COMPARATIVE STUDIES ON THE PHOTOCATALYTIC DEGRADATION OF 2,4,6-TRICHLOROPHENOL UNDER VARIOUS IRRADIATION SOURCES

Dissertation

Submitted in partial fulfillment of the requirement for the award of degree of

Masters of Technology
in
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By

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CERTIFICATE

This is to certify that thesis entitled, “**Comparative Studies On The Photocatalytic Degradation Of 2,4,6-Trichlorophenol Under Various Irradiation Sources** “submitted by Ms. Navdeep Kaur in partial fulfillment of the requirements for the award of Masters in Technology Degree in Environmental Science & Technology at Thapar University, Patialais an authentic work carried out by her under our supervision and guidance.

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

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DECLARATION

I, the undersigned, hereby declare that the research work presented in the M.Tech project entitled "**Comparative Studies On The Photocatalytic degradation Of 2,4,6-trichlorophenol Under Various Irradiation Sources**" has been carried out by me under the supervision and guidance of *Dr.Amit Dhir,* School of Energy and Environment, Thapar University, Patiala. Further, I declare that no part of this Dissertation has been submitted for a degree or any other qualification of any other university or examining body in India/elsewhere.

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Navdeep Kaur

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ABSTRACT

With the increasing industrialization because of the development taking place all around the globe the large amount of industrial waste water is being produced and discharged in nearby water streams. Restoring waste water quality is essential to avoid further pollution of the environment. Biodegradable pollutants present in industrial wastewater can be treated by various biological treatment technologies available and are already being used, but there are few biorecalcitrant organic contaminants which can't be degraded in conventional waste water treatment plants and need special attention. AOPs are the promising technologies which degrade organic compound by hydroxyl radicals. The versatility of AOPs is also enhanced by the fact that they offer different possible ways for OH radical production, thus allowing a better compliance with the specific treatment requirements. Among AOPs heterogeneous photocatalysis has been emerged as an effective way for degradation of organic contaminants.It involes the acceleration of the photoreaction in the presence of semiconductor, photocatalyst and UV irradiation.Chlorophenols (CPs) are a group of special interest due to their high toxicity and low biodegradability. CPs are resistant to biodegradability and even a low concentration can pose health problem. 2,4,6-trichlorophenol was chosen as a model compound, which is also listed in EPA's list of priority pollutants. 2,4,6-trichlorophenol which(TCP) is used as a wood and glue preservative, as an antimildew agent for textiles, in pesticide formulations (herbicides, fungicides, bactericides) and in leather tanning and fishing industries. It has been detected in the emission from fossil fuel combustion, municipal waste incineration, and chlorination of water containing phenols or certain aromatic acids with hypochlorite or during the disinfection of drinking water sources, river water, landfill leachate, chemical plant and sew-age treatment plant effluents and in ambient air. 2,4,6-TCP is a toxic, mutagenic and carcinogenic pollutant. 2,4,6-trichlorophenol is a weak acid which can easily permeate into the human skin in vitro and is readily absorbed by the gastro-intestinal tract. It is also very harmful to the aquatic life if it is discharged into the river, lake and sea as well. The stable carbon-chlorine bond and the position of chlorine atoms relative to the hydroxyl group are responsible for their toxicity, carcinogenic properties, structural stabilization and persistence in the environment, making the removal of 2,4,6-trichlorophenol from the environment very crucial.

The photocatalytic degradation of 2,4,6-trichlorophenol was carried out in slurry mode in a photoreactor. The target was to compare the degradation efficiency among different irradiation

sources. The UV/Vis spectrophotometer was used for analysing the concentration of 2,4,6-trichlorophenol in solution at different time interval during the experiment. The degradation was examined in terms of change in absorbance at 207nm.First the degradation was accessed at different catalyst dose and pH and the optimum value as found. The optimized catalyst dose (TiO_2) &pH was found to be 1g/L and pH was 4.5respectively. The degradation with 1g/L catalyst dose and pH 4.5 under UV was found to be 84.2% and under sunlight was77.5% after 6hr of exposure. The results exhibit that the degradation was higher in case of direct UV exposure than by exposure under sunlight followed by exposure under visible light (53.1%) and least in dark conditions (47.5%). From the results it is clear that sunlight is the cheaper and efficient alternative but its non-availability throughout the day, and dependence on topography etc. are the factors which doesn't allow it to be chosen as the irradiation source making UV exposure to chosen as an option. Further under UV irradiation two different irradiation sources i.e.UV tubes and UV LEDs were used. The degradation in UV tube(64 watt) reactor was 68.4% and in UV LED(10 watt) reactor was 62.8% at comparable intensity. From the results it is clear that UV LEDs are effective in degradation of the recalcitrant compound at reduced recurring cost. Further, the cost effectiveness can be achieved using more intense LEDs (as these can be customized as per the requirement) which will ultimately means the industrial applicability of AOPs as economic process.

LIST OF FIGURES

ABBREVIATIONS

- AOPs-Advanced Oxidation Processes
- Approx..-approximately
- CPs-Chlorophenols
- e.g- Example
- eq-equation
- Fig-Figure
- i.e.-That is
- LED- Light Emitting Diode
- resp- respectively.
- TCP- Trichlorophenol
- UV -Ultraviolet
- w.r.t- with respect to

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Water shortage is one of the greatest concerns of the beginning of this century. New industries are being set up at a great pace due to globalization, urbanization and industrialization which along with growth and production also leads to the generation of large amount of wastewater. Restoring water quality is essential to avoid further pollution of the environment and for its reuse in order to decrease freshwater consumption. Biodegradable pollutants can be treated by various treatment technologies available and are already being used but there are few recalcitrant organic contaminants which can’t be treated in conventional waste water treatment plants. Among such pollutants one class is of chlorophenols which are a group of chemicals in which chlorines (between one and five) have been added to phenol. In all, there are 19 different chlorophenols out of which 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,5-trichlorophenol, 2,4,6--trichlorophenol, 2,3,4,5-tetrachlorophenol, 2,3,4,6-tetrachlorophenol, and 2,3,5,6-tetrachlorophenol, pentachlorophenols are found in EPA list of priority pollutants.

chlorophenols(CPs) are used worldwide as broad-spectrum biocides and antisapstain fungicides in the cut-lumber industry and typically used as intermediates in making preservatives, antiseptics, disinfectants, insecticides, other organic compounds etc. These are also found in waste, waters of petroleum industries, landfills leachate, mining, pesticide industry,pharmaceutical, dye processing, textile, paper and pulp industry. CPs have a long half-life in water and organic sediments and due to their numerous origins, can be found in waste water, ground water, or soil.

Chlorophenols(CPs) are a group of special interest due to their high toxicity and low biodegradability. CPs are resistant to biodegradability and even a low concentration can pose serious health problem. These are lipophobic and can transport through cell membrane where they get bioaccumulated, have high endocrine distrupting potency and genotoxicity.

1.2 TREATMENT TECHNOLOGIES

There is growing interest in developing new and efficient technologies for environmental remediation and protection. As the pollution increases, there is increased environmental awareness too. Several technologies for the degradation of such pollutants has drawn attention e.g.: physical, chemical, biological and their combinations. For biological treatments sludge disposal and lower reaction rates are the problem, also a strict control over parameters like pH, temperature, nutrients etc. is required. There are compounds which can't be treated using these technologies especially in lower concentrations. Available wastewater technologies such as adsorption, coagulation etc. concentrate the pollutants but do not completely eliminate them. Other traditional water treatment methods such as filtration, membrane technologies involve high operation cost and could produce toxic pollutants. These toxic contaminants can be redundant and had been fretful. Chlorination is widely used disinfection process but the by-products are harmful. Because of limitation of above discussed treatment technologies, there is need to focus on environmental friendly technologies for the treatment of such biorecalcitrants. One of the most trending and promising technology these days is advanced oxidation processes to achieve complete degradation of pollutants without generation of hazardous by-products.

1.3 ADVANCED OXIDATION PROCESSES

AOPs constitute a promising technology for the treatment of wastewaters containing non-biodegradable and toxic organic compounds. These (AOPs) have been proven to be powerful and efficient treatment methods for degrading recalcitrant materials or mineralizing stable, inhibitory, or toxic contaminants. AOPs have shown great potential in treating wastewater for the reason that the organic components that are thermodynamically unstable to the oxidation are not transferred from one phase to another. Among many alternative method available for the destruction of chlorophenols, AOPs are suitable and considered as a highly competitive water treatment technology. All AOPs are designed to produce hydroxyl radicals, which act with high efficiency to destroy organic compounds. These technologies could be applied for contaminated groundwater, surface water, wastewaters containing recalcitrant, inhibitory and toxic compounds with low biodegradability as well as for the purification and disinfection of drinking water. AOPs include ozone (O_3), ultraviolet (UV),hydrogenperoxide(H_2O_2) and/or catalyst to offer a powerful water treatment solution for the reduction and/or removal of residual organic compounds as measuredby COD, BOD or TOC. The versatility of AOPs is also enhanced by the fact that they offer different possible ways for OH radicals production, thus, allowing a better compliance with the specific treatment requirements.

Advanced Oxidation Processes are recognized in the early 1970s as the promising field of study for pollutant degradation, and much research and development work is being undertaken to commercialize some of these processes. AOPs have found applications as diverse as ground water treatment, municipal wastewater sludge destruction and VOCs control. AOPs can mainly be divided into two categories, homogeneous AOPs and heterogeneous AOPs.

1.3.1 HOMOGENOUS AOPs

Homogenous AOPs (single phase system) used to treat contaminated water and involves the use of an oxidant to generate hydroxyl radical ($^{\bullet}HO$) in the presence of UV light which attacks the organic pollutant to start the reaction. There are number of techniques available in literature which are really promising and small changes in the processes lead to the discovery of a new AOP techniques. Few of the techniques are stated below:

Fenton Process involves production of OH radicals by Fenton reagent occurs by means of addition of H_2O_2 to Fe^{2+} salts.($H_2O_2 + Fe^{2+} \rightarrow OH\bullet + OH^- + Fe^{3+}$).Another widely used homogeneous AOP is photo-Fenton process, which is a UV-induced degradation process which uses metal ions as catalysts, which, depending on the treatment objective and the substance of the wastewater, may lead to a better process efficiency. It uses solutions containing iron are used as catalysts. On the basis of various photoreactions, hydroxyl radicals are generated via photoreductionof the metal ions and initiate the degradation process. To avoid the disadvantages of traditional Fenton oxidation such as potential risk in transportation of H_2O_2, a loss of reactive activity and sludge production, a modified process called Electro-Fenton method (EF) was developed. The EF method has the advantage of allowing a better control of hydroxyl radical production; in the EF method, soluble Fe^{3+} can be cathodically reduced to Fe^{2+} which is known as electrochemical catalysis with. Thus, the fast generation of Fe^{2+} accelerates the production of •OH. The electro- Fenton process can generate •OH by the simultaneous electrochemical reduction of O_2 in the presence of catalytic amount of ferrous ions.Ozoneis an unstable molecule which readily gives up one atom of oxygen providing a powerful oxidizing agent and the process is named as Ozonation. Other widely used homogenous AOPs uses UV radiation, Ultrasound energy and Electrical energy, an overview is given in Fig 1.1.

1.3.2 HETEROGENOUS AOPs

Heterogenous AOPs (bi-phase or multi-phased system) employs semiconductors as photocatalyst and has established its efficiency in degrading a wide variety of refractory into readily biodegradable compounds and eventually mineralize them into harmless end products. Semiconductor photocatalytic degradation has shown a great potential as an environmental friendly and sustainable treatment technology to align with the“zero” waste scheme in the water/wastewater industry. The widely used catalysts for the process are TiO_2, ZnO, Fe_2O_3, CdS, ZnS etc. Many doped catalysts are also being used these days. The process can be driven by various irradiation sources like UV, solar, visible light. The ability of this advanced oxidation technology has been widely demonstrated to remove persistent organic compounds and microorganisms in water. Various AOPs have been demonstrated in Fig1.1.

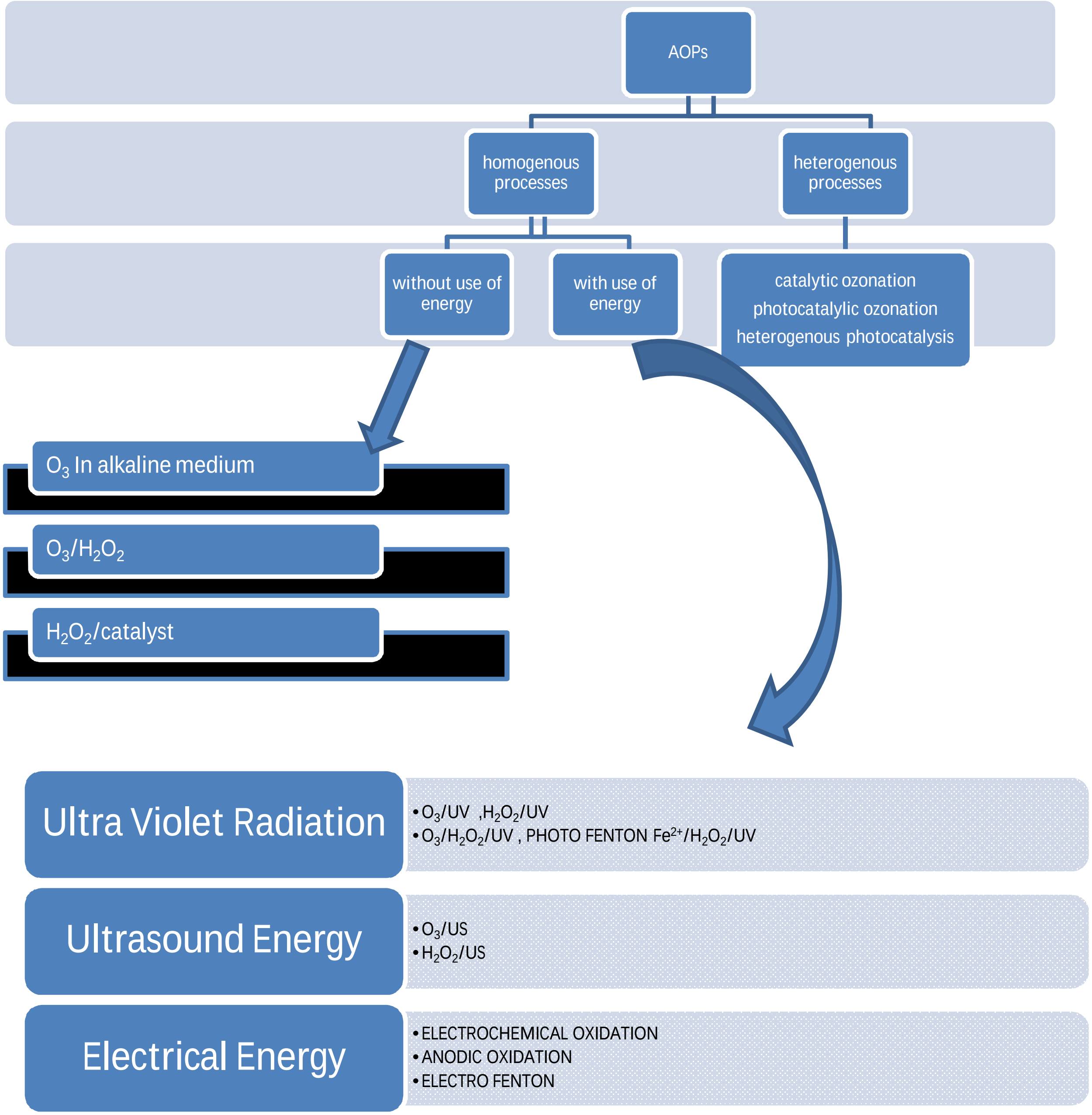

Fig 1.1.Various types of Advanced Oxidation Processes(chart form)

Fig 1.2 briefly demonstrates the application of aops for waste water treatment

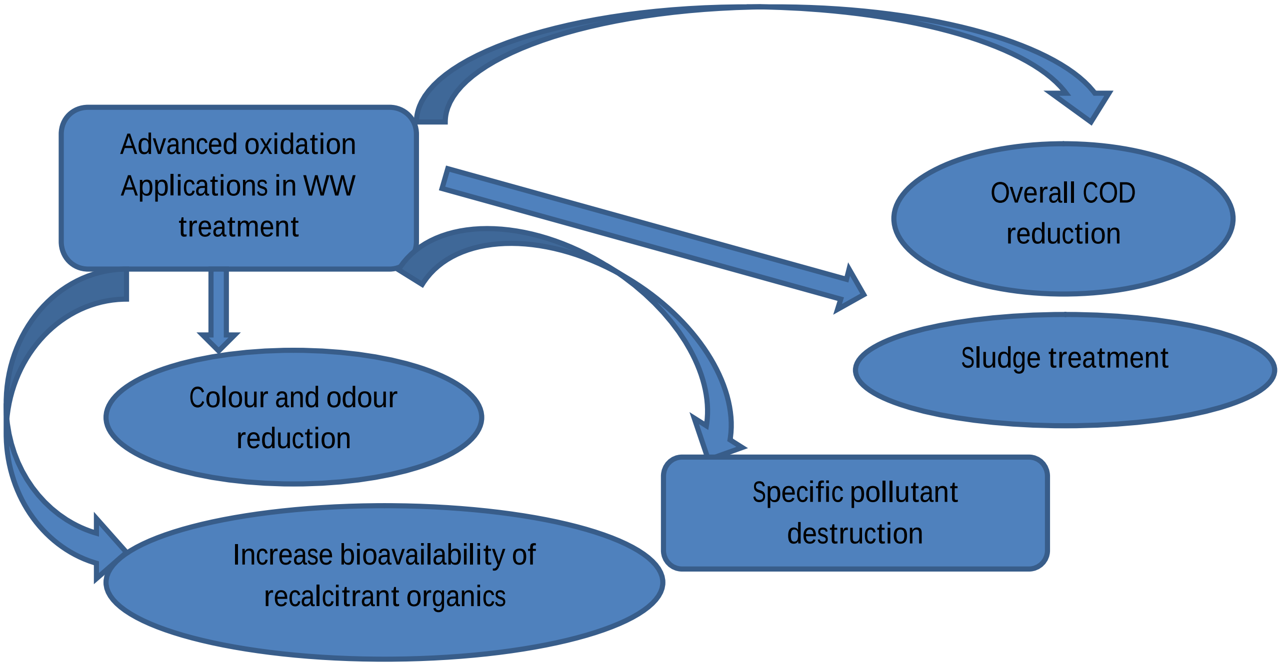

Fig 1.2 Applications of AOPs represented in diagram form.

1.4 COMPONENTS OF PHOTOCATALYTIC PROCESS.

Important and fundamental elements for successful photocatalytic system are the type of photo catalyst, the light source and the reactor configuration.

1.4.1 PHOTOCATALYST

A broad range of semiconductors may be used for photocatalytic oxidation of organic pollutants such as TiO_2, ZnO, ZnS and CdS and other doped catalysts etc. Among these TiO_2 has received the greatest interest in research of photocatalysis technology. Titanium Dioxide exhibits strong oxidizing photoactivity when irradiated by UV ray. TiO_2 has high oxidizing ability as oxidative OH radicals produced by TiO_2 have high oxidation potential. It is chemically stable and not dissolved in water although some other semi conductive photocatalytic compounds are dissolved when irradiated in water. It is regarded as a safe and inert material in general.

1.4.2 MECHANISM OF PHOTOCATALYTIC OXIDATION PROCESS

In the photocatalytic oxidation process, organic pollutants are degraded in the presence of photocatalyst (semiconductor), an energetic light source and an oxidizing agent such as oxygen or air. With the light energy, photocatalyst decomposes pollutants mainly made of organic compounds into carbon dioxide and water. A semiconductor is described by an electronic band structure in which highest energy band is called valence band(vb) and the lowest empty band is called as conduction band (cb) and the difference in vb and cb is band gap(bg).

When a photocatalytic surface is illuminated by light (e.g.-UV) with energy equal to or greater than bandgap, it excites the electron in the valence band to the conduction band resulting in the generation of electron-hole pair(positive hole in valence band and an electron in conduction band). The positive hole(p+) oxidizes either pollutant directly or water to produce hydroxyl radicals, whereas the electron in conduction band reduces oxygen adsorbed to photocatalyst.

The mechanism described above can be represented by equations given below

$$\text{SC(photocatalyst)} \longrightarrow (e^-) + (p^+) \qquad (1)$$

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

$$p^+ + \text{organic compound} \longrightarrow CO_2 \qquad (3)$$

$$p^+ + H_2O \longrightarrow HO^{\cdot} + H^+ \quad (4)$$

$$HO^{\cdot} + \text{organic compound} \longrightarrow CO_2 \qquad (5)$$

In the photocatalytic Degradation of pollutants, when the reduction of oxygen (eq.2) and oxidation of pollutant (eq.3&4) do not proceed simultaneously, there is an electron accumulation in the conduction band, thereby causing recombination of electron and positive hole. Therefore, efficient consumption of electron is essential to promote photocatalytic oxidation. The Fig 1.3 shows the mechanism of photocatalysis.

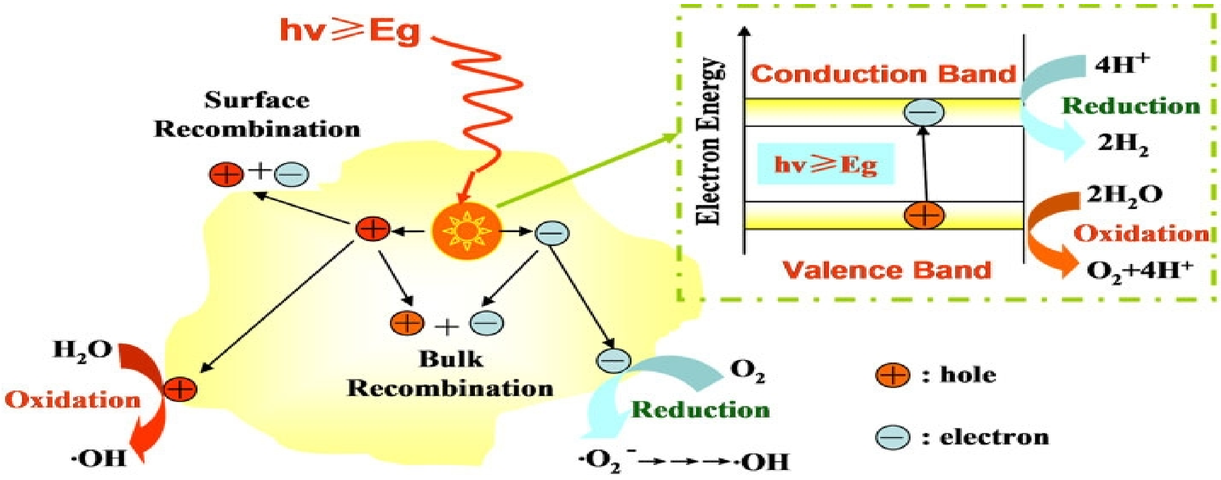

Fig1.3 Schematic representation of the mechanism of photocatalytic activity (photochemical activation and electron –hole formation)

1.4.3 IRRADIATION SOURCES

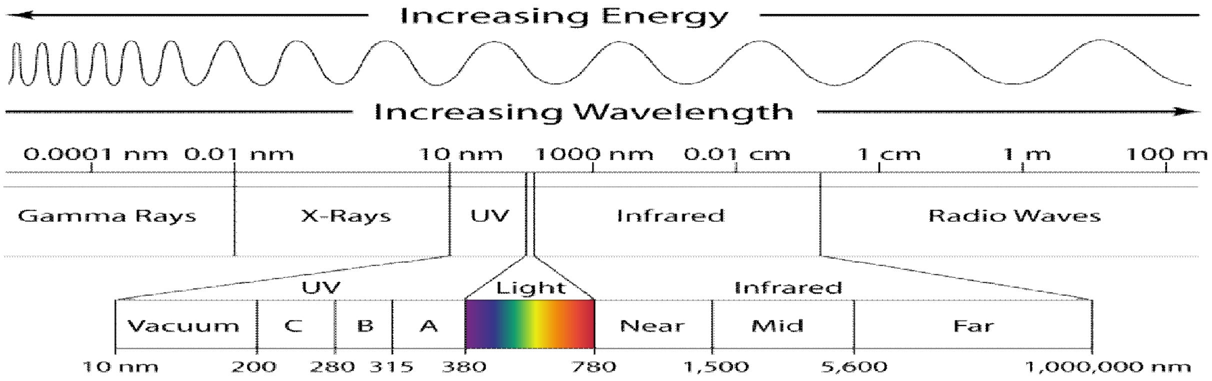

Fig 1.4 The electromagnetic spectra showing wavelenght corresponding to different components.

Sunlight Light: Sunlight is broken down into three major components: (1) visible light, with wavelengths between 0.4 and 0.8 micrometre, (2) ultraviolet light, with wavelengths shorter than 0.4 micrometre, and (3) infrared radiation, with wavelengths longer than 0.8 micrometre. The visible portion constitutes nearly half of the total radiation received at the surface of the Earth. It has 8% UV light reaching earth surface which can be used as irradiation source. AOP in the presence of sunlight is a cheap process. But the sunlight is not available throughout the day and all time of the year. Even on the sunny day it is available only for around 6 hours, that too with varying intensity. Cloudy skies reduce its effectiveness and huge areas of land are required to capture the solar energy. As the industries operate round the clock so there is continuous generation of wastewater and it requires a reliable disposal unit before discarding the waste so as to meet the discharge standards. Hence sunlight cannot be used as only irradiation source for the photocatalytic degradation.

UV Light: The UV spectrum encompasses all wavelengths between 100nm and 400nm and is commonly broken down into three distinct subfields:

- UV-A: 315-400 nanometers (also known as long wave UV),
- UV-B: 280-315 nanometers (also known as medium wave UV), and
- UV-C: 100-280 nanometers (also known as short wave UV).

1.4.4 UV LEDs AS A LIGHT SOURCE

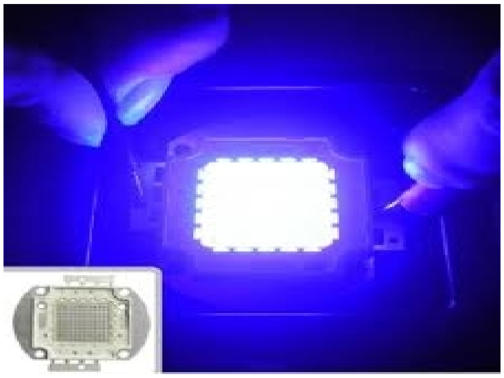

Fig 1.5 Picture of irradiated UV LED.

UV LEDs can shrink the size and cost of sterilization systems for medical and food industries as well as biological and chemical analysis. UV-C, sometimes called deep UV (DUV), is the band generally used for sterilization, and DUV LEDs have advantages over the mercury vapor lamps currently used in water purification systems. Semiconductor-based sterilization reactors can be smaller, can potentially cost less, contain no mercury, and could be more easily powered by low-voltage sources such as batteries or solar panels. UV LEDs also provide significant performance benefits compared to alternative technologies. UV LEDs can provide tight beam angle and uniform beam pattern. Because of the challenges in optical efficiency inherent to UV LEDs, most design engineers are looking for a specific beam angle that maximizes the output over the targeted area. With ordinary UV lamps, the engineer has to rely on flooding the area with enough light to try and achieve the right combination of uniformity and intensity. With UV LEDs, the lensing allows for a much tighter emission angle, allowing the majority of the UV LEDs output to be focused directly where it is required. To match this performance, alternate technologies would require secondary lenses with additional cost and space requirements. The combination of tight beam angle and uniform beam patterns without the need for a secondary lens, reduced energy consumption and enhanced durability allows UV LEDs to provide up to 50% cost savings compared to CCFL technology

Other advantages of LEDs are:

- Intensity of light doesn't change with depth
- Recent technological advancements are moving the UV LED market segment into a whole new level of product innovation and performance. Design engineers are taking note as emerging UV LED technologies generate significant cost, energy, and space savings compared to alternate technologies
- Environmental Impact - Lower energy consumption, Reduced waste and no hazardous materials
- Enhanced Life Span: Over the last ten years, UV LED technology has been challenged by insufficient life spans. New technology has emerged that has solved this engineering challenge. For example the epoxy lenses were replaced with a robust TO-46 package with glass lens allowing the technology to last at least ten times longer, providing a life span of more than 50,000 hours. UV LED technology has become an attractive option for a growing number of applications.

Moreover the flexibility offered in case of LEDs is more as these can be customized according to the requirement of the user. There are many manufacturing units offering variety of manufacturing offers for e.g.SETi (sensor electronic technology INC.),Tao Yuan electron (HK) limited. etc.

CHAPTER 2

REVIEW OF LITERATURE

Advanced Oxidation Processes are recognized in the early 1970s as the promising field of study for pollutant degradation. Lot of research and development work is being undertaken to commercialize some of these processes. AOPs have been widely studied for the degradation of diverse types of industrial wastewaters. The influence of different AOP on the degradation and mineralization of several different classes of organic pollutants such as pesticides, pharmaceutical formulations and dyes is widely studied. AOP and their applications have attracted the attention of both the scientific community and of corporations interested in their commercialization. The search using "advanced oxidation processes”, yields approximately 840 publications (source: Science Finder Scholar database (version 2012)) and which nicely reflects the rapid growth in interest AOP, given the unique characteristics and the versatility of application of AOP.

2.1 PHOTOCATALYTIC DEGRADATION OF CHLOROPHENOLS

Phenols and their chlorinated derivatives represent one of the most abundant families of industrial toxic compounds which are resistant to biodegradation and persist in the environment for long periods. Several strategies have been followed to remove CPs from the environment. Heterogeneous photocatalysis is one of the most promising techniques to completely destroy CPs (HuanhuanJi et al, 2013) .Various processes which allow the efficient degradation of a variety of organic pollutants at low concentration levels in aqueous wastes had been studied. Mogyorósiet al.,(2002) studied the removal and decomposition of 2-chlorophenol (2-CP) and degradation of 2-CP by three different oxidation processes were compared: direct photolysis, heterogeneous photocatalysis in a TiO_2 suspension, and the decomposition of substrate adsorbed on HDPM in the presence of TiO_2 and the effect of catalyst load on photocatalytic degradation of 2-chlorophenol was studied by (Barakat et al., 2005). The use of oxidants is known to aid the increase in rate of reaction.Momani et al., (2004) investigated advanced oxidation processes (AOPs) using UV, UV/H_2O_2, Fenton and photo-Fenton treatment laboratory scale for aqueous solutions of 2,4-dichlorophenol (DCP). The effects on degradation of different reactant concentrations, irradiation time, temperature and pH were assessed. All the studies primarily focus on optimizing the process parameters and different combinations were being tried to bring down the cost. The photochemical oxidation of phenols and chlorophenols was studied using UV irradiation, hydrogen peroxide and TiO_2 and a rough comparison of energy consumption shows that UV/H_2O_2/TiO_2 process reduced the energy consumption by 40-50% compared with the UV/H_2O_2 and UV/TiO_2 processes by (Dixit etal.,2010). Catalyst modification is one of the ways to bring down the degradation time, doping of catalysts with some metal/non-metal/ion is known to increase the reaction rate. Ghorai in (2011) studied the photocatalytic degradation of 4-chlorophenol (4-CP) in aqueous solution using Cu-MoO_4^- doped TiO_2 nanoparticles under Visible light radiation. The photocatalysts were synthesized by chemical route from TiO_2 with different concentration of $CuMoO_4$. The photodegradation process was optimized by using $Cu_xMo_xTi_{1-x}O_6$ (x = 0.05) catalyst at a concentration level of 1 g/l. Parameters affecting the photocatalytic process such as catalyst loading, concentration of the catalyst and the dopant concentration, solution pH, and concentration of 4-CP have been investigated. The photochemical oxidation of 4-chlorophenol in aqueous solutions in a batch reactor using ultraviolet irradiation, hydrogen peroxide and nickel oxide was investigated and the efficiency of the system was evaluated with respect to reaction time, pH, feed concentration of reactants, catalyst load, light intensity, and the reaction rate constant. The optimum conditions were found out by (Alimoradzadeh et al., 2012). The photocatalytic degradation of 2,6-DCP in aqueous phase using titania (PC-105) as a photocatalyst under UV irradiation was studied the rate of degradation was estimated from residual concentration spectrophotometrically for process optimization, The photocatalytic degradation of chlorophenols (2-chlorophenol or 2,4-dichlorophenol) evaluated under direct solar radiation using commercial ZnO catalyst and the effects of several parameters such as a catalyst loading, pH of solution and initial concentration on the degradation process were investigated.(Kansal et al., 2012;Ba-Abbad et al.,2013).

2.2 DEGRADATION OF 2,4,6-trichlorophenol(TCP)

Among the chlorophenols, 2,4,6-trichlorophenol is one of the most representative compounds of this group it is present in several wastewaters and specially abundant in effluents from the pulp bleaching process, and it is soluble enough at ambient temperatures to exceed EPA standards. (Benitez et al, 1999). The stable carbon-chlorine bond and the position of chlorine atoms relative to the hydroxyl group are responsible for toxicity, carcinogenic properties, structural stabilization of 2,4,6- trichlorophenolwhich makes the removal of 2,4,6-TCP from the environment very crucial. Besides, 2,4,6-TCP has been classified as one of the primary pollutants as enacted by the Department of Environment (DOE), Malaysia in Environmental Quality Act 1979 (Sewage and Industrial Effluent). The chemical decomposition of aqueous solutions of various chlorophenolslike 4-chlorophenol(4-CP), 2,4-dichlorophenol (2-DCP), 2,4,6-trichlorophenol

(2,4,6-TCP) and 2,3,4,6-tetrachlorophenol (2,3,4,6-TeCP), which are environmental priority pollutants was studied by means of single oxidant (hydrogen peroxide, UV radiation, Fenton's reagent and ozone), and by the Advanced Oxidation Processes (AOPs) constituted by combinations of these oxidants (UV/H_2O_2, UV/Fenton's reagent and O_3/UV) (Benitez et al., 2000). The versatility of AOP is also enhanced by the fact that they offer different possible ways for OH radical production thus allowing a better compliance with the specific treatment requirements so various alternate technologies can be developed by making small change in the process. Chen et al., (2002) studied the synergistic effect due to the application of ultrasound on the photocatalytic degradation of phenol and chlorophenols, in the presence of TiO_2 suspensions in sonophotocatalytic reactor. Chlorophenols namely, 4-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenolthe study suggested that the generation of chloride radicals ($Cl^{\bullet}$) might assist the degradation of the organic compounds before substantial chloride anions (Cl^-) were formed to inhibit the photocatalysis and the solubility of the examined organic compounds has a significant influence on the performances of the photocatalytic and sonochemical reactions. Thereafter doped catalysts have been used to enhance the degradation efficiency of organic compound. A series of Ag-TiO_2nanocatalysts by a sol–gel method with a doping content up to 2 w%-Ag. The photocatalytic activity of the Ag-TiO_2 was evaluated in the 2,4,6-trichlorophenol (TCP) degradation and mineralization in aqueous solution under UV-A illumination. The effect of La loading on the photocatalytic activity of La-doped ZnO in the degradation of 2,4,6-trichlorophenol (TCP) was studied and the results were compared with the pure ZnO and TiO_2.(Rengaraj et al., 2006; Anandan et al., 2007) . By thermal evaporation and sol-gel coating techniques nanostructured thin ZnO films had been fabricated and used in mineralization of 2,4,6-TCP under UV irradiation. (Aal et al., 2009).Zhang et al., (2011) used an integrated photocatalytic-biological reactor (IPBR) for accelerated degradation and mineralization of 2,4,6-trichlorophenol (TCP) through simultaneous, intimate coupling of photocatalysis and biodegradation in one reactor. Hassan et al., (2011) studied the photocatalytic activity of pure TiO_2 and silver doped TiO_2 , Ag-TiO_2 used for the photocatalytic degradation of 2,4-dichlorphenol (99% degradation), 2,5-dichlorophenol (98% degradation), and 2,4,6-trichlorophenol (96% degradation) in 1 hour. The degradation time of 2,4,6-trichlorophenol could further brought down to 0.70h by using Graphitic carbon nitride g-C3N4. (Huanhuan et al., 2012)

2.3 PHOTOCATALYTIC DEGRADATION USING LEDs

Continuous effort is being put on to bring down the cost of degradation process for various pollutants in AOPs .The recent advancement in this field is use of light emitting diodes (LEDs) as alternative to traditional mercury lamps for the removal of micropollutants by Advanced Oxidation Processesdue to their low energy consumption and potential for high efficiency and long lifetime. Dai et al., (2010) did study on the Development of UV-LED/TiO_2Device and their applications for Photocatalytic Degradation of Methylene Blue .The decomposition in aqueous solution by TiO_2 photocatalytic process with the UV-LED was found to be technically feasible. The results have shown a promising technique for organic waste-water treatment by the UV-LED/TiO_2 method. Another similar work where LEDs has been used as irradiation source is done by Rojviroon et al., (2012). They checkedthe photocatalytic Activity of Toluene under UV-LED Light with TiO_2 Thin Films. The kinetics of the photocatalytic processes under a UV-LED light source was explained by the Langmuir-Hinshelwood kinetic model and observed that the increase in Fe^{3+} dopant concentration could enhance the photocatalytic activity of toluene decomposition as a result of lower optical band gaps, smaller grain size, and higher surface area. Autin et al., (2013) observed the growing interest in using light emitting diodes (LEDs) as alternative to traditional mercury lamps for the removal of micropollutants by advanced oxidation processes due to their low energy consumption and potential for high efficiency and long lifetime and did evaluation of a UV-light emitting diodes unit for the removal of micropollutants in water for low energy advanced oxidation processesstudied the Application of Photocatalysts and LED Light Sources in Drinking Water Treatment was studied by (Izadifardet al., 2013).

2.4 GAPS IN LITERATURE

AOPs permit the conversion of organic pollutants with a wide range of chemical structures into substances that are less toxic and/or more readily biodegradable. Homogeneous and heterogeneous processes have been widely used for degradation of recalcitrant compounds but still literature on this aspect has some lacuna.

- The AOPs using UV irradiation for producing radical can't be implemented at large scale due to large initial and recurring cost. Solar light as a source of UV poses problems as it is not available throughout the day varies with season and with topography.
- Due to scale up problems and the design of photoreactors, the industrial implementation remains limited
- Very limited reports on degradation of chlorophenols using UV-LED as light source is available. LEDs are being explored but major breakthroughs are still lacking.
- Studies focusing on performance improvement by optimising photon transfer remain limited and needs to be done explored.

Research in photochemical and photocatalytic technology is very promising for the development of viable alternatives for the treatment of polluted waters. Keeping in view the above mentioned technological gaps, further study is being expanded to investigate the photocatalytic degradation using UV LEDs as irradiation source. And comparison among the degradation using various irradiation sources is done in the present study.

2.5 OBJECTIVES OF PRESENT STUDY

New economically viable and efficient methods for degradation using AOPs for pollution control and prevention arerequired for environmental protection so that the effluent discharge into the environment must have minimal impact on human health, natural resources and the biosphere. The present study is subjected towards finding out the economically viable alternative for the traditional UV sources, which are used for the irradiation in a photocatalytic process so as to commercialize the process. Thus, the objectives of the present study are mentioned below:

- Designing of a photoreactor having UV LED as light source
- Photocatalytic degradation 2,4,6-trichlorophenol using photocatalyst in UV/solar light.
- Comparison of degradation efficiency and cost under UV TUBE photoreactor and UV LED photoreactor

CHAPTER 3

MATERIAL AND METHODS

3.1 MATERIALS

3.1.1 Chemicals and reagents

The model compound used in the present study is 2,4,6-trichlorophenol and was purchased from TCI chemicals ,Tokyo. The photocatalyst used in is TiO_2. Titania P-25(surface area 50m^2/g and average particle size 30nm)was obtained from Degussa, Germany. And all the reagents were prepared in double distilled water. pH of the solutions was adjusted using 1M HCI or 1M NaOH as required in the study.

3.2 INSTRUMENTS AND EQUIPMENT

3.2.1 Photoreactor

For the comparative studies two photoreactors were used, one with UV tube as a light source and other with UV LEDs as irradiation source. The UV tubes has specifications:365nm,32 watt each. UV LEDs were imported from ebay Canada, with specification (10 watt ,365-395nm)

3.2.1.1 UV Tube Photoreactor

UV reactor used was rectangular having dimensions of 45inch*30inch*35inch and was made up of cast iron. Roof of the reactor was made up of wood having provision for seven UV tubes(36 watt each) attached with the roof. Temperature inside the reactor was maintained by an exhaust fan. Four magnetic stirrers were fitted in the reactor to carry out the photocatalytic reaction in slurry mode.

3.2.1.2 UV LED Photoreactor

The reactor having UV LEDs as a irradiation source was made up of wood and had inner lining of cast iron which act as a sink and absorb excessive heat.The dimensions of the container are 45inch*28inch*28inch.The reactor has been divided into three chambers as shown in Fig3.1. The partition was done using sliding cast iron sheets. The whole chamber ispainted black from the innerside.

Fig 3.1 Lab scale UV LED reactor showing the partitions(Front view)

The exhaust fan was provided for removing the heat if produced during run time of the reaction due to stirring.as shown in in Fig 3.1. The fan is provided in the centre chamber which takes out heat from all the compartments of the reactor as there is some space provided behind the parting cast iron sheets for the circulation of air. The 1stchamber of the reactor has UV LED of 10 watt,365 nm as depicted in Fig 3.2

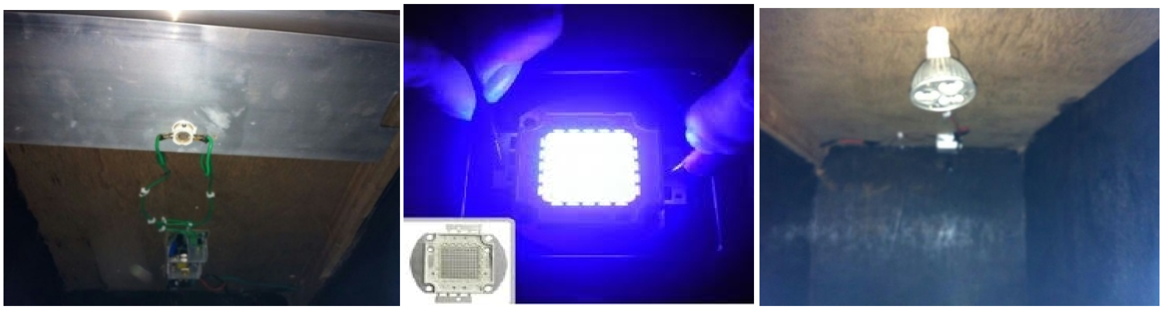

Fig 3.2 The LEDs used as irradiation source for the present study.

2nd chamber of the reactor has to be equipped with another LED yet to be imported and 3rd chamber had LED emitting visible light as shown in Fig 3.2

These LEDs can be changed as per the requirement and even the sliding partition can also be removed making it into a single chamber having more space. Each of three chambers can accommodate 2 reaction assemblies one behind the other. Dimension of each individual chamber is 15inch*28inch*28 inch. Each chamber is fitted with its own individual power input plugs to power magnetic stirrer and aerators. The power input of LEDs and exahust fan is via a switch over the top of the reactor.

3.2.2 Radiometer

Intensity of ultraviolet and solar light was measured using Radiometer(Eppley USA)

3.2.3 pH meter

A digital desktop, pH Meter was used to measure the pH of the solution. Freshly prepared buffer solution of pH 4, 7 and 9 were used to calibrate the instrument from time to time throughout the research work.

3.2.4 UV-Vis Spectrophotometer

The spectrophotometric readings were taken with UV-Vis spectrophotometer(LABINDIA,UV-3200 double beam spectro). The degradation studies were conducted by measuring absorbance in UV-Vis spectrophotometer having a wavelength from 190-1100nm using 1 cm quartz cell at wavelength 207nm.

3.3 METHODS

3.3.1 Preparation of 2,4,6-trichlorophenol(TCP) solution

The concentration of TCP solution used in the experiment was in 10 mg/L i.e. 10ppm. First a stock solution of 30 ppm was prepared by adding 15mg of 2,4,6-trichlorophenol in 1ml ethanol in order to solubilize it, which was then added to distilled water to make its volume upto500ml in volumetric flask. The stock solution was stirred overnight over a magnetic stirrer. From the stock solution, working solution of 10 ppm was prepared by adding 333.4ml of 30ppm TCP into remaining volume of distilled water to make the volume upto 1000ml. The solution was stirrer and used for the experiment.

3.3.2 Standard curve

To make the standard curve various concentrations varying from 0 ppm to 12 ppm were made from 30ppm stock. The complete wavelength scan was done for 2,4,6-trichlorophenol and the maximum absorbance was observed at 207nm So, further readings(absorbance) were taken under UV-Vis spectrophotometer at 207nm throughout the research work.

3.3.3 Slurry mode experiment

For the slurry mode experiment, the photocatalyst in the form of powder was added to a solution which is to be degraded and the solution was kept under constant stirring using magnetic stirrer and aeration was carried out with the help of traditional aerator. The ambient temperature of the reaction vessel and UV chamber was maintained by exhaust fan. The concentration of 2,4,6-trichlorophenol stock solution used in the present study was 10mg/L i.e10 ppm. Photocatalytic experiments were performed under various parametric conditions including varying catalyst dose, pH etc. The aqueous suspension was subjected to irradiation under UV using UV tube and UV LEDs and solar light for fixed interval of time. The solution was withdrawn and was filtered through syringe filter. The degradation studies were conducted by measuring absorbance in UV-Vis spectrophotometer at wavelength 207nm.

3.3.4 Determination of degradation efficiency

The aqueous suspension was magnetically stirred and subjected to irradiation under UV light for a period of 6h. After regular time intervals of 1 h, aliquot was taken out with the help of a syringe and then filtered through a Millipore syringe filter (0.45μm). The degradation of the model compound was evaluated by monitoring absorbance as a function of irradiation-time using spectrophotometer. The degradation efficiency of was studied in terms of changes in absorption spectra recorded at λ_{max} 207 nm.

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 photo irradiation. The experimental medium was extended by varying different parameters like the dosage of photocatalyst, pH of solution, time and different irradiation sources.

3.3.5 Process Economics

In order to sustain the effective running of the industry, the processes must be economically viable. Therefore it is vitally important to assess the economic benefits of using alternate process (here it is the use of alternate UV source i.e UV LEDs) to ensure that the venture is economically viable and sustainable. So, after checking the degradation efficiency under different irradiation sources,the cost incurred for degradation of compound in water under UV Tube and UV LEDs as irradiation source was calculated to see which among the two UV sources is cost effective.

CHAPTER 4

RESULTS AND DISCUSSION

In this chapter the result of photocatalytic degradation of 2,4,6-trichlorophenol carried out using TiO_2 as catalyst under various UV irradiation sources has been discussed.to find the most economic UV source among UV tubes and UV LEDs. The degradation efficiency has been asscessed by varying different process parameters like pH, catalyst dose.

4.1 STANDARD CURVE

The complete wavelength scan was done for 2,4,6-trichlorophenol and the maximum absorbance was observed at 207nm . A standard curve was plotted using the UV spectrometer at wavelength 207 nm to use as a method of detection after treatment The degradation efficiency of the model compound was recorded in terms of change in absorbance of the solution. Fig 4.1 shows the change in absorbance w.r.t concentration generated from measuring the absorbance at pre-determined known concentrations of 2,4,6-trichlorophenol.

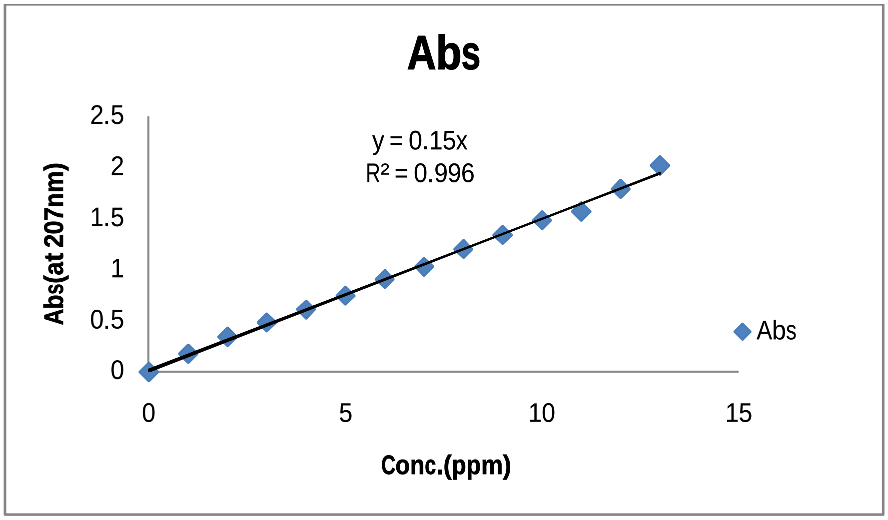

Fig 4.1 Standard curve to evaluate the concentration of 2,4,6-TCP from the absorbance

4.2 PHOTOCATALYTIC DEGRADATION OF 2,4,6-trichlorophenol(TCP)

The experiments were carried out in order to assess the most favorable conditions for the photocatalytic degradation of 2,4,6-trichlorophenol using TiO_2 with varying catalyst dose, pH, light intensity etc.

4.2.1 Catalyst dose

In order to the optimum catalyst dose, experiments were conducted by varying catalyst dose(TiO_2) from 0.5g/L to 2g/L in 10ppm solution of 2,4,6-trichlorophenol at natural pH under UV irradiation . The graph in Fig 4.2 shows the variation of concentration with time at different catalyst dose. The maximum degradation was observed at a catalyst dose of 1g/L after 6 h of UV exposure. The probable reason for the decrease in degradation efficiency might be the decrease in absorbance as the light scattering increases with increased catalyst dose. However, with the increase in catalyst dose beyond 1g/L the degradation efficiency decreases. Similar results have been reported in the study conducted by Kansal et al., 2007 for the Optimization of photocatalytic process parameters for the degradation of 2,4,6-trichlorophenol in aqueous solutions.

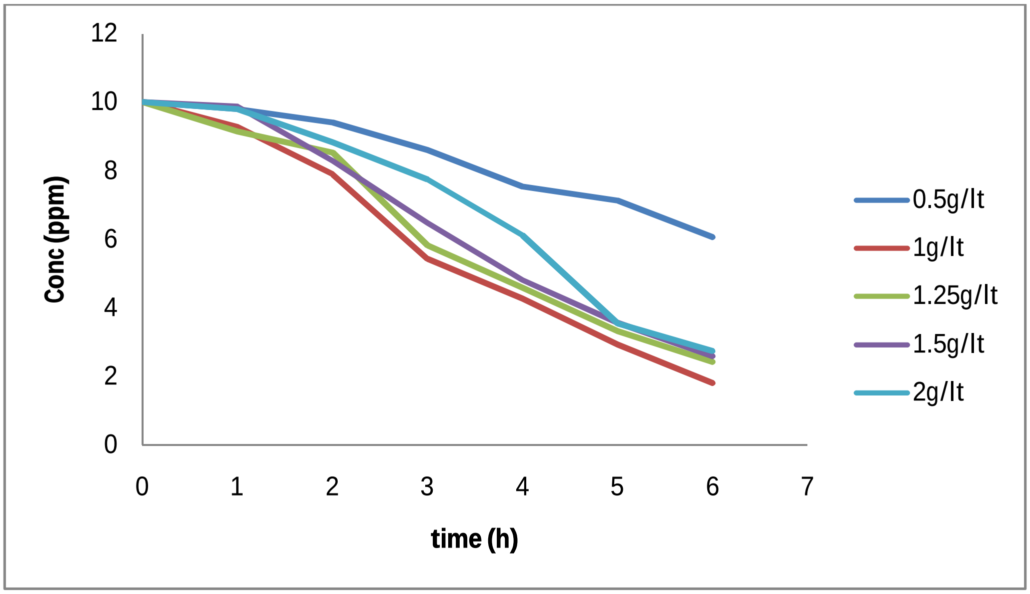

Fig 4.2 Effect of variation of catalyst dose on degradation of 2,4,6-trichlorophenol w.r.t time at different concentrations of catalyst(TiO_2)

4.2.2 Variation of pH

pHplays a vital role in the photocatalytic reaction. The optimum pHvalue was assessed for the maximum degradation of the compound at a catalyst dose(TiO_2) of 1g/L TiO_2 .The pH of solution was varied from 4 to 8 and the degradation profile is shown in Fig 4.3.At pH 4.5the maximum degradation was of 98% observed.2,4,6- trichlorophenol is known to show better adsorption on TiO_2 at slightly acidic pH , with the increased adsorption, catalytic activity improves. Thus, there is a increased degradation at pH 4.5. The observations are in agreement with the previouswork on the effects of pH on photocatalysis of 2,4,6-trichlorophenol in aqueous suspensions (Tanaka et al., 1994)

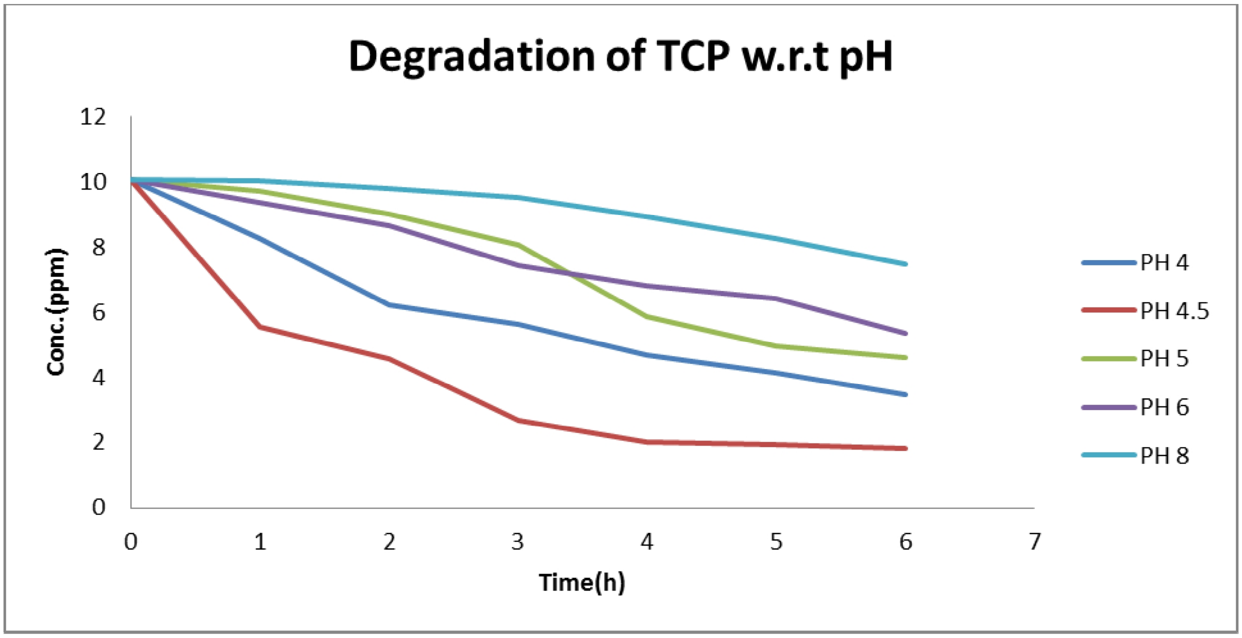

Fig4.3 Effect of change of pH on degradation of 2,4,6-trichlorophenol

4.3 LIGHT SOURCES.

Photocatalytic degradation of 2,4,6-trichlorophenol using TiO_2 was conducted under the illumination by various irradiation sources. The degradation was assessed under sunlight, UV tubes, UV LEDs and in dark at pH 4.5 and catalyst dose 1g/L . 2,4,6-trichlorophenol(10ppm) model compound at pH 4.5 and 1g/L TiO_2 was exposed to UV light, sunlight, visible light and in dark at the above mentioned conditions. Thedegradation was observed to be 84.2, 77.5, 53, 47.5% in UV light, sunlight, visible light and dark conditions respectively and degradation was minimum under dark.Fig4.4 shows the change in concentration of 2,4,6-trichlorophenol w.r.t time under different irradiation sources. Fig 4.5 shows the % degradation of 2,4,6-trichlorophenol w.r.t time under various irradiation sources.

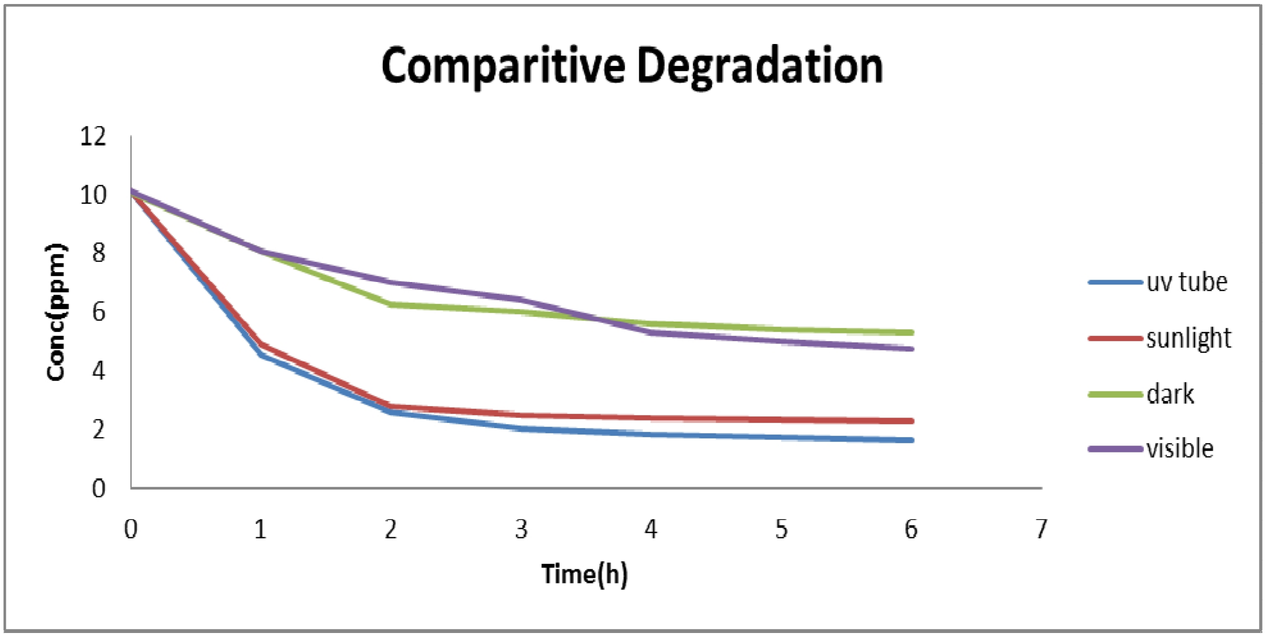

Fig4.4 Variation of irradiation source for change in concentration of 2,4,6-trichlorophenol w.r.t time

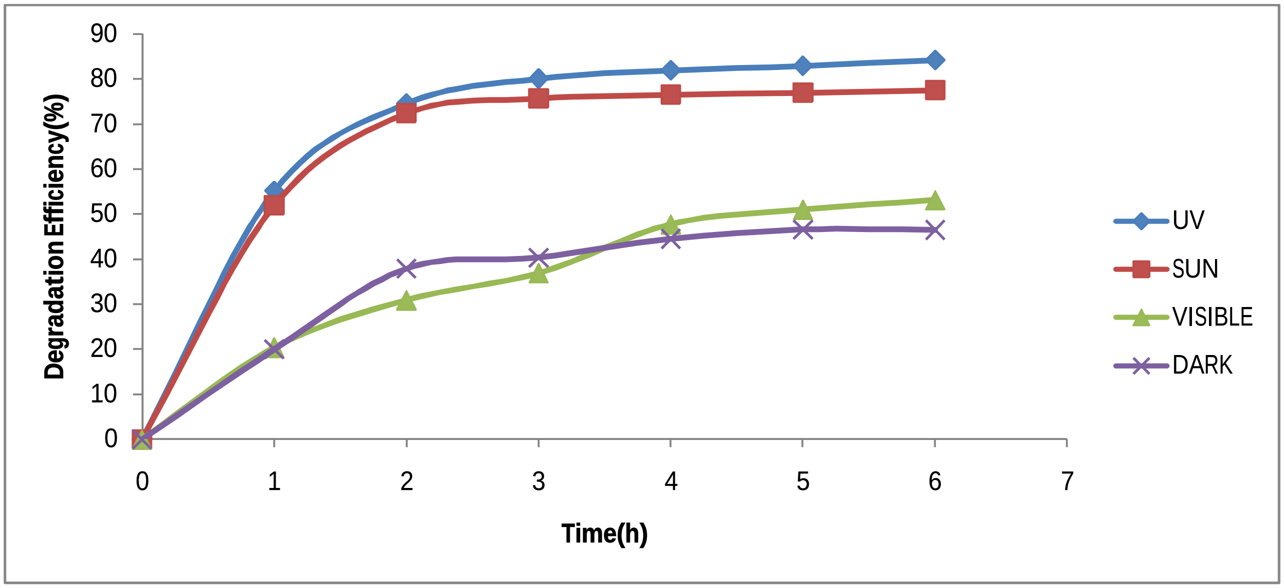

Fig 4.5. Time dependent degradation efficiencyof 2,4,6-trichlorophenol w.r.t time under various irradiation sources.

It is evident from the results that the maximum degradation of the model compound was observed when exposed under UV light. The probable reason for more degradation under UV light is the energy carried by the photons, which is more at smaller wavelength (Fig 1.4). A photon is characterized by either a wavelength, denoted by λ or equivalently energy, denoted by E having inverse relationship. The degradation efficiency achieved under solar light was comparable to UV light. Although Sunlight is cheap and freely available source of energy but the sunlight is not available throughout the day and all seasons of the year.Even on the sunny days it is only available for around 6 hours, that too with varying intensity. Cloudy skies also reduce its effectiveness. Moreover, large area of land is required to capture the solar energy. As the discharge of effulents from process industries is round the clock and the treatment of wastewater/effulent with AOP require the continuous availability of light source so such process cannot rely on sunlight as a source irradiation. AOPs have the major limitation of high operation cost due to use of expensive UV light, which limits its use at industrial scale. In a direction to reduce the operation cost UV LEDs were tested for the degradation of the model compound under tested conditions (pH 4.5, 1 g/L $TiO_{2)}$ and compared with other irradiation sources.

Fig 4.6 shows that UV LED with a power of 10 watt shows similar degradation profile when compared to 64 watt UV tube thus consuming less electricity and subsequently results in low operation cost.

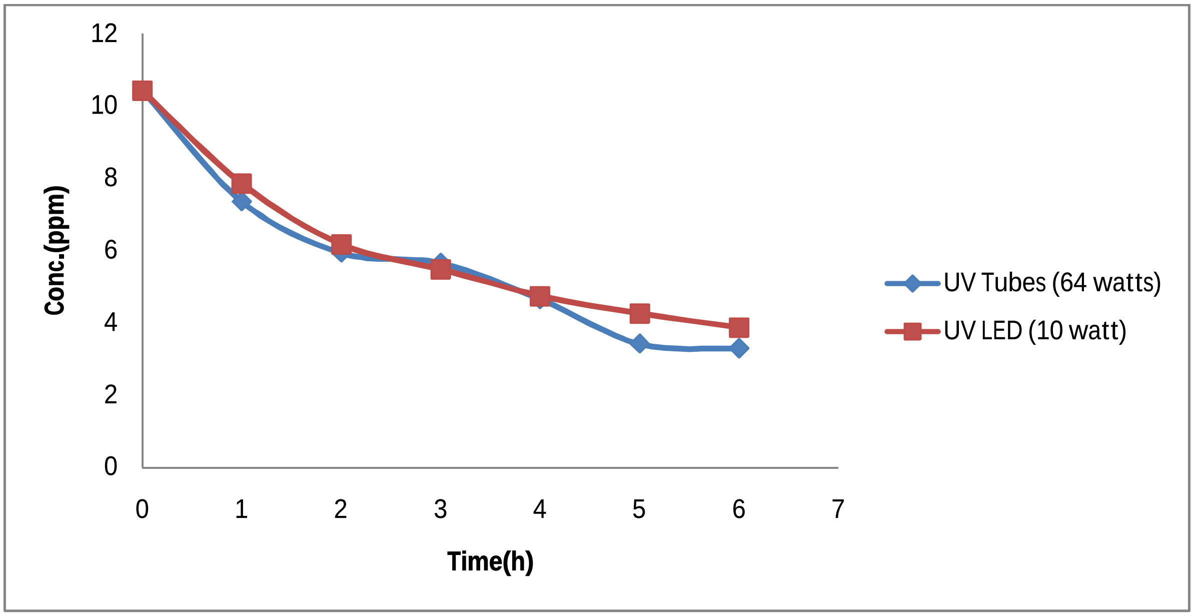

Fig 4.6 The change in concentration of 2,4,6-trichlorophenol with time under irradiation by UV tube and UV LED.

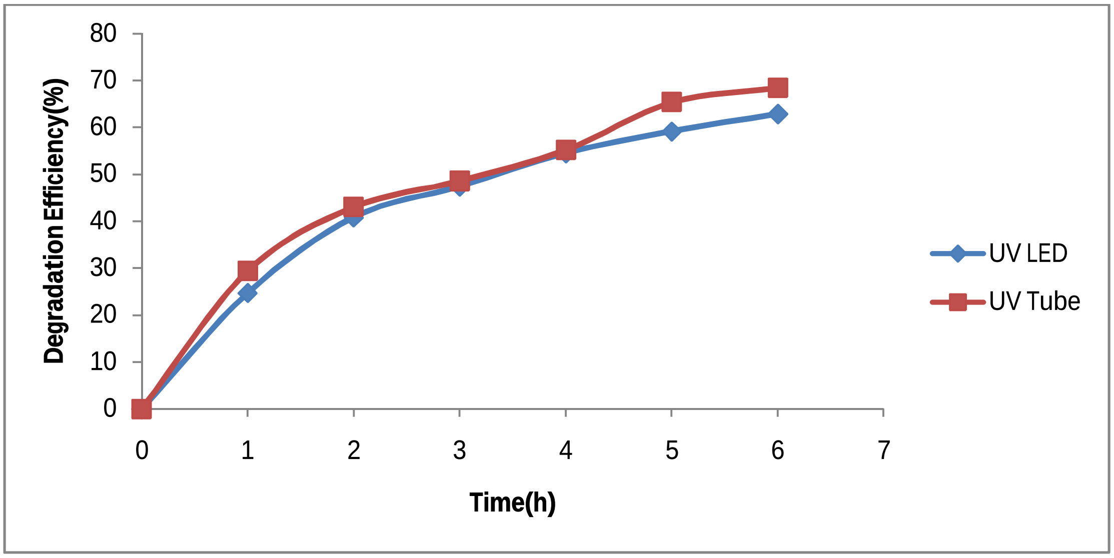

Fig 4.7 % Degradation of 2,4,6-trichlorophenol with time under irradiation by UV tube and UV LED.

Moreover, the flexibility offered in case of LEDs is more as these can be customized according to the requirement of the user. However, in literature little data was available to address the central question, whether UV-LEDs could serve as an effective photon source in heterogeneous photocatalytic oxidation.The above graph (Fig 4.6, 4.7) clearly indicates the degradation of 2,4,6-trichlorophenol compound at similar intensity is comparable under both UV irradiation sources. This shows that UV LEDs can be efficient replacement for traditional UV tubes and can be considered as an alternative UV source for photocatalysis.

4.4 COST COMPARISON

As per the well-known saying "Energy saved is energy produced". Treatment technologies for the degradation of recalcitrant compounds are energy intensive thus, expensive. It is very essential to consider all the economical parameters to assess the feasibility of practical implementation at pilot scale and then to industrial scale. Light-emitting diodes (LEDs) are compact, reliable and long-lasting devices. LEDs are driven by direct current, can accommodate rapid “on” and “off” toggling. Ultra-violet-light-emitting diodes (UV-LEDs) have a life expectancy of 50,000 hours, about five times that of traditional UV tubes/ lamps. Cost analysis was conducted in order to identify if LEDs are efficient and economically viable replacement for UV tubes or not.

The LED's cost comparative studies were done on the basis of lab scale experiment conducted in present study. The dimensions of the UV tube reactor are 114 cm*76 cm*89 cm and the dimensions of the reaction vessel for this UV tube reactor can be 100cm*50cm*4cm (i.e 1m*0.5m*0.04m). Since the water can't be filled till the top of the reaction vessel,the volume of water that can be treated inside the vessel can be calculated as 1m*0.5m*.03m(considering 1cm as free head) and Volume =0.015m^3 (15 L.)

Similarly the dimensions of UV LED reactor are 114 cm*71 cm*71 cm and that of reaction vessel for UV LED reactor can be 72cm*56cm*4 cm. The volume of water that can be treated using this reaction vessel is 0.72m*0.56m*0.03 m i.e. 0.012m^3 (12L.)

Assuming 1000L of flow of wastewater, to treat 15L of water 2 UV tubes (32 watt each) and to treat 12L of water, one UV LED of 10 watt was used. The electricity units consumed for the treatment of wastewater can be calculated as (no.of tubes*power*time in hours)=N Unit(kWh).

Let the industrial electricity tariff be X, then the electricity cost would be{X}*{no. of electricity units consumed.}.e.g. considering above mentioned case in Punjab state, India for the treatment is given below.

Considering the plant to be running for 24 h, the electricity units consumed by UV tubes is (134*32*24)/1000=102.912 Unit and by UV LEDs is (84*10*24)/1000=20.160 units

As per the electricity tariff (Punjab)= Rs6.33/unit +10% electricity duty.(1 unit=1kWh)

Electricity cost incurred for UV tubes =(103*6.33)+{0.10*(103*6.33)}≈Rs.720/day/1000L

Electricity cost incurred for UV LEDs=(21*6.33)+{0.10*(21*6.33)}≈150/day/1000L.Thus the electricity saved using UV LEDs instead of UV tubes for irradiation in this photocatalytic process is approximately 82 Units and cost saved ≈Rs.570/day/1000L which further implies that the amount saved on electricity cost =Rs0.57/day/L. or Rs 2,08,000/m^3/year. E.g. for industry generating 1000m^3 /day then the approximate saving =Rs 570,000/day

The price of the UV tubes used in this study was Rs.1200 (approx.) for the UV tube alone and the price of UV LED was Rs.800 (approx). As per the available literature, the life expectancy of LEDs is 4-5 times that of traditional UV tubes, so even the money is saved in maintenance also, as UV LEDs don't require frequent replacements, the cost benefit of using the LEDs may outweigh the marginally better performance of the UV tubes. Thus, the results depicts that UV LEDs has proven to be efficient in photon transfer for the present photocatalytic process and are economical also when compared to UV tubes. Therefore,LEDs may be the more viable option for similar photocatalytic processes also.

CHAPTER 5

CONCLUSION

5.1 CONCLUSION

Heterogenous photocatalytic process has been efficient in the degradation of 2,4,6-trichlorophenol present in aqueous solution. In the present study, the photocatalytic degradation of 2,4,6-trichlorophenol was assessed.The target was to compare the degradation efficiency of 2,4,6-trichlorophenol among different irradiation sources such as UV tubes, UV LEDs, Sunlight and in dark. The residual concentration in the aqueous solution was measured by UV/Vis spectrophotometer at 207 nm to analyze the concentration of 2,4,6-trichlorophenol in solution at different time interval during the experiment. The degradation was accessed at different catalyst dose varying from0.5g/L to 2 g/L and pH varying from 2 to 8 and the maximum degradation wasobserved using TiO_2 1 g/L and pH to 4.5. The degradation under UV was found to be 84.2% and under sunlight was 77.5% after 6h of exposure in the presence of 1g/L TiO_2 as catalyst at pH 4.5. The results exhibit that the maximum degradation was found in direct UV exposure than by exposure under sunlight followed by exposure under visible light(53.1%) and least in dark conditions(47.5%).Further under UV irradiation, two different irradiation sources i.e. UV tubes and UV LEDs were used. The degradation in UV tube (64 watt) reactor was 68.4% and in UV LED (10 watt) reactor was 62.8 % at comparable intensities. It is evident from the results that UV LEDs are effective in degradation of the recalcitrant compound 2,4,6-trichlorophenol at a reduced operating cost when compared when compared to UV tubes. UV LEDs has proven to be efficient in photon transfer for the photocatalytic process and are economical also. So,LEDs may have more practical applicability as irradiation source in the AOP induced degradative studies.

5.2 FUTURE RECOMMENDATIONS

While this present study did provide data that suggests that the UV-LEDs perform comparable to the UV tubes in terms of degradation,it is clear that UV LEDs can be considered as an alternative source for irradiation in photocatalytic processes and is economical as compared to traditionally used irradiation sources, a thorough investigation of the energy considerations and an economic analysis involved with UV-LED photolysis on improved wavelengths, more intensity etc. would provide an important supplement to the study. This would allow for a more comprehensive picture of the environmental, energy, and economic advantage of using UV-LEDs as opposed to other light sources UV LEDs as irradiation source for AOPs is a recent development and needs to be explored in more details but there is a scope of process improvement and needs to be explored in more details as few reports are available in literature where LEDs has been used as irradiation source for the degradation of pollutant and various improvements can be done, few of them are listed here:

- LEDs with different intensities needs to be done to see the effect of intensity on degradation efficiency
- As LEDs can be customized, LEDs with different wavelengths can be tested for their effectiveness in degrading pollutants as smaller wavelengths carry more energy(Energy of a photon $E=hc/\lambda$. where λ is wavelength, c=speed of light and h is Plank's constant)
- Effect of height/depth of aqueous stream in the reaction vessel upon degradation needs to be further explored.

CHAPTER 6

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