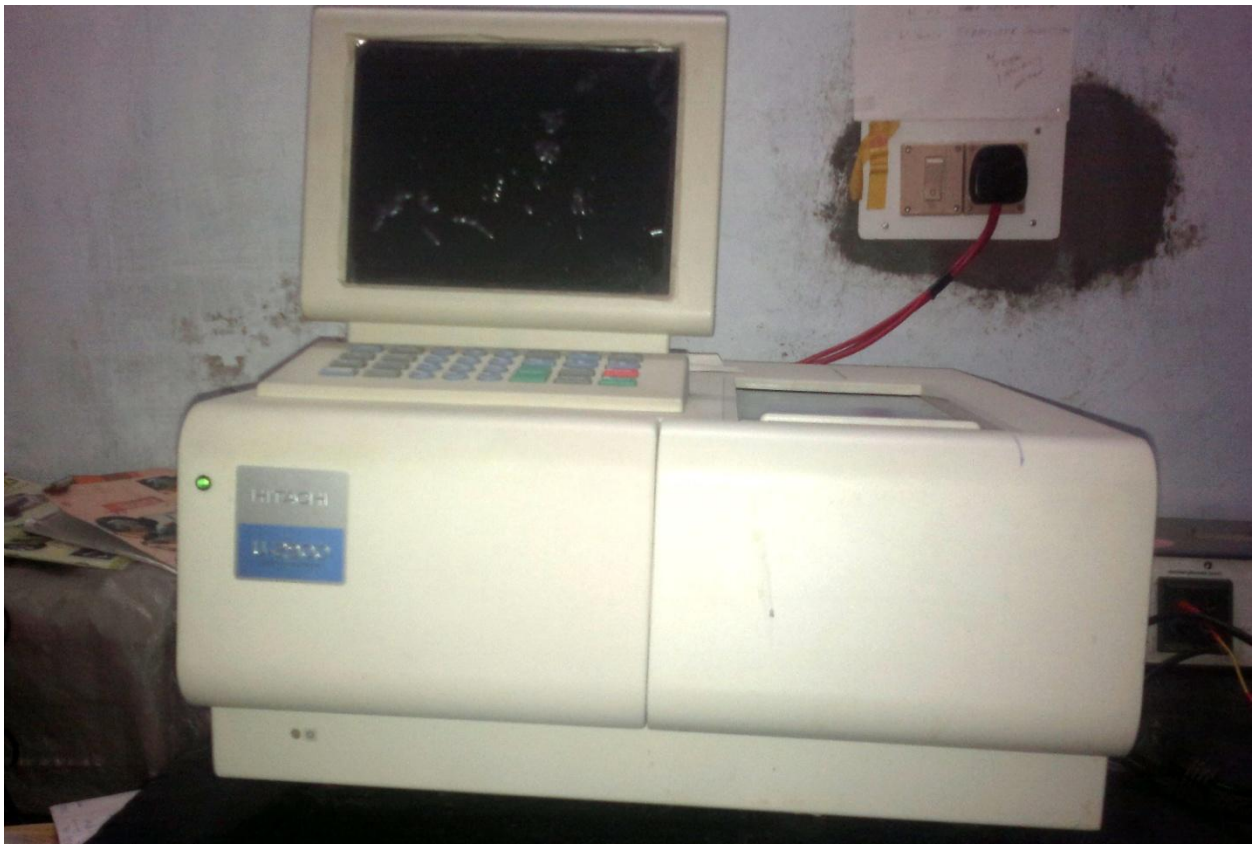


Fig 3.5 UV-Vis spectrophotometer

3.3 Methodology

3.3.1 Preparation of solution

- **Acrylonitrile solution:** ACN compound solutions of 50 mg/L concentration was prepared by dissolving 62.5 µL of Acrylonitrile in double distilled water and make the solution quantity to 1 L. The solutions was prepared by adding known amount of compound into a small amount of deionized water in 1-litre volumteric flask and filling it to the mark with double distilled water. The flasks were covered with aluminium foil to avoid degradation by the laboratory fluorescent lights. Before the oxidation experiments

could be performed, it was necessary to choose the appropriate concentration of compound solution.

- **Hydrogen Peroxide:** Hydrogen peroxide (30% w/v) was obtained from S.D. fine-chem. Limited having M.W. of 34.01. It implies that 100 ml of solution contains 30 g or 1 ml contains 300 mg (2.5 mM/L to 10mM/L oxidant dose was used in the experiment).
- **Sodium hypochlorite:** Sodium hypochlorite (4% Cl_2 available, BDH Merk) was used as an oxidant. 10 % NaOCl was prepared by adding 10 ml of NaOCl to 90 ml of distilled water.

3.3.2 Photocatalytic Treatment

Photocatalytic treatment was carried out for Acrylonitrile solution. The compound solution was treated and the various parameters like the catalyst dose, pH, area to volume ratio of the reaction vessel, UV intensity and concentration of oxidants were varied and optimized. 50 mg/L of acrylonitrile solution was prepared using double distilled water. The experiments were also carried out in dark, UV and solar light under the same conditions. Double distilled water was used for the all the dilutions.

- Initial pH of the sample was checked and all the parameters were varied to optimize the value of catalyst dose, pH, concentration of oxidant (hydrogen peroxide and sodium hypochlorite) under UV light and then compared to the photocatalytic activity with solar light.
- 200 ml of sample taken in the reaction vessel (1000ml quantity) and the vessel was covered with the transparent thin foil; air is also supplied by the aerator during the experiments.
- The aqueous suspension was magnetically stirred and subjected to irradiation under UV light for a period of 2 hours.
- The sample was withdrawn at every 15 minute interval, filtered through the syringe filter of 0.45 µm pore size and absorbance was taken at 204 nm with the spectrophotometer.
- The percentage degradation was calculated as follows:

$$\%Degradation = 100 \times \left[\frac{C_o - C}{C_o} \right]$$

where C_0 = initial concentration of solution,

C = concentration of solution after photoirradiation

3.4 Box–Behnken design

Box and Behnken (1960) have proposed some three-level designs for fitting response surfaces. Box–Behnken design requires an experiment number according to $N=K^2 + K + C_p$, where, (k) is the factor number and (C_p) is the replicate number of the central point. These designs are formed by combining 2^k factorials with incomplete block designs. Box–Behnken is a spherical, revolving design, viewed as a cube and consists of a central point and the middle points of the edges. The resulting designs are usually very efficient in terms of the number of required runs, and they are either rotatable or nearly rotatable as shown in Fig. 3.6.

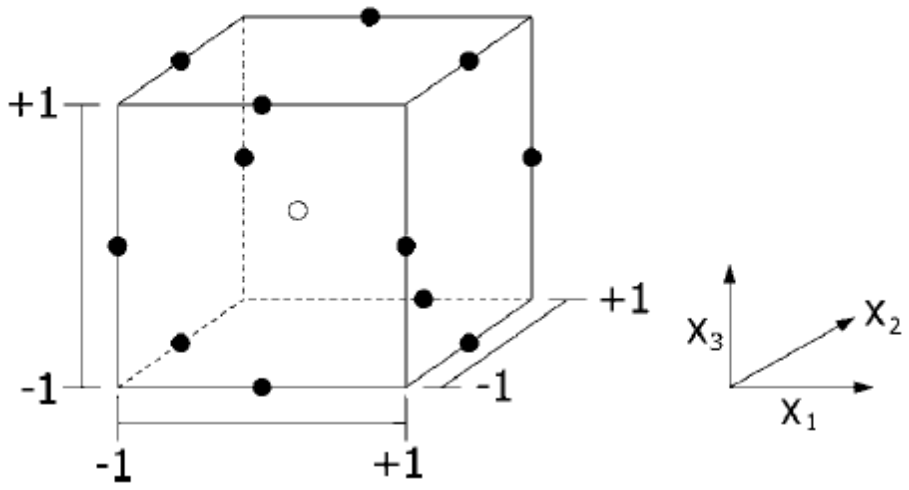


Fig 3.6 A Box–Behnken design for three factors (k=3)

A three-variable Box-Behnken design is presented by *Evans, 2003*. It has been applied for optimization of several chemical and physical processes.

$$q = b_0 + \sum_{i=1}^{n} b_i x_i + \left(\sum_{i=1}^{n} b_{ii} x_i\right)^2 + \left(\sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} x_i x_j\right)$$

This design is generally used for fitting the second order polynomial model as given by following equation where q is the predicted response, b_0 = constant coefficients, b_i is the slope or linear coefficients of the input factor x_i, b_{ii} is the linear by linear interaction coefficients or

quadratic coefficients between the input factor x_i and x_j, b_{ij} is the interaction coefficients of input factor x_i.

It is important to include the second order model to provide good prediction throughout the region of interest. The second order response surface design is rotatable; this means that the variance of the predicted response is the same at all points. Rotatability is a reasonable basis for the selection of response surface design. Because the purpose of response surface methodology (RSM) is optimization and as the location of the optimum is unknown prior to running the experiment, it makes sense to use design that provides equal precisions of estimation in all directions.

Cubic model was found to be aliased and cannot be used for further modelling of experimental data. A model is aliased means that not enough experiments have been run to independently estimate all the terms for that model. Whenever, there are fewer independent points in the design than there are terms in the model, some parameters cannot be estimated independently. A model is aliased means that model is inappropriate for further investigation.

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

- ZnO dose (A)
- pH (B)
- H_2O_2 conc. (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 designation. The response parameter in the present study was degradation efficiency. In each test, degradation efficiency was calculated by change in the concentration of that component. 17 experiments were conducted according to the plan mentioned in Table 4.1 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: ZnO dose (g/L)	0.50	1.75	3.00
B: pH	2.00	7.00	12.00
C: H_2O_2 conc. (mM/L)	2.50	6.75	10.00

CHAPTER 4

RESULTS AND DISCUSSIONS

In the photocatalytic oxidation process, organic pollutants are destroyed in the presence of semiconductor 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 acrylonitrile compound which was carried out using ZnO and TiO_2 catalysts. A matrix of experimental variables was developed in which the catalyst dose, pH, intensity of UV light, area to volume ratio of the reaction vessel, concentration of oxidants and light source (UV/solar) were varied and applied to the model compound. In addition, efficacy of degradation was also evaluated in mixed catalyst (ZnO and TiO_2) under UV light.

4.1 UV –Vis spectra of Acrylonitrile (ACN)

The degradation efficiency of ACN (50 mg/L) was recorded in terms of change in the intensity of characteristic peak at 204 nm. Fig. 4.1 shows the UV-Vis Spectra of 50 mg/L of acrylonitrile solution.

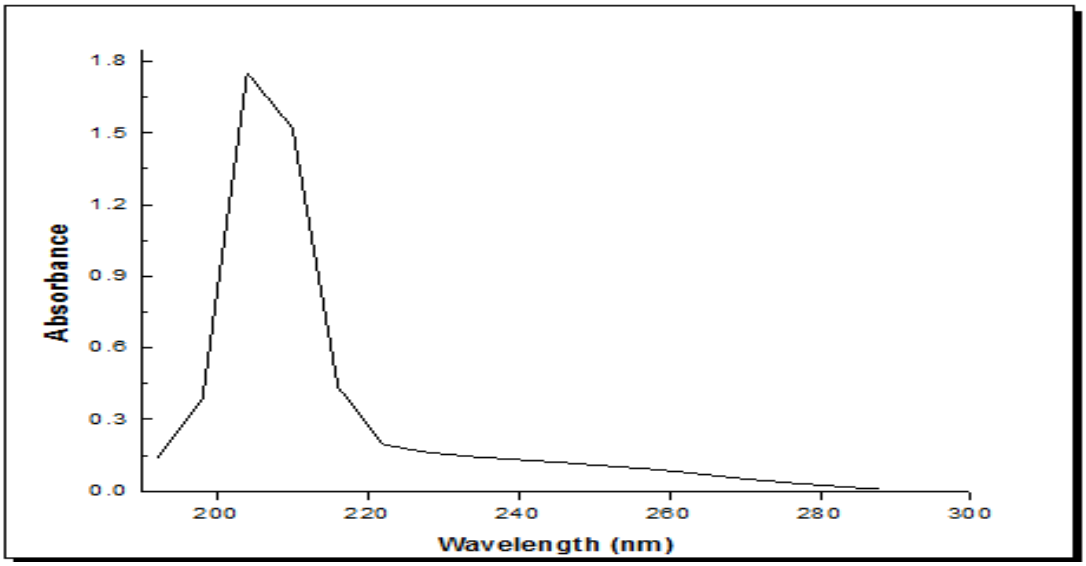


Fig 4.1 Full scanning spectrum of ACN

4.2 Adsorption studies of Acrylonitrile (ACN)

The Degradation adsorption of ACN on catalyst surface was studied by carrying out experiments under dark conditions through UV/ZnO, UV/TiO_2, Dark/ZnO and Dark/TiO_2. The photocatalytic degradation of ACN under these experimental conditions is shown in Fig 4.2. The degradation efficiency was recorded in terms of change in the intensity of characteristic peak at

204 nm. The experiments were carried out under dark conditions using ZnO and TiO_2 to assess the adsorption of ACN on the surface of photocatalyst which was observed to be 36.2% and 17%, respectively. This degradation efficiency refers to adsorption of ACN on catalyst surface. Then the UV induced photocatalytic experiments were conducted using both the catalysts at substrate concentration of 50 mg/L and catalyst loading of 1.5 g/L. The pH was maintained at 8.0 with ZnO and 4.0 in case of TiO_2. 86.7% degradation efficiency was achieved with in 60 min using ZnO whereas 78.7% degradation efficiency was observed using TiO_2 in the same duration. This shows that ZnO exhibits higher photocatalytic activity as compared to TiO_2.

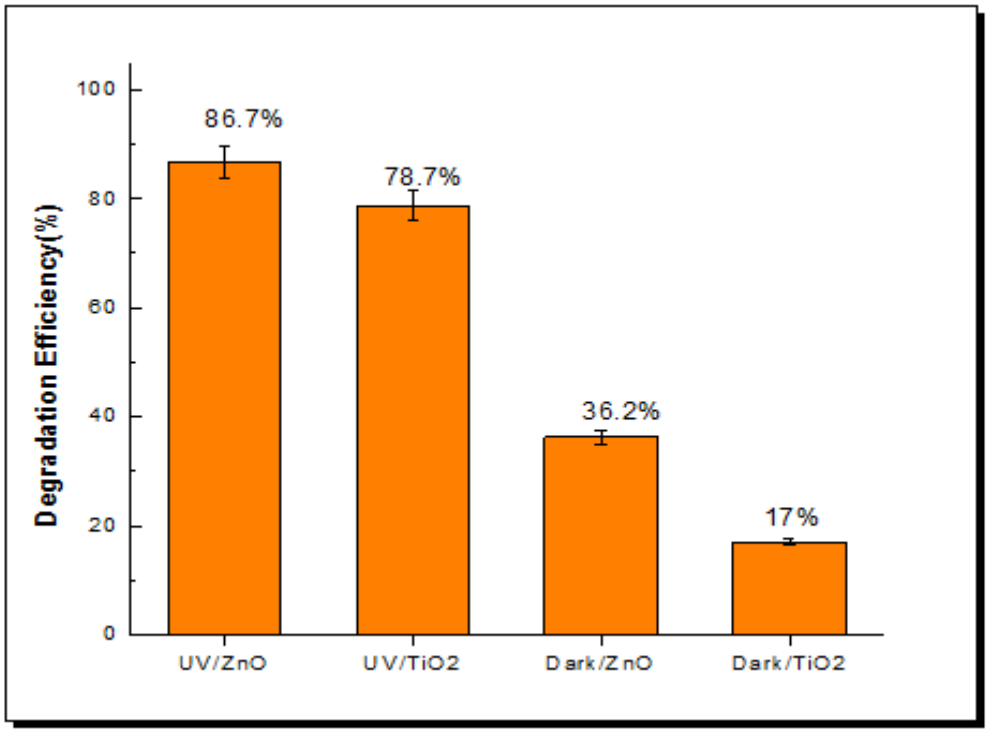


Fig 4.2 Photocatalytic degradation of ACN under UV/Dark conditions [ZnO]=1.5 g/L, [TiO_2]= 1.5 g/L, [Conc.]= 50 mg/L, [wavelength]= 204 nm, [Time]= 60 min

4.3 Effect of catalyst loading

It has been suggested that the amount of catalyst plays an important role in the degradation of organic compound in photocatalysis. It is necessary to find the optimum loading for the efficient degradation of acrylonitrile in order to avoid the excess use of ZnO and TiO_2 to obtain the highest photocatalytic activity at minimum operational cost. A series of experiments were conducted with 50 mg/L ACN in order to assess the optimum catalyst loading by varying

the catalyst dose from 0.5-2.0 g/L at natural pH 7.6. The effect of the catalyst loading on the degradation efficiency of acyrlonitrile under UV irradiation is shown in Fig 4.3(a) and 4.3(b), respectively. The results demonstrated that as the catalyst concentration (ZnO) was increased from 0.5 to 1.5 g/L, the degradation efficiency increased from 75% to 83% after 60 min of irradiation. However, in case of TiO_2, the degradation efficiency increased from 60.4% to 84.1% by increasing the catalyst dose from 0.5 to 1.5 g/L. 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).* Part of the catalyst surface probably became unavailable for photon absorption and substrate adsorption under such conditions, thus bringing little stimulation to catalytic reaction (*Gao et. al., 2006).* The results demonstrate that an optimal concentration of the catalyst is necessary for enhancing the rate of degradation and reducing its wastage. So, the optimal concentration of ZnO and TiO_2 came out to be 1.5 g/L.

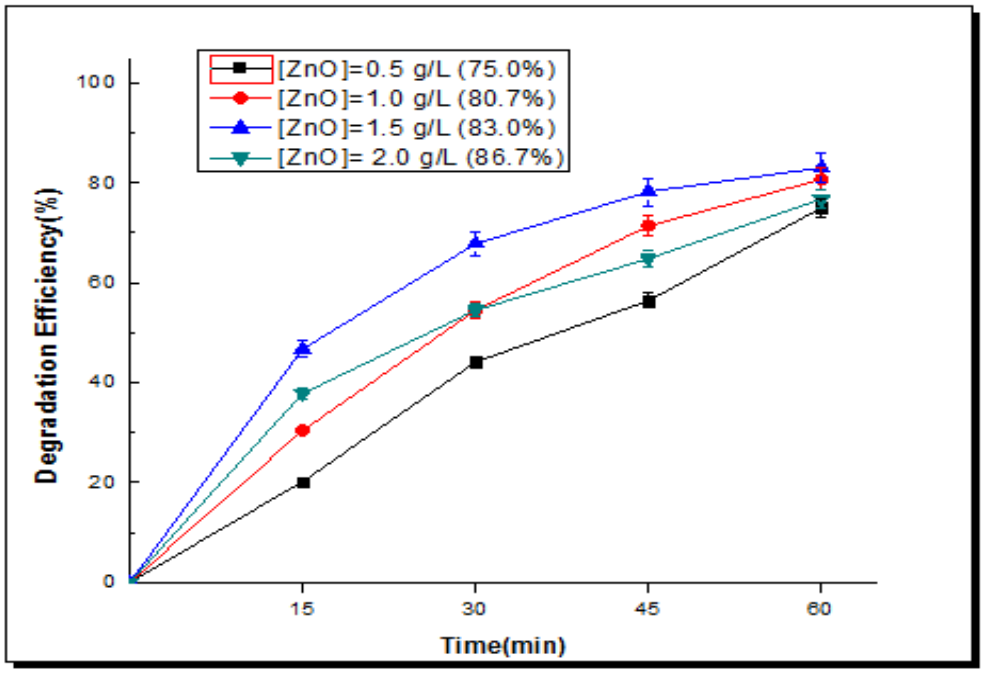


Fig 4.3(a) Effect of ZnO dose on photocatalytic degradation of ACN [pH]= 7.6, [Conc.] = 50 mg/L, [wavelength]= 204 nm, [Time]= 60 min

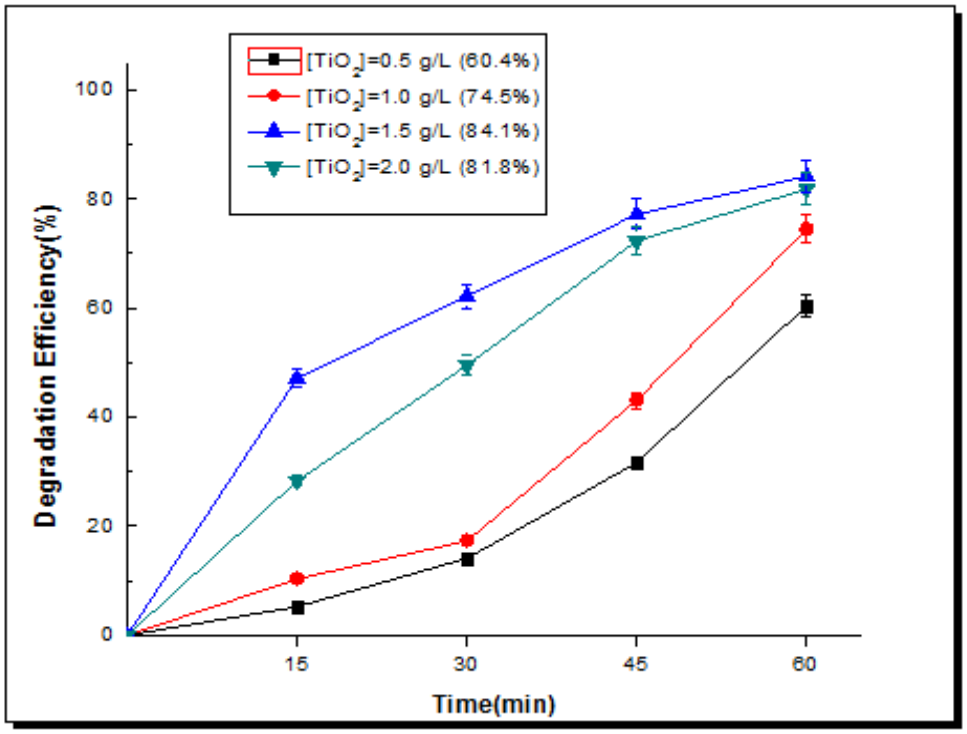


Fig 4.3(b) Effect of TiO_2 dose on photocatalytic degradation of ACN [pH]=7.6, [Conc.] = 50 mg/L, [wavelength]= 204 nm, [Time]= 60 min

Behnajady et. al., 2005 investigated the kinetic study on photocatalytic degradation of C.I. Acid Yellow 23 by ZnO photocatalyst and found the similar results where the increase in the catalyst concentration increased the degradation efficiency up to a certain limit but after that the increase in catalyst loading did not affect the degradation significantly. *Dixit et. al., 2010* reported the photochemical oxidation of Phenol and Chlorophenol by UV/H_2O_2/TiO_2 process and observed that the degradation rate for the decomposition of both phenol and p-chlorophenol in the presence of TiO_2 increases with the increase in catalyst concentration and a further increase in catalyst concentration leads to a decrease in the degradation rate.

4.4 Effect of pH

The amphoteric behaviour of most semiconductor oxides influences the surface charge of the photocatalyst. Therefore, it is important to consider the effect of pH on the degradation efficiency. To study this aspect, experiments were carried out at pH values ranging from 2–12 using 50 mg/L ACN keeping the ZnO/TiO_2 concentration of 1.5 g/L. Fig. 4.4(a) and 4.4(b)

shows the effect of pH on the degradation efficiency using ZnO and TiO_2, respectively. The results show that in case of ZnO, the maximum degradation efficiency of 86.4% and 86.7% was observed at pH 4.0 and pH 8.0, respectively. Since pH 8.0 is closer to the natural pH of ACN which was 7.6, therefore, pH 8.0 was chosen as the optimum pH. However in case of TiO_2, maximum degradation of 78.7% was obtained at pH 4.0 which was taken as the optimum pH for the further experimentation. The effect of pH can be explained on the basis of acid base property of metal oxide and zero point charge of TiO_2 and ZnO. The adsorption of H_2O molecules at surficial metal sites is followed by the dissociation of OH^- groups leading to coverage (4–10nm^2) with chemically equivalent metal hydroxyl groups (M–OH). Due to the amphoteric behaviour of most metal hydroxides, the following two equilibria are considered.

$$M\,OH + H^+ \longrightarrow MOH_2^+ \,(pH \leq pzc) \qquad (1)$$

$$M\,OH \longrightarrow MO^- + H^+ \,(pH \geq pzc) \qquad (2)$$

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. The zero point charge (zpc) pH_{zpc} for TiO_2 (Degussa P25) is 6.8. TiO_2 surface is positively charged in acidic media (pH 6.8) whereas it is negatively charged under alkaline condition (pH>6.8). At pH lower than the pH_{zpc} of TiO_2, the higher the adsorption, the higher is the degradation. When the pH increases, the rate of degradation decreases, because the change of surface charge of TiO_2 leads to a supplementary repulsive phenomenon.

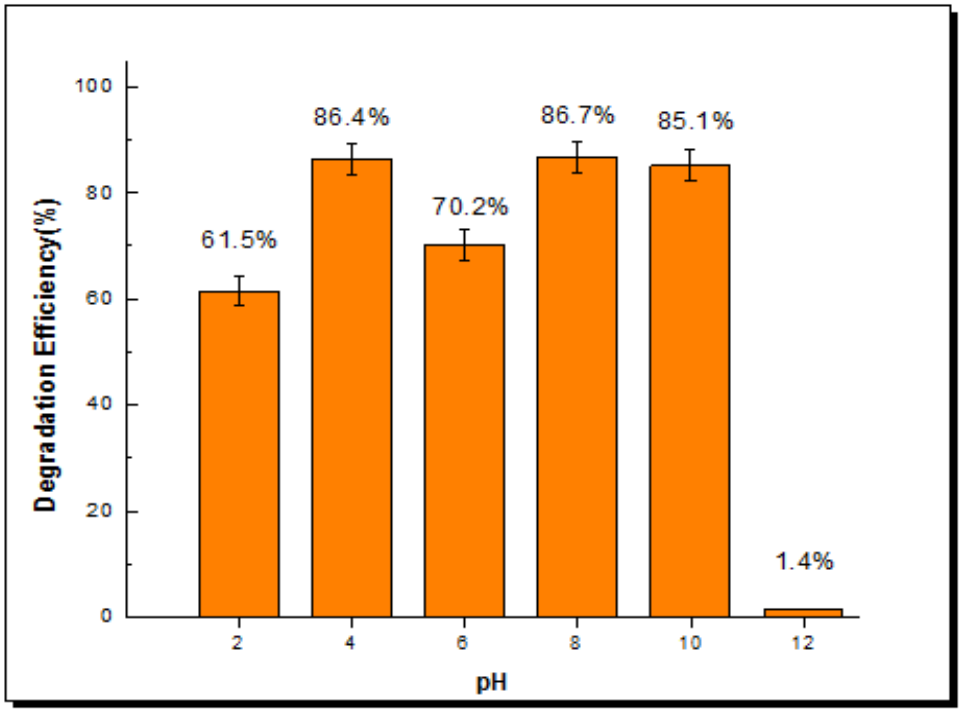


Fig 4.4(a) Effect of pH on photocatalytic degradation of ACN with ZnO [ZnO]=1.5 g/L, [Conc.]= 50mg/L, [wavelength]= 204 nm, [Time]= 60 min

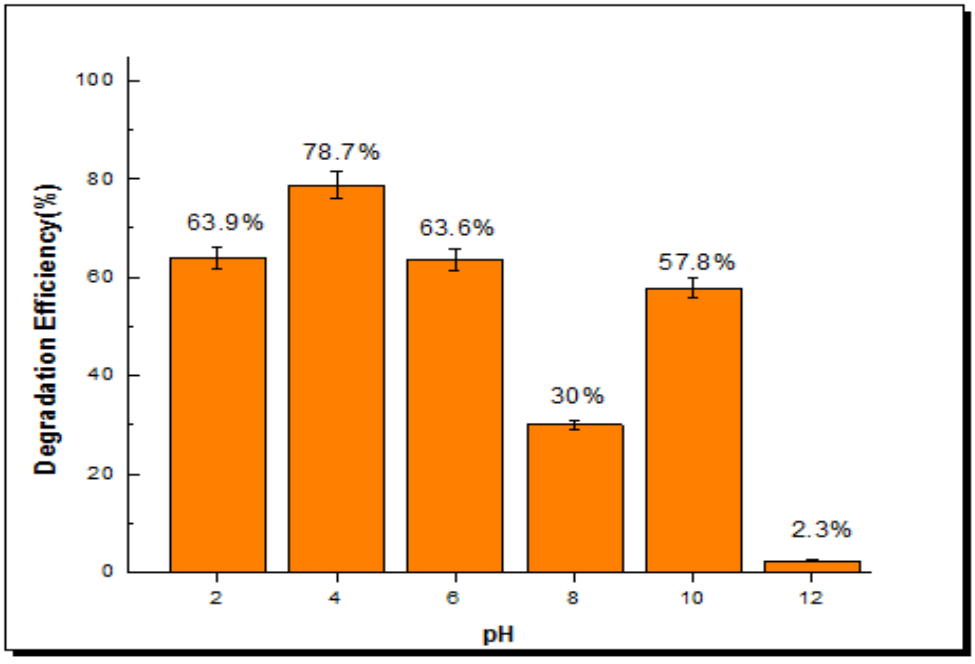


Fig 4.4(b) Effect of pH on photocatalytic degradation of ACN with TiO_2 [TiO_2]= 1.5 g/L, [Conc.]= 50 mg/L, [wavelength]= 204 nm, [Time]= 60 min

Sakhtivel et. al., 2003 observed similar kind of results with ZnO and TiO_2 where the rate of degradation increases with increase in pH exhibiting maximum rate of degradation at pH 10 with ZnO. But in the case of TiO_2, it was observed reversely, the rate of degradation increases with decrease in pH.

4.5 Effect of UV intensity

The effect of UV light intensity on the degradation efficiency of acrylonitrile (50 mg/L) has been studied with catalyst loading of 1.5 g/L TiO_2/ZnO at pH 4.0 and pH 8.0, respectively. The Fig. 4.5(a) and 4.5(b) shows the effect of UV intensity on the degradation efficiency using ZnO and TiO_2, respectively. It is evident from the graphs that as the light intensity increases, the photodegradation efficiency increases. Because the UV irradiation generates the photons required for the electron transfer from the valence band to the conduction band of a semiconductor photocatalyst and the energy of a photon is related to its wavelength, the overall energy input to a photocatalytic process is dependent on light intensity. As more radiations fall on the catalyst surface, the rate of degradation increases and hence producing more hydroxyl radicals *(Daneshvar et. al., 2004; Konstantinou et. al., 2004).*

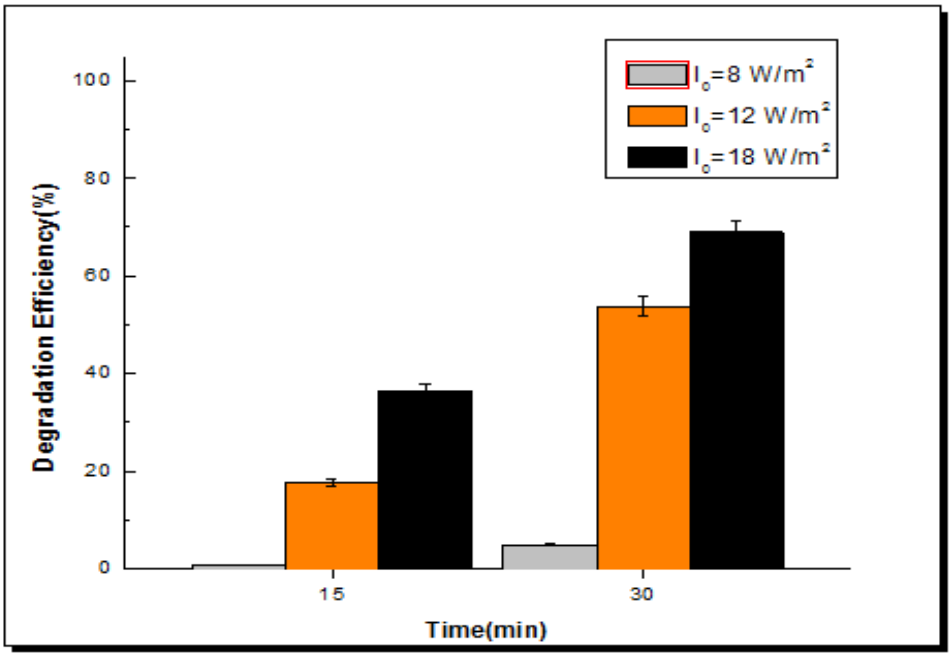


Fig 4.5(a) Effect of UV intensity on photocatalytic degradation of ACN with ZnO [ZnO]= 1.5 g/L, [pH]= 8.0, [Conc.]= 50 mg/L, [wavelength]= 204 nm, [Time]= 30 min

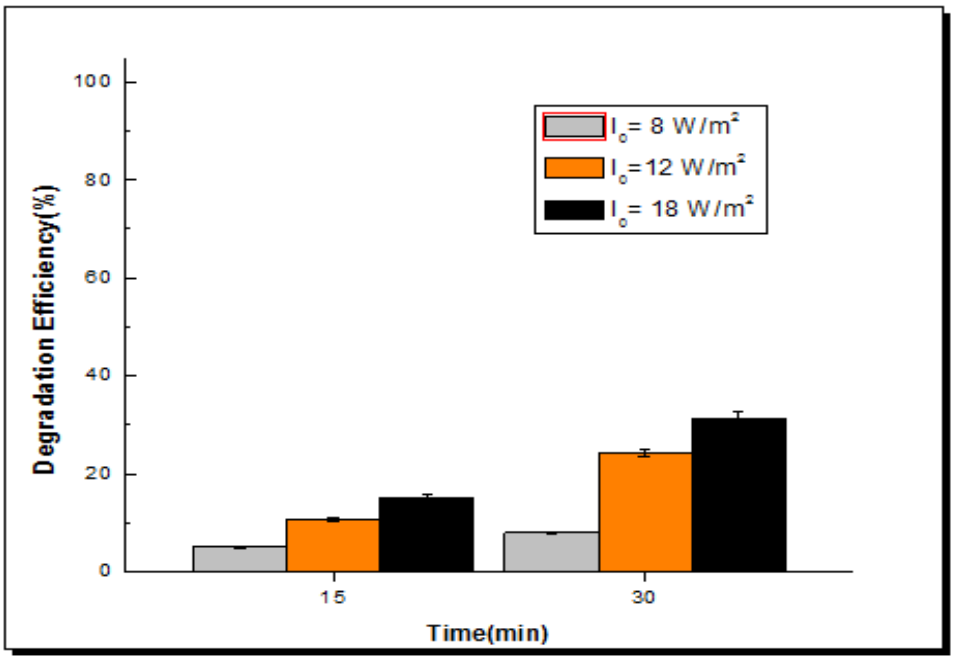


Fig 4.5(b) Effect of UV intensity on photocatalytic degradation of ACN with TiO_2 [TiO_2]= 1.5 g/L, [pH]= 4.0, [Conc.]= 50 mg/L, [wavelength]= 204 nm, [Time] = 30 min

Behnajady et. al., 2005; Swaminathan et. al., 2006 investigated the effect of UV/solar light intensity on the degradation efficiency of acid yellow 23 and Reactive Yellow 14 at different light intensities. They reported that the photodegradation efficiency increases with the increase in intensity of UV/solar light.

4.6 Effect of area to volume ratio of the reaction vessel

The area and volume of the reaction vessel are the two different parameters which affect the degradation of the pollutants. If surface area is increased keeping the same volume, there will be more degradation because of more surface area which will be available for light to come in contact with the solution. As a first case, the volume of reaction mixture was 200 ml and the surface area of the reaction vessel was 78.5 cm^2 so the area to volume ratio was 0.39 cm^2/ml, whereas in the other case the area to volume ratio was 3.14 cm^2/ml as the surface area was 314 cm^2 and the volume taken was 100 ml. The effect of varying area to volume ratio of the reaction vessel on the photocatalytic degradation of acrylonitrile is shown in Fig 4.6(a) and 4.6(b) which depict that as the area to volume ratio increases, the degradation efficiency was increased from

58.5% to 86.7% using ZnO. However, with TiO_2, the degradation efficiency observed was 60.4% and 91.6% with the area to volume ratio of 0.39 cm^2/ml and 3.14 cm^2/ml, respectively.

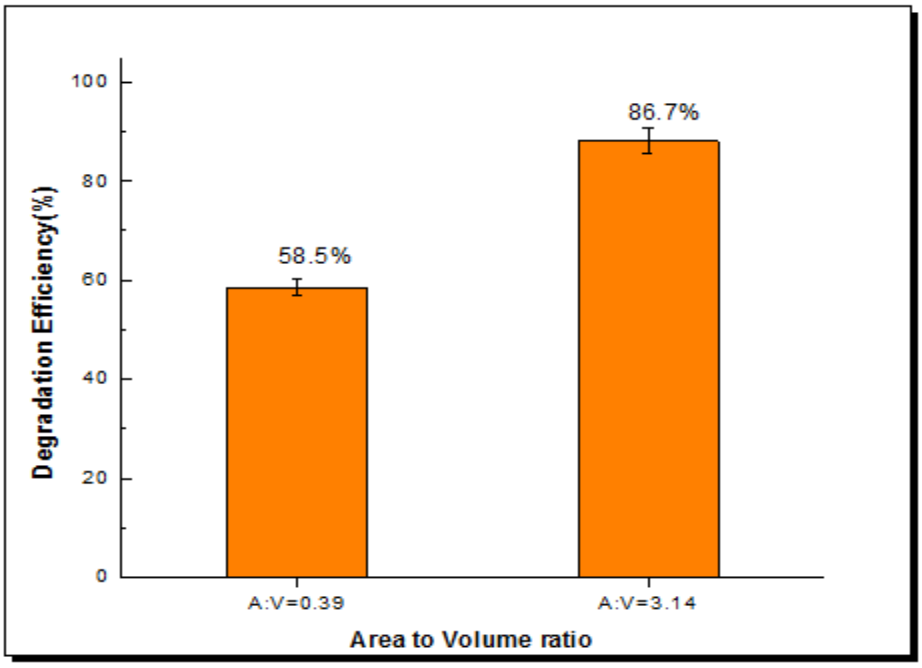


Fig 4.6(a) Effect of area to volume ratio on photocatalytic degradation of ACN with ZnO [ZnO]= 1.5 g/L, [pH]= 8.0, [Conc.]= 50 mg/L, [wavelength]= 204 nm, [Time]= 60 min

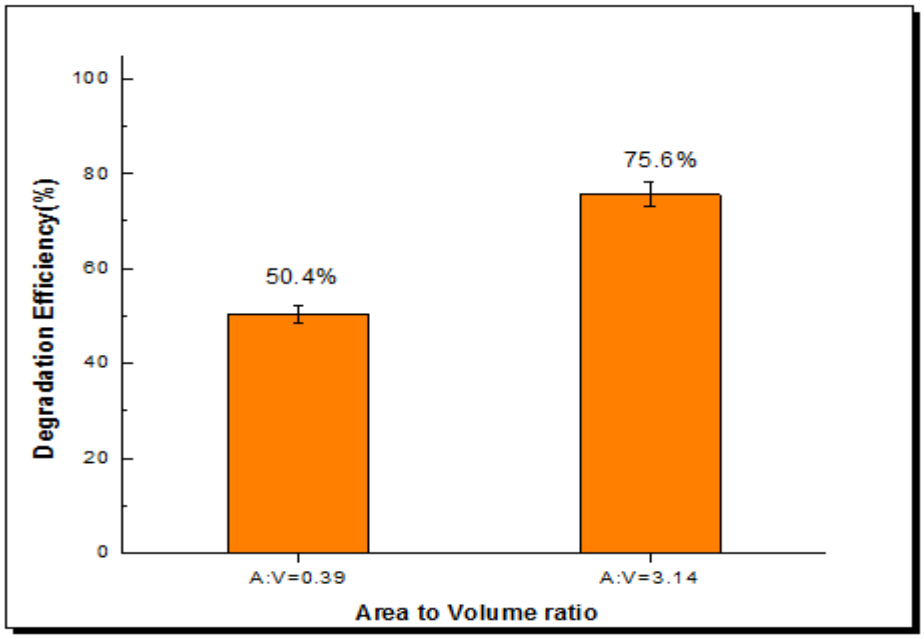


Fig 4.6(b) Effect of area to volume ratio on photocatalytic degradation of ACN with TiO_2 [TiO_2]=1.5 g/L, [pH]= 4.0, [Conc.]= 50 mg/L, [wavelength]= 204 nm, [Time]= 60 min

Toor et. al., 2007 reported that the degradation rate increased with the increasing area to volume ratio of the shallow pond type reactor used for the treatment of bleaching effluent from the pulp and paper industry by photocatalytic oxidation.

4.7 Effect of oxidant dose

The effect of oxidant dose on the photocatalytic degradation of ACN was studied using hydrogen peroxide and sodium hypochlorite. The rate of photocatalytic degradation of organic compounds is significantly improved in the presence of oxidizing agent. The experiments were conducted by varying the dose of hydrogen peroxide and sodium hypochlorite from 2.5-10 mM/L with the catalyst dose of 1.5 g/L at pH 8.0 in case of ZnO and 1.5 g/L at pH 4.0 in case of TiO_2. As the oxidant concentration was increased, the rate of photocatalytic degradation of acrylonitrile increased initially up to certain limit and then decreased with further increase in oxidant concentration. The dual effect of H_2O_2 can be explained by radical reaction mechanisms. The reaction is accelerated by added H_2O_2 producing hydroxyl radicals from scavenging the electrons and absorption of UV light. By addition of excess H_2O_2, it acts as hydroxyl radical or hole scavenger to form the perhydroxyl radicals (HO_2•) which is a much weaker oxidant than hydroxyl radicals. The effect of hydrogen peroxide concentration using ZnO and TiO_2 is shown in Fig 4.7(a) and 4.7(b), respectively. The results show that degradation efficiency of 78.9% and 46.3% was achieved up to 5 mM/L H_2O_2 with ZnO and TiO_2 after 30 min of UV exposure, Above 5 mM/L H_2O_2, the degradation efficiency decreases. Thus, H_2O_2 was optimized to be at 5 mM/L.

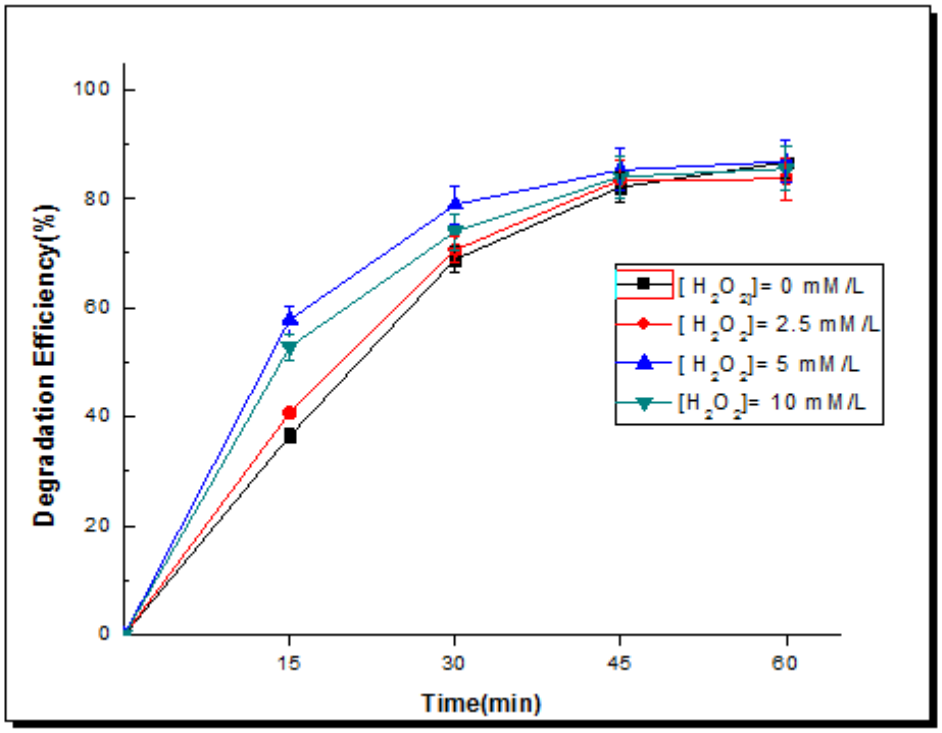


Fig 4.7(a) Effect of hydrogen peroxide on photocatalytic degradation of ACN with ZnO [ZnO]= 1.5 g/L, [pH]= 8.0, [Conc.]= 50 mg/L, [wavelength]= 204 nm, [Time]= 60 min

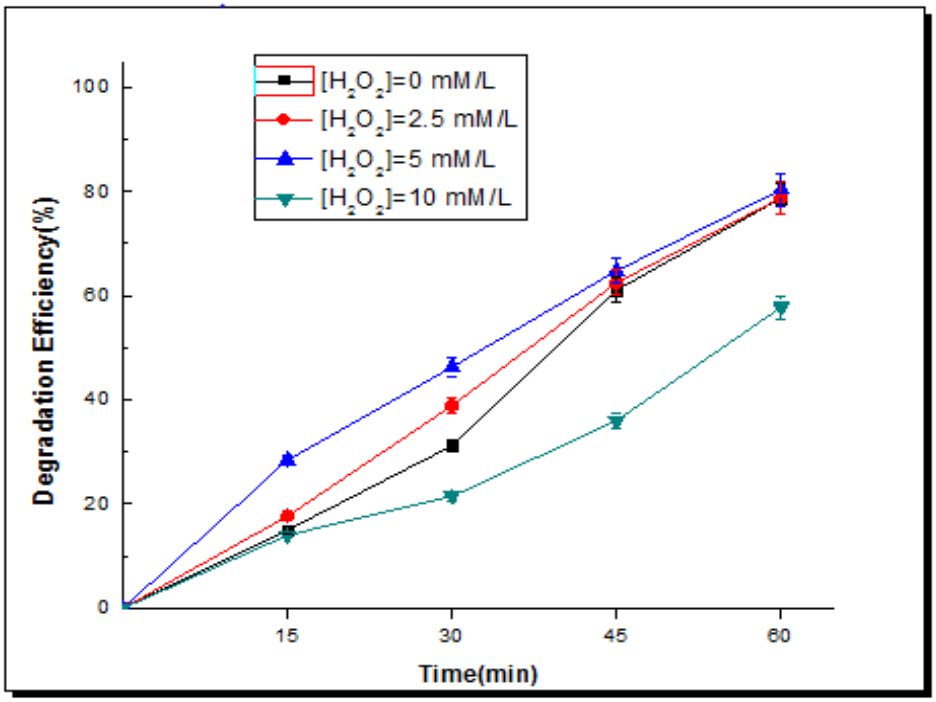


Fig 4.7(b) Effect of hydrogen peroxide on photocatalytic degradation of ACN with TiO_2 [TiO_2]= 1.5 g/L, [pH]= 4.0, [Conc.]= 50 mg/L, [wavelength]= 204 nm, [Time] = 60 min

The results are in agreement with the previous findings of *Daneshvar et. al., 2003* who documented the effect of H_2O_2 in the photocatalytic degradation of Acid Red 14 dye and the degradation rate was reported to increase with the increasing H_2O_2 concentration up to certain limit.

When NaOCl was used as an oxidant, then it was observed that degradation efficiency did not increase with ZnO. The effect of sodium hypochlorite on TiO_2 is shown in Fig 4.7 (c). The results indicated that the addition of NaOCl in the concentration range of 2.5–10 mM/L enhanced the rate of degradation up to 5 mM/L NaOCl. After 30 min of UV exposure, degradation efficiency of 71.1% was noted in the presence of 5 mM/L NaOCl. A reason for this could be the availability of hypochlorite ion (OCl^-), which is unstable and ultimately gets degraded to chloride and chlorate ions which results in oxidation of more organic matter. Further increase in the concentration of NaOCl may be contributing towards the slight increase in COD value due to more consumption of potassium dichromate by hypochlorite ion, so degradation decreases with 10 mM/L NaOCl.

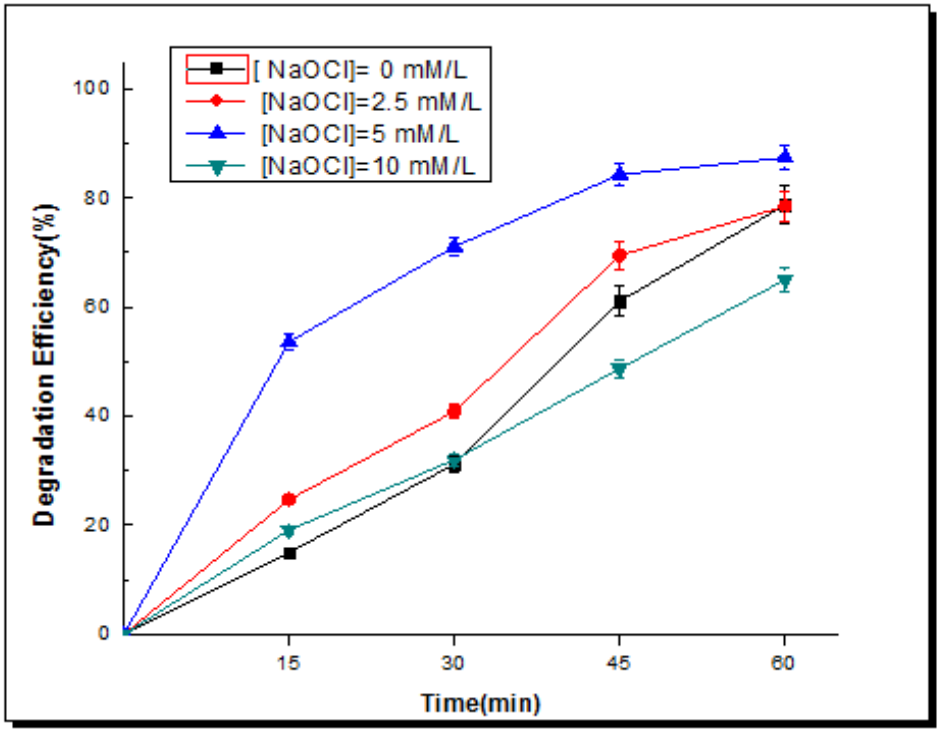


Fig 4.7(c) Effect of sodium hypochlorite on photocatalytic degradation of ACN with TiO_2 [TiO_2]= 1.5 g/L, [pH]= 4.0, [Conc.] = 50 mg/L, [wavelength]= 204 nm, [Time]= 60 min

Dhir et. al., 2012 reported the similar results for the photocatalytic degradation of 4-chlorocatechol (4-CC) and bleach mill effluents where the addition of NaOCl along with TiO_2 was found to enhance the rate of degradation of 4-CC. The presence of oxidant (sodium hypochlorite) along with ZnO at pH 8 did not result in increase in the degradation efficiency of 4-CC.

Fig 4.7(d) shows the Time dependent degradation of ACN using TiO_2, ZnO, TiO_2+H_2O_2, TiO_2+ NaOCl, ZnO+H_2O_2, ZnO +NaOCl at optimized conditions. The results clearly indicate that ZnO exhibits higher photocatalytic activity as compared to TiO_2 and H_2O_2 has proved to be better oxidant than NaOCl.

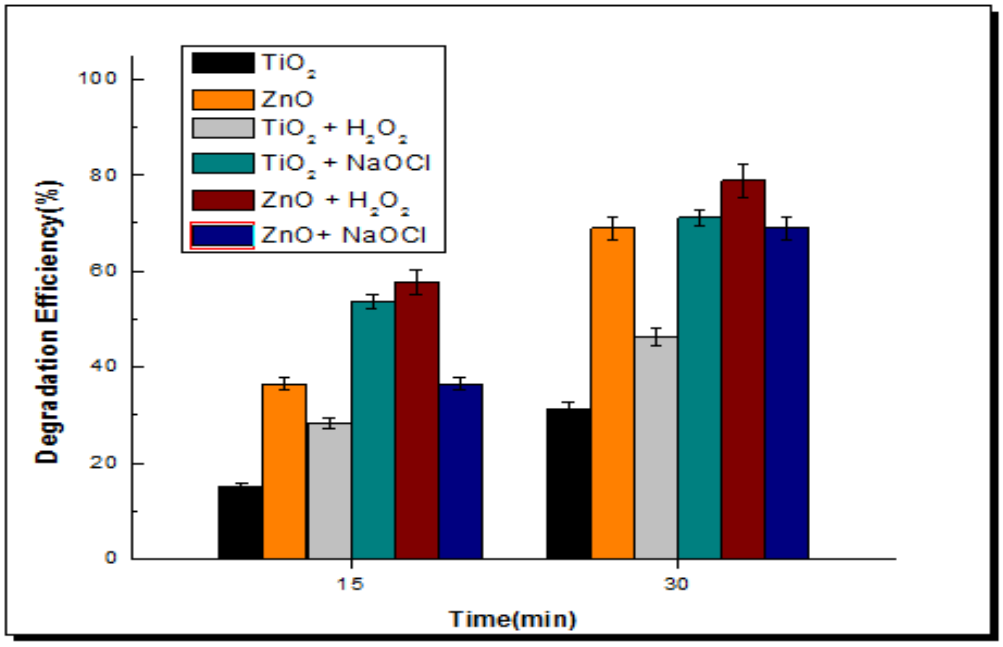


Fig 4.7(d) Time dependent degradation of ACN using TiO_2, ZnO, TiO_2+H_2O_2, TiO_2+NaOCl, ZnO+H_2O_2, ZnO +NaOCl at optimized conditions, [Time]= 45 min

4.8 Effect of light source (UV/solar)

In order to reduce the operating cost of the process, investigations were carried out using solar light and compared to UV irradiation. The aqueous suspensions of ACN (50 mg/L) were exposed to UV and solar light under optimized conditions (1.5 g/L ZnO, pH 8.0 in the presence of 5 mM/L H_2O_2 and 1.5 g/L TiO_2, pH 4.0 in the presence of 5 mM/L NaOCl). The respective degradation efficiency was found to be 82% and 78.4% in solar light as compared to 78.9% and

71.1% degradation efficiency achieved in UV with in 30 min of irradiation (Fig 4.8(a) and 4.8(b)). The percentage degradation in solar light was in close proximity with the UV light which is due to their ability to absorb part of visible light. The adsorption of chemical molecule on the catalyst surface results in excited states caused due to visible illumination and these excited states facilitate transfer of electrons to the conduction band of TiO_2 particles. The results indicate efficient use of solar light for the photocatalytic degradation of ACN.

Similar trend have been reported by *Toor et. al., 2007* where the results indicated the efficient use of solar light for the treatment of bleaching effluent from pulp and paper by photocatalytic oxidation.

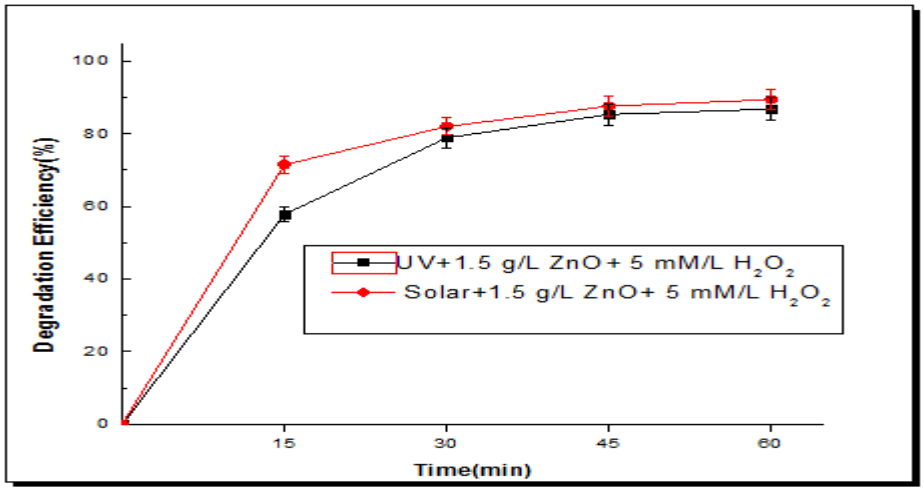


Fig 4.8(a) Effect of UV/solar light on photocatalytic degradation of ACN with ZnO [ZnO]= 1.5 g/L, [pH]= 8.0, [Conc.]= 50 mg/L, [wavelength]= 204 nm, [Time]= 60 min

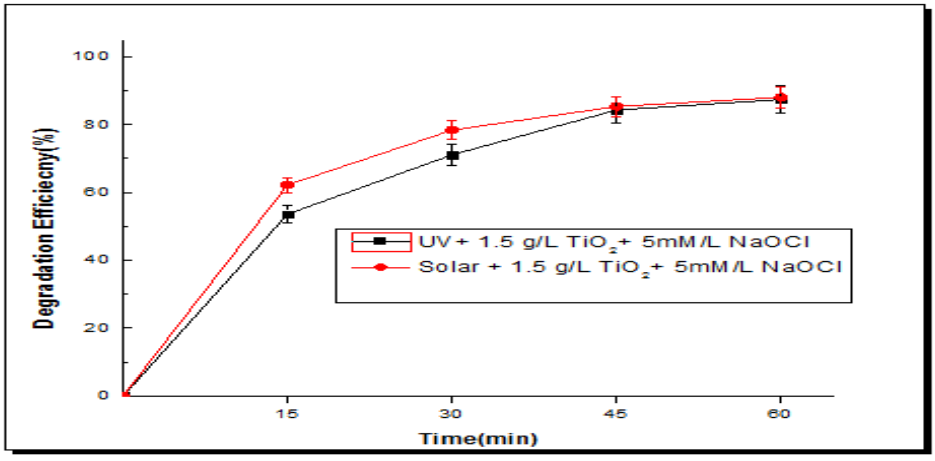


Fig 4.8(b) Effect of UV/solar light on photocatalytic degradation of ACN with TiO_2 [TiO_2]=1.5 g/L, [pH]= 4.0, [Conc.]= 50 mg/L, [wavelength]= 204 nm, [Time]= 60 min

4.9 Effect of mixed catalyst

The influence of mixed catalyst was investigated on the photocatalytic degradation of ACN. In these experiments, varying proportions of ZnO and TiO_2 such as (ZnO:TiO_2) (90:10), (70:30), (50:50), (30:70), (10:90) were applied to 50 mg/L acrylonitrile solution at pH 8. The degradation efficiency achieved is shown in Fig 4.9. The results showed that 100% ZnO was most effective for the degradation of ACN which result in 86.7% degradation efficiency after 60 min of UV exposure. As the ZnO proportion in the catalyst decreases, the degradation efficiency decreases from 82.5% at 90% ZnO to 30% with pure TiO_2.

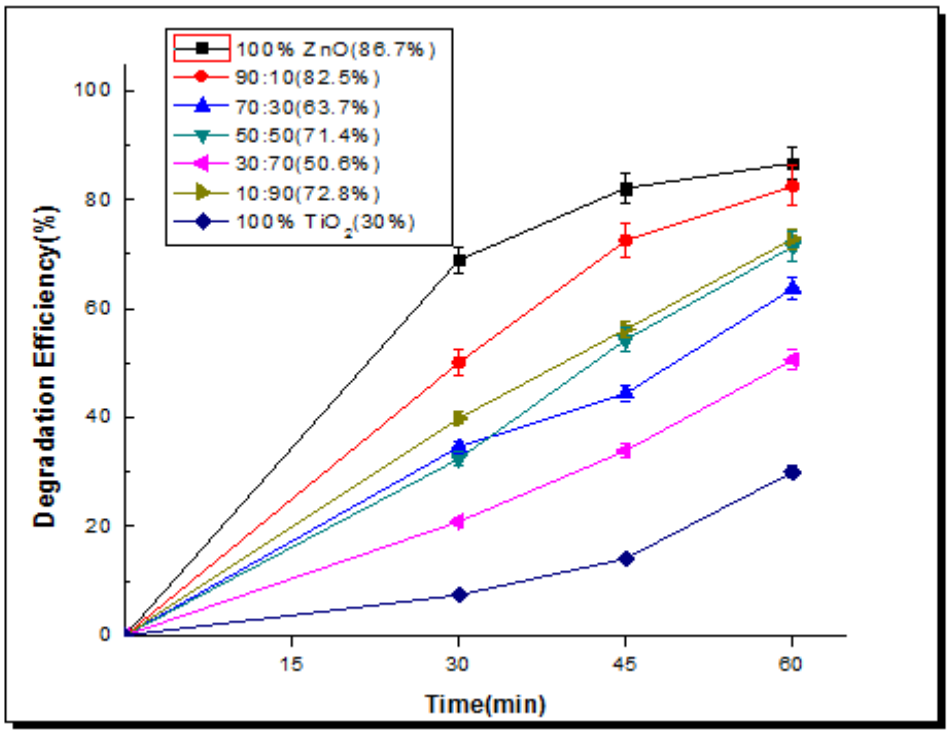


Fig 4.9 Effect of mixed catalyst on photocatalytic degradation of ACN pH=8.0, [Conc.]= 50 mg/L, [wavelength]= 204 nm, [Time]= 60 min

4.10 Optimization of the photocatalytic process parameters for degradation of ACN

4.10.1 Model fitting and statistical analysis

The experimental design as given by the 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 (ZnO dose)	Factor 2 (pH)	Factor 3 (H_2O_2 conc.)	Response (Degradation Efficiency)
3	1	Block 1	0.50	12.00	6.25	0.30
9	2	Block 1	1.75	2.00	2.50	87.3
7	3	Block 1	0.50	7.00	10.00	86.1
16	4	Block 1	1.75	7.00	6.25	83.2
17	5	Block 1	1.75	7.00	6.25	87.2
10	6	Block 1	1.75	12.00	2.50	0.60
15	7	Block 1	1.75	7.00	6.25	88.9
11	8	Block 1	1.75	2.00	10.00	85.0
1	9	Block 1	0.50	2.00	6.25	83.9
14	10	Block 1	1.75	7.00	6.25	88.2
2	11	Block 1	3.00	2.00	6.25	84.5
6	12	Block 1	3.00	7.00	2.50	81.09
5	13	Block 1	0.50	7.00	2.50	74.2
12	14	Block 1	1.75	12.00	10.00	0.56
13	15	Block 1	1.75	7.00	6.25	86.1
8	16	Block 1	3.00	7.00	10.00	82.6
4	17	Block 1	3.00	12.00	6.25	0.45

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 ACN. Cubic model was not recommended as the Box–Behnken matrix has sufficient data to interpret the outcome of the present system. To decide about the adequacy of model for ACN 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. The results of the quadratic model for degradation efficiency in the form of Analysis of Variance (ANOVA) is given in Table 4.3. The analysis shows that the form of the model chosen to explain the relationship between the factors and the response is correct.

Table 4.2 Selection of adequate model for degradation of ACN

Sequential Model Sum of Squares						
Source	Sum of squares	d.f	Mean square	F	P	Remark
Mean	3.19	1	3.19			
Linear	3.81	1	1.27	7.62	0.0034	
2FI	0.028	3	9497E-003	0.044	0.9868	
Quadratic	2.06	3	0.69	65.84	<0.0001	Suggested
Cubic	0.073	3	0.024	12408.95	<0.0001	Aliased
Residual	7.862E-006	4	1.956E-006	--	--	
Total	9.16	17	0.54	--	--	
Lack of Fit Tests						
Source	Sum of squares	d.f	Mean square	F	P	Remark
Linear	2.17	9	0.24	1.225E+005	<0.0001	
2FI	2.14	6	0.36	1.813E+005	<0.0001	
Quadratic	0.073	3	0.024	12408.95	<0.0001	Suggested
Cubic	0.000	0	--	--	--	Aliased
Pure Error	7.862E-006	4	1.965E-006	--	--	--
Model Summary Statistics						
Source	Std.Dev.	R^2	Adj.R^2	Pre.R^2	Press	Remark
Linear	0.41	0.6375	0.5538	0.3267	4.02	
2FI	0.46	0.6423	0.4276	-0.4827	8.86	
Quadratic	0.10	0.9878	0.9720	0.8041	1.17	Suggested
Cubic	402E-003	1.000	1.0000		+	Aliased

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

Source	Sum of squares	d.f	Mean square	F	P	Remark
Model	5.90	9	0.66	62.75	<0.0001	Highly significant
catalyst dose	0.014	1	0.014	1.37	0.2085	
pH	3.80	1	3.80	363.08	<0.0001	Highly significant
H_2O_2 conc.	1.749E-004	1	1.749E-004	0.017	0.9007	
(catalyst dose)^2	0.033	1	0.033	3.15	0.1194	
$(pH)^2$	1.99	1	1.99	190.56	<0.0001	Highly significant
$(H_2O_2 conc.)^2$	0.030	1	0.030	2.88	0.1336	
catalyst dose *pH	0.028	1	0.028	2.68	0.1457	
catalyst dose*H_2O_2 conc.	1.333E-005	1	1.333E-005	1.275E-003	0.9725	
pH*H_2O_2 conc.	4.812E-004	1	4.812E-004	0.046	0.8362	
Residual	0.073	7	0.010			
Lack of Fit	0.073	3	0.024	12408.95	<0.0001	Highly significant
Pure Error	7.862E-006	4	1.965E-006			
Cor Total	5.98	16				

Std. Dev.	0.10	R-Squared	0.9878
Mean	0.43	Adj R-Squared	0.9720
C.V.	23.62	Pred R-Squared	0.8041
PRESS	1.17	Adeq Precision	21.459

From the ANOVA of the empirical second order polynomial model, F value for the model is 62.75, 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 12408.95 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 0.8041 is in reasonable agreement with the "Adj R-Squared" of 0.9720, 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 21.459 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 sofware is given below:

$$\frac{1}{sqrt(\%degradation\ efficiency)}$$

$$= +0.34689 - 0.14050 * catalyst\ dose - 0.22766 * pH + 0.071616 * H_2O_2$$
$$+ 0.05655 * (catalyst\ dose)^2 + 0.027513 * (pH)^2 - 6.01159E - 003$$
$$* (H_2O_2)2 - 0.013386 * catalyst\ dose * pH + 3.89387E - 004$$
$$* catalyst\ dose * H_2O_2 + 5.84979E - 004 * pH * H_2O_2$$

Fig 4.10 displays the normal probablity 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.

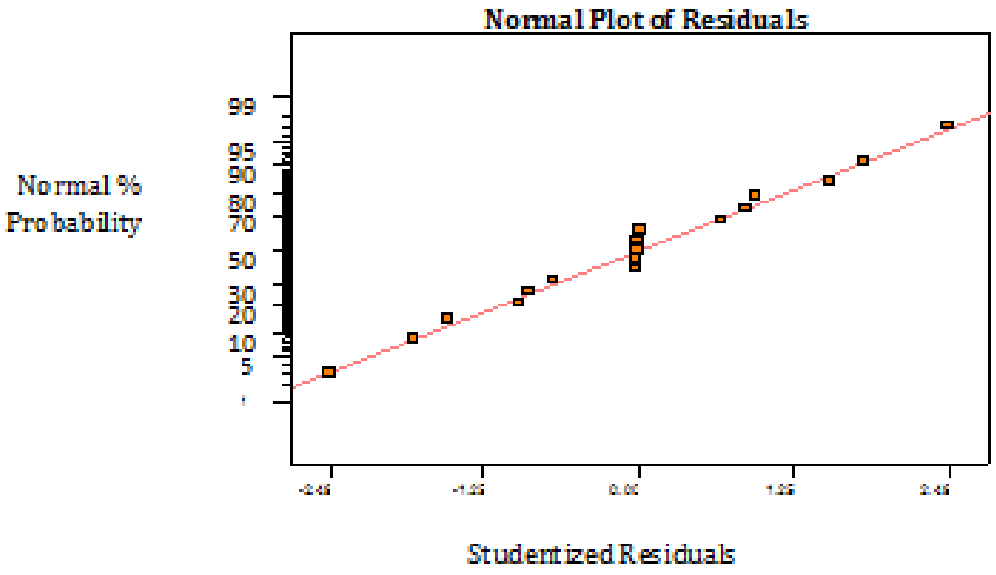


Fig 4.10 Normal probablity plot of the residuals for percentage degradation

4.10.2 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. The results of the interactions between the three independent variables and the response are shown in Fig 4.11 (a), 4.11 (b) and 4.11 (c). Fig 4.11 (a) illustrates the effect of ZnO dose and pH on the response (R) which is inversely related to the degradation efficiency of ACN. As pH is the highly significant factor, so maximum degradation was achieved at pH 7.0 and 1.48 g/L ZnO dose with minimum value of R.

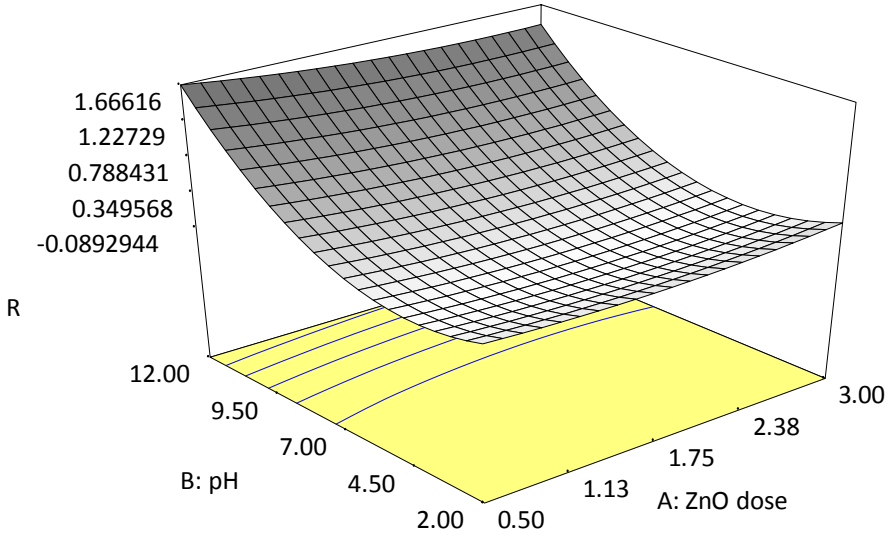


Fig 4.11(a) Effect of pH and ZnO dose on degradation efficiency of ACN
R= 1.0/Sqrt(%deg eff.), X= A: ZnO dose, Y= B:pH, Actual Factor C: H_2O_2= 4.22 mM/L

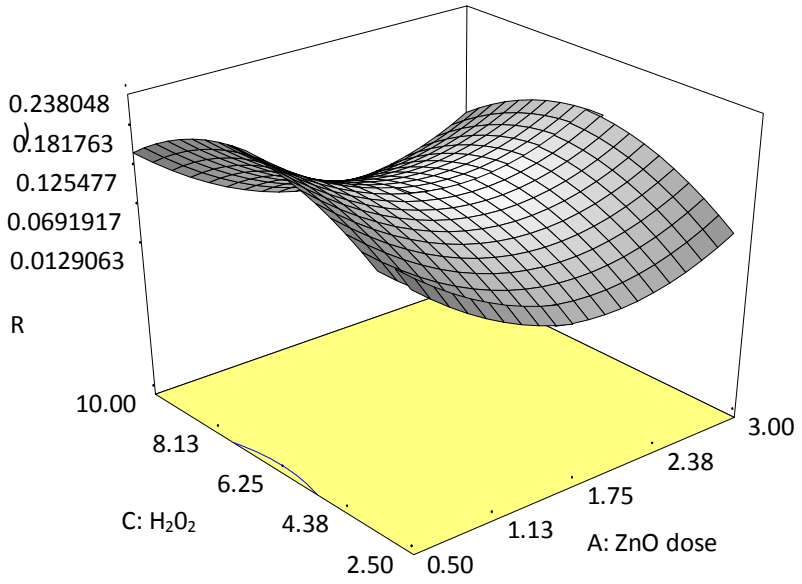


Fig 4.11(b) Effect of H_2O_2 and ZnO dose on degradation efficiency of ACN
R= 1.0/Sqrt(% deg eff.), X= A: ZnO dose, Y=C: H_2O_2, Actual Factor B: pH=7.00

The effect of ZnO dose and H_2O_2 on response (R) = 1.0/Sqrt (% deg eff.) is shown in Fig 4.11(b). As the ZnO dose and H_2O_2 conc. increases, the degradation efficiency increases and at 1.48 g/L ZnO dose and H_2O_2 conc. of 4.2 mM/L, R is minimum and the corresponding degradation efficiency is maximum. Fig 4.11(c) illustrates the effect of H_2O_2 and pH on R= 1.0/Sqrt (% deg eff.). It was found that degradation efficiency increases with increasing pH and H_2O_2 conc. and maximum degradation efficiency was achieved at pH 7.0 and H_2O_2 conc. of 4.2 mM/L with minimum value of R and beyond that degradation efficiency decreases as R increases.

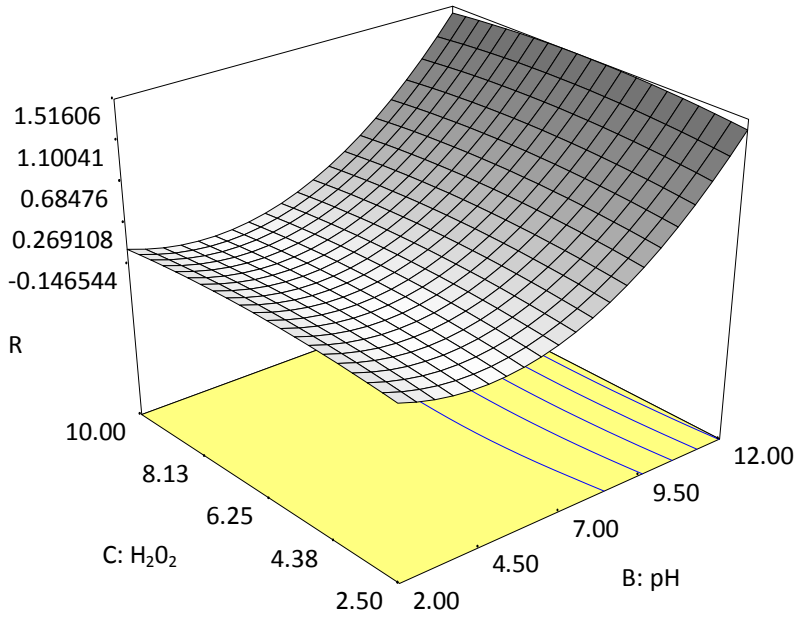


Fig 4.11(c) Effect of H_2O_2 and pH on degradation efficiency of ACN
R= 1.0/Sqrt(%deg eff.), X= B: pH, Y=C: H_2O_2, Actual Factor B: ZnO dose= 1.48 g/L

The optimum conditions for the degradation of ACN were found to be ZnO dose (1.48 g/L), pH (7.00) and H_2O_2 concentration (4.22 mM/L). To confirm the adequacy of the model for predicting the maximum percentage degradation of ACN, a verification experiment was carried out under the optimum conditions. A maximum degradation of 89.6% was obtained from the experiment, as shown in Table 4.4. The good agreement between the predicted value and the experimental value confirms the validity of the model for stimulating the photocatalytic degradation of ACN.

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

		ACN degradation (%)	
Variables	Optimum value	Predictive	Experimental
ZnO dose(g/L)	1.48	89.9%	89.6%
pH	7.00		
H_20_2 conc. (mM/L)	4.22		

The results are in agreement with *Tantriratna et. al., 2011* where BBD based on RSM was applied for the UV phototocatalytic degradation of paraquat and the results indicated that the quadratic model fitted well with the experimental data and the good agreement between the predicted and the experimental values confirmed the validity of the model.

CHAPTER 5

CONCLUSION

Heterogeneous photocatalytic process has been proved to be efficient 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 Acrylonitrile, which is listed third in the EPA list of 129 priority pollutants, typically found in acrylic industry wastewater has been successfully achieved using ZnO and TiO_2. The effect of varying various parameters like catalyst dose, pH, area to volume ratio, UV intensity, oxidant concentration (H_2O_2 and NaOCl) etc. has been investigated. With 50 mg/L ACN concentration, ZnO dose was optimized to be 1.5 g/L, at operating pH 8.0 in the presence of 5 mM/L H_2O_2. In case of TiO_2, the optimized conditions were 1.5 g/L catalyst dose and pH 4.0 in the presence of 5 mM/L NaOCl. 78.9% and 71.1% degradation efficiency has been observed with ZnO and TiO_2, respectively under the optimized conditions in 30 min of UV irradiation. Hydrogen peroxide (H_2O_2) used as an oxidant, has proved to be better oxidant than NaOCl since NaOCl had shown no significant effect with ZnO. The results clearly demonstrate that ZnO exhibits better photocatalytic activity as compared to TiO_2 in the photodegradation of ACN. The experiments were also carried out with solar light under optimized conditions (1.5 g/L ZnO, pH 8.0 in the presence of 5 mM/L H_2O_2 and 1.5 g/L TiO_2, pH 4.0 in the presence of 5 mM/L NaOCl) where 82% and 78.4% degradation efficiency was achieved after 30 min 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. The influence of mixed catalyst was also investigated where the results showed that 100% pure ZnO was most effective for the degradation of ACN. Box Behnken design based on response surface methodology has been applied to further optimize the conditions of ACN degradation using ZnO. Three independent variables were assigned as the factor limits, namely ZnO dose (0.5-3.0g/L), pH (2-12) and H_2O_2 dose (2.5-10 mM/L). The optimum conditions that yielded the maximum degradation efficiency of ACN (89.6%) were 1.48 g/L ZnO dose, pH 7.0 and 4.2 mM/L H_2O_2 concentration. The quadratic model fitted well with the experimental data with R^2 and R^2 adjusted correlation coefficients of 0.9878 and 0.9720, respectively. Hence, it can be concluded that photocatalytic process in tandem with solar light can be efficiently and cost effectively used for the degradation of ACN.

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