THE PHOTOCATALYTIC DEGRADATION OF PRIORITY POLLUTANTS

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DECLARATION

I hereby declare that the work embodied in dissertation entitled **“The photocatalytic degradation of priority pollutants”** is 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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CERTIFICATE

This is to certify that the dissertation entitled, **"The photocatalytic degradation of priority pollutants"**, is an authentic work carried out by Miss Sumit Rana student of M.Tech. (Env. Sc. & Tech.) Thapar University, Patiala, during the year 2008-2009, in partial fulfilments for the award of the Degree of Master of Technology and that the dissertation has not formed the basis for the award previously of any degree, associate ship, fellowship or any other similar title to any other university or institute.

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ABSTRACT

Industrial development is pervasively connected with the disposal of number of toxic pollutants. Nonbiodegradable Pollutants present in wastewater is a point of major concern in many countries. Some of these pollutants require a high priority of treatment for development of water quality criteria and effluent limitation guidelines because they are frequently found in wastewater such type of pollutants are referred to as priority pollutants. Therefore, it becomes imperative to completely degrade these pollutants which cannot be completely degraded by well established techniques like conventional wastewater treatment methods. The main objective of destructive oxidation processes is to mineralize organic contaminants, i.e., convert them to carbon dioxide, water and the oxidised inorganic anions of any heteroatoms present. These processes frequently include the addition of oxidizing agents in the presence of a Catalyst or UV light. These types of processes are collectively called as Advanced oxidation processes (AOP's). The principal mechanism of AOP's function is the generation of highly reactive free radicals. TiO_2 has been demonstrated to be excellent catalyst and its behaviour is well documented in the literature.

In order to meet international standards treatment of industrial wastewater containing pollutants is mandatory. The attention is being given to alternative photocatalytic oxidation processes for wastewater treatment. Taking all these facts into consideration, in the present study, 2-nitroaniline was chosen as a model compound. Photo degradation of 2-nitroaniline was performed in specially designed reaction vessel in the photoreactor equipped with UV tubes and constant stirring of solution was ensured at constant temperature. Experiments were performed in slurry mode in both UV and solar light at optimized condition. The degradation of 2-nitroaniline compound has been investigated in terms of change in color by measuring absorbance and reduction in COD. Various process parameters like catalyst dose, pH, effect of UV/solar, initially pollutant concentration was varied and their effects have been analyzed.

The work done has been presented in four chapters. After introducing the problem and its content in the first chapter, the study begins with the literature review on photocatalytic degradation of various priority pollutants and aniline and its derivatives in the second chapter. In the third chapter, experimental materials and methods have been discussed in detail. Results and their discussion of photocataytic degradation of model 2-nitroaniline compound and real effluent have been presented in fourth chapter.

In the case of 2-nitroaniline (25ppm), TiO_2 dose was optimized to be 4g/l, at operating pH of 2.0 with UV intensity of 25 W/m^2. In case of 2-nitroaniline 89.5% and 98.9% degradation

was achieved in UV at 282nm and 411nm and 93% and 99.3% degradation was achieved at 282nm and 411nm in solar light under the optimized parameters. While the treatment of real effluent yields COD reduction from 80 to 8.4 mg/l in UV and 80mg/l to 5.6mg/l in solar at 282nm and 60mg/l to 2mg/l in UV and 60 to 1mg/l in solar at 411nm was observed.

The results of photo degradation of 2-nitroaniline showed that heterogeneous photo catalytic could be used as efficient and environmental friendly technique for the complete degradation of recalcitrant organic pollutants which will increase the chances for the reuse of wastewater. The investigations demonstrate the importance of selecting the optimal degradation parameters for practical applications of this operation.

The results depict that solar light can be effectively used for the degradation of 2-nitroaniline and this will help in the economical viability of the process at industrial scale.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

Water pollution is a major cause of concern in most of the countries such as India and other developing nations. Several methods of water purification have been practiced since many decades; approximately 23% of the world's population live in developed countries, consume 78% of the resources and produce 82% of the waste products *(Blanco and Malato, 1996).* At present, there are some five million known substances registered, of which approximately 70,000 are widely used worldwide, and it is estimated that 1,000 new chemical substances are added to the list each year. Speedy industrialization has provided much comfort to human beings; however, its adverse effects have emerged in the shape of environmental deterioration. Industries discharging pollutants into the environment include oil refineries, tanneries, textile plants, and the food, pharmaceutical, paint, and coal processing industries. Many of these pollutants from industrial and municipal waste are toxic, persistent, and not readily biodegradable.

Photocatalysis is a promising technique, for photodegradation of various hazardous chemicals that are encountered in waste waters. The great significance of this technique is that, it can degrade (detoxify) various complex organic chemicals, which has not been addressed by several other methods of purification. The object of destructive oxidation processes is to mineralize organic contaminants, i.e., convert them to carbon dioxide, water and the oxidised inorganic anions of any heteroatoms present. These processes frequently include the addition of oxidizing agents such as hydrogen peroxide and ozone in the presence of a Catalyst or UV light. Hydroxyl radicals are known to be involved in most of these processes. Examples include UV/H_2O_2, Fenton's Reagent, UV/O_3, H_2O_2/O_3, O_3/pH, high energy radiation and photo catalytic oxidation. Because the application of photocatalysis for water treatment is a comparatively recent development and because it offers certain advantages over the preceding oxidation processes, it will be the main subject of this thesis. The photocatalysis does not require the consumption of expensive oxidizing chemicals; and catalyst is non-hazardous,but it requires the light to activate the catalyst with long wavelength UV transmitted by glass, or by the natural UV component of sunlight, the oxidation is powerful and indiscriminate leading to the mineralization of the majority of organic pollutants present in wastewater.

1.1 PRIORITY POLLUTANTS

Priority Pollutants refer to a list of specific pollutants that includes heavy metals and specific organic chemicals. The priority pollutants are a subset of "toxic pollutants" as defined in the Clean Water Act (USA). These pollutants were assigned a high priority for development of water quality criteria and effluent limitation guidelines because they are frequently found in wastewater. Many of these are heavy metals, pesticides, and other chemicals listed here are on the priority pollutant list:

Heavy Metals (Total and Dissolved): "Heavy Metal" in the water treatment field refers to heavy, dense, metallic elements that occur only at trace levels in water, but are very toxic and tend to accumulate.

Pesticides: Pesticides comprise a large class of compounds of concern. Typical pesticides and herbicides include DDT, Aldrin, Chlordane, Endosulfan, Endrin, Heptachlor, and Diazinon. Surprisingly, concentrations of pesticides in urban runoff may be equal or greater than the pesticides in agricultural runoff.

Polycyclic Aromatic Hydrocarbons (PAHs): Polycyclic Aromatic Hydrocarbons include a family of semi-volatile organic pollutants such as naphthalene, anthracene, pyrene, and benzo(a)pyrene. There are typically two main sources of PAHs: spilled or released petroleum products (from oil spills or discharge of oil production brines) and combustion products that are found in urban runoff.

Polychlorinated biphenyls (PCBs): Polychlorinated biphenyls are organic chemicals that formerly had widespread use in electrical transformers and hydraulic equipment. This class of chemicals is extremely persistent in the environment and has been proven to bio-concentrate in the food chain, thereby leading to environmental and human health concerns in areas such as the Great Lakes.

1.2 CLASSIFICATION OF PRIORITY POLLUTANTS

The purpose of the Priority Pollutants database is to serve as a convenient and practical spectral reference for research, industry and all others who are engaged in analyzing, monitoring, controlling or studying environmental, physiological or occupational pollutants and toxic substances.

Table 1.1: Classification of priority pollutants

TYPE	NO.
HYDROCARBONS	44
HALOGENATED HYDROCARBONS	76
NITROGEN CONTAINING COMPOUNDS	164
AMINES	94
PYRIDINES	4
QUINOLINES	4
HYDRAZINES	4
AZO COMPOUNDS (-N=N-)	15
TRIAZENES(-N=N-NH-)	3
NITRILES(-CN)	8
NITROSO COMPOUNDS(-N=O)	17
NITRO COMPOUNDS(-NO2)	35
PHOSPHORUS CONTAINING COMPOUNDS	22
SULFUR CONTAINING COMPOUNDS	46
OXYGEN CONTAINING COMPOUNDS	281
ETHERS	33
ALCOHOLS(R-OH)	71
KETONES(R-C(=O)-R)	19
ALDEHYDES(R-C(=O)-H)	11
ACID HALIDES(R-C(=O)-X)	4
ANHYDRIDES(R-C(=O)-O-C(=O)-R)	4
AMIDES	10
IMIDES(R-C(=O)-NH-C(=O)-R)	1
HYDRAZIDES(R-C(=O)-NH-NH2)	1
UREAS(R-NH C(=O)-NH2)	3
HYDANTOINS, URACILS, BARBITURATES	6
CARBOXYLIC ACIDS(R-C(=O)-OH)	58
ESTERS	50
INORGANICS	10
MISCELLANEOUS	8

Table 1.2 Black lists of chemicals substances selected by the E.U. (Harrinson, 1992)

Group	Included substances
Chloride Hydrocarbons	Aldrin, dieldrin, chlorobenzene, dichlorobenzene, chloronaphthalene, chloroprene, chloropropene, chlorotoluene, endosulfane, endrin, hexachlorobenzene, hexachlorobutadiene, Hexachlorocyclo-hexane, hexachloroethane, PCBs, tetrachlorobenzene, trichlorobenzene.
Chlorophenol	Monochlorophenol, 2, 4-dichlorophenol, 2-amino-4-chlorophenol, pentachlorophenol, 4-chloro-3-methylphenol, trichlorophenol.
Pesticides	Cyanide chloride, 2,4-dichlorophenoxyacetic acid and derivatives, 2,4,5 trichlorophenoxyacetic acid and derivatives, DDT, demeton, dichloroprope, dichlorvos, dimethoate, disulfoton, phenitrothion, phenthyon, linuron, malathion, MCPA, mecoprope, monolinuron, omethoate, parathion, phoxime, propanyl, pirazone, simacine, triazofos, trichlorofon, trifularin and derivatives.
Chloroanilines and nitrobenzenes	Monochloroanilines, 1-chloro-2,4 dinitrobenzene, dichloroaniline, 4-chloro-2-nitrobenzene, chloronitrobenzene, chloronitrotoluene, dichloronitrobenzene.
Polycyclic Aromatic Hydrocarbons	Antracene, biphenyl, naphthalene, PAHs
Inorganic substances	Arsenic and its compounds, cadmium and its compounds, mercury and its compounds.
Solvents	Benzene, carbon tetrachloride, chloroform, dichloroethane, dichloroethylene, dichloromethane, dichloropropane, dichloropropanol, dichloropropene, ethyl benzene, toluene, tetrachloroethylene, trichloroethane, trichloroethylene.
Other	Benzidine, chloroacetic acid, chloroethanol, dibromomethane, dichlorobenzidine, dichloro-diisopropyl-ether, diethylamine, dimethylamine, isopropyl benzene, Tributylphosphate, trichlorotrifluoroethane, vinyl chloride, xilene.

The presence of such type of pollutant in an aqueous dissolution is especially problematic as the residual waste cannot be stored indefinitely (as is the case with some solid waste) and it has the peculiarity that a small volume of water is able to contaminate much greater volumes of water. It must also be pointed out that a wide spectrum of compounds can transform themselves into potentially dangerous substances during the drinking water treatment process, particularly by chlorination, as is the case of the precursor compounds of the formation of chlorocarbons.

1.3 TREATMENT TECHNIQUES FOR PRIORITY POLLUTANTS

The treatments processes of different types of effluents to be used must guarantee the elimination or recuperation of the pollutant in order to reach the strict authorized levels for the discharge of these effluents. The levels of pollutants allowed in discharge waters, are directly related with the type of present pollutant in the effluent.

In general, the elimination of organic pollutants in aqueous solution needs one or various basic treatment techniques *(Weber and Smith, 1986; Chuang et al., 1992)*: chemical oxidation, air desorption, liquid-liquid extraction, adsorption, inverse osmosis, and ultra-filtration and biological treatment. Depending on the present compound in solution the methods to use can be destructive as for example, chemical oxidation, incineration or degradation, which only allow the efficient elimination of the pollutant from an aqueous form; and the non-destructive methods, among which is liquid-liquid extraction and absorption, that allow the recuperation of the pollutant. On the other hand, the application of one or other of the methods depends on the concentration of the effluent. It is necessary to choose the most adequate method according to the characteristic of the effluent. Once again, it has to be chosen between those techniques, which are useful for high concentrations of pollutants, like incineration or some chemical oxidation methods, and those techniques for low concentrations of pollutants, for example adsorption, membrane techniques, and some chemical oxidation methods as well. But now days the most promising techniques are like photochemical process, advanced oxidation process.

1.3.1 ADVANCED OXIDATION PROCESS (AOP)

In the last 15 years, a lot of research projects have been addressed to a special class of oxidation techniques defined as Advanced Oxidation Processes (AOP’s), pointing out its potential prominent role in the wastewater purification (Ollis and Ekabi, 1993)**.** It was shown that AOP’s could successfully solve the problem of biorecalcitrant water pollutants working at or near ambient temperature and pressure (Bahnemann et al., 1994; Bolton and Cater, 1994). All AOP’s are characterized by the same chemical feature: the production of hydroxyl radical’s .OH. These radicals are extremely reactive species and attack mainly every organic molecule with rate constants usually in the order of 106-109 mol l-1 s-1 (Hoigne, 1997). .OH radicals are also characterized by a low selectivity of attack which is a useful attribute for an oxidant used in wastewater treatment and for solving pollution problems. The versatility of AOP’s 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. Table 1.3 shows that .OH has the highest thermodynamic oxidation potential, which is perhaps why .OH -based oxidation processes have gained the attention of many advanced oxidation technology developers. In addition, most environmental contaminants react 1 million to 1 billion times faster with .OH than with O_3, a conventional oxidant (US EPA, 1998).

Table 1.3 Oxidation potential of several oxidants in water (CRC Handbook, 1985)

OXIDANT	**OXIDATION POTENTIAL(eV)**
.OH	**2.80**
$O(^1D)$	**2.42**
O_3	**2.07**
H_2O_2	**1.77**
Permanganate ion	**1.67**
Chlorine	**1.36**
O_2	**1.23**

The oxidation reactions involving hydroxyl radical and organic substrates (RH or PhX) in aqueous solutions may be classified with respect to their character *(Boossmann et al., 1998):*

- abstraction of hydrogen
- addition reactions
- electron transfer

$$.OH + RH \rightarrow R. + H_2O$$

$$.OH + PhX \rightarrow HOPhX.$$

$$.OH + RH \rightarrow [R - H]^{+.} + HO^-$$

Only wastewater with relatively small Chemical Oxygen Demand (COD) contents can be suitably treated by these techniques *(Andreozzi et al., 1999)* in order to avoid an excessive consumption of expensive reactants. Wastes with massive pollutant contents are more conveniently treated by wet oxidation or incineration *(Mantzavinos et al, 1997;Luck, 1999)*

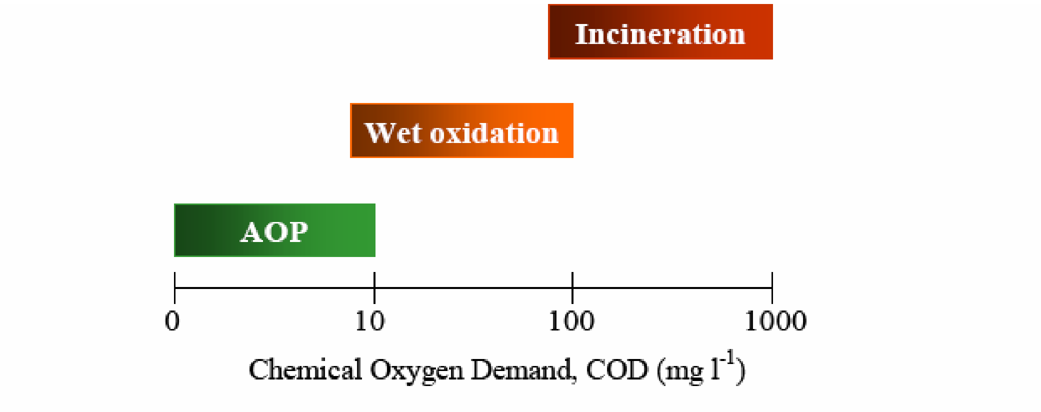


Fig-1.1 Application of AOP

AOP can be classified according to the reaction phase (homogeneous or heterogeneous) or to the methods used to generate the •*OH* radicals (chemical, electrochemical, sonochemical or photochemical). The main used AOP are illustrated in Figure 1.2.

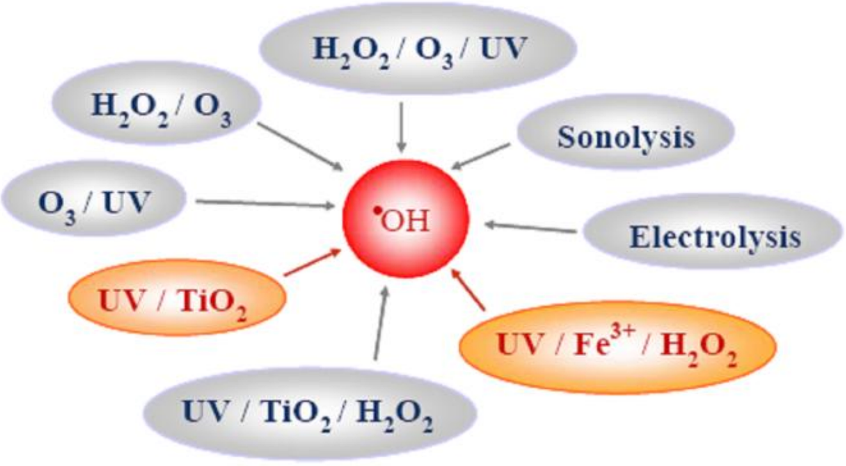


Fig-1.2 Main advanced oxidation processes (AOP).

An interesting class of AOP consists of the so-called Advanced Photochemical Oxidation (APO) processes (US EPA, 1998). APO processes are characterized by a free radical mechanism initiated by the interactions of photons of a proper energy level with the molecules of chemical species present in the solution or with a catalyst.

The most used APO technologies can be broadly divided into the following groups: (1) heterogeneous photocatalysis, (2) homogeneous photocatalysis, and (3) the photo-Fenton process. These APO technologies are briefly described below.

1.3.2 HETEROGENEOUS PHOTOCATALYSIS

Since 1972, when *Fujishima and Honda (1972)* reported the photocatalytic decomposition of water on TiO_2 electrodes, photocatalysis has been used with great success in the degradation of a wide variety of contaminants, including alkanes, alcohols, carboxylic acids, alkenes, phenols, dyes, PCBs, aromatic hydrocarbons, halogenated alkanes and alkenes, surfactants, and pesticides *(Ollis and Ekabi, 1993; Blake, 2001)***.** Heterogeneous photocatalysis is a technology based on the irradiation of a catalyst, usually a semiconductor, which may be photoexcited to form electron-donor sites (reducing sites) and electron-acceptor sites (oxidizing sites), providing great scope as redox reagents. The process is heterogeneous because there are two active phases, solid and liquid.

Among several semiconductors, titanium dioxide has proven to be the most suitable for widespread environmental applications. TiO_2 is stable to photo and chemical corrosion, and inexpensive. TiO_2 has an appropriate energetic separation between its valence and conduction bands (VB and CB, respectively), which can be surpassed by the energy of a solar photon. The VB and CB energies of the TiO_2 are estimated to be +3.1 and -0.1 volts, respectively, which means that its band gap energy is 3.2 eV and absorbs in the UV light (wavelength $\lambda<387$ nm). Hydroxyl radical (*•OH)* is the main oxidizing species responsible for photo-oxidation of the organic compounds *(Legrini et al., 1993; Valavanidis et al., 2006).* The first event, after absorption of near ultraviolet radiations at $\lambda<387$ nm, is the generation of electron/hole pairs separated between the CB and VB.

$$TiO_2 + hv \rightarrow TiO_2\,(e^- + h^+)$$

Some of the numerous events which take place after the UV light absorption by TiO_2 particles are presented in figure 1.3. The subsequent generation and separation of electrons (e^- CB) and holes (h^+ VB) are also mentioned. In particular, three oxidation reactions have been experimentally observed: electron transfer from R, HO_2 and $-OH$ adsorbed on the catalyst surface.

It has been shown that the photocatalytic degradation of a water contaminant can be enhanced by addition of H_2O_2, a better electron acceptor than O_2 *(Ollis et al., 1991; Pichat et al., 1995;*

Diller et al., 1996). This effect has been explained by the formation of hydroxyl radicals during the reaction with CB electrons:

$$H_2O_2 + e^-_{CB} \rightarrow .OH + OH.$$

It limits the electron-hole recombination rate and increases the hydroxyl radical concentration at the TiO_2 surface.

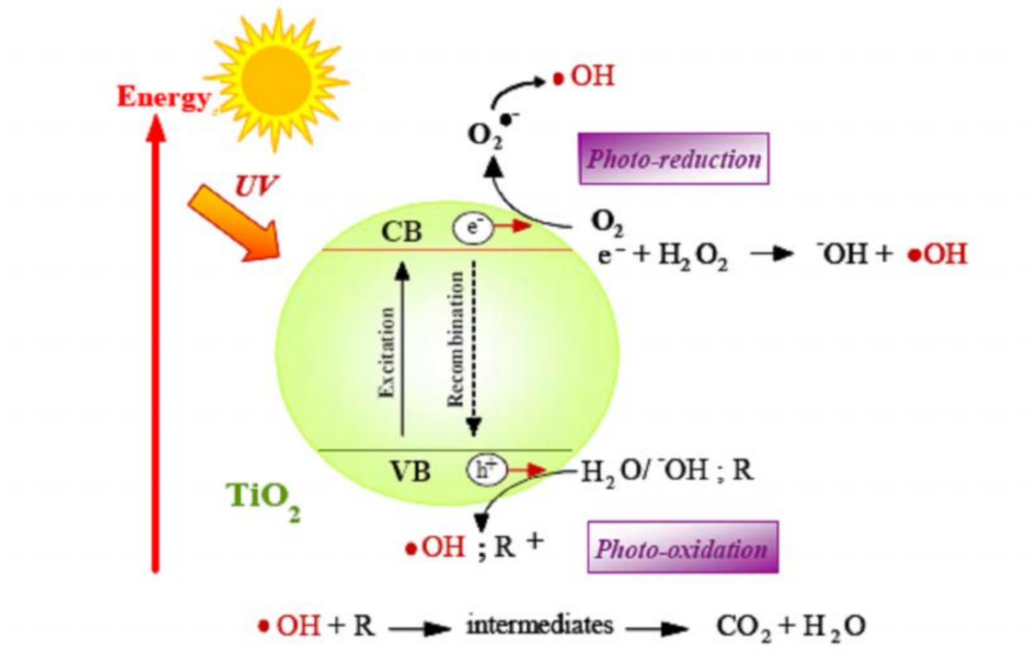


Fig-1.3 Irradiated TiO_2 semi-conductor particle

1.3.3 HOMOGENEOUS PHOTODEGRADTION

The former applications of homogeneous photo degradation (single-phase system) to treat contaminated waters concerned the use of UV/H_2O_2 and UV/O_3. The use of UV light for photodegradation of pollutants can be classified into two principal areas:

- Direct photodegradation, which proceeds from direct excitation of the pollutant by UV light, and
- Photo-oxidation, where light leads oxidative processes principally initiated by hydroxyl radicals.

This process involves the use of an oxidant to generate radicals, which attack the organic pollutants to initiate oxidation. The three major oxidants used are: hydrogen peroxide (H_2O_2), ozone, and photo-Fenton system (Fe^{3+}/H_2O_2).

1.3.4 FENTON AND PHOTO-FENTON REACTION

The Fenton reaction was discovered by *H.J.Fenton in 1894 (Fenton, 1894).* Forty years later the *Haber-Weiss (1934)* mechanism was postulated, which revealed that the effective oxidative agent in the Fenton reaction was the hydroxyl radical. Since then, some groups have tried to explain the whole mechanism that will be treated in details in the next two chapters. The Fenton reaction can be outlined as follows:

$$M^{n+} + H_2O_2 \longrightarrow M^{(n+1)+} + HO^- + HO^*$$

Where M is a transition metal as Fe or Cu. In the absence of light and complexing ligands other than water, the most accepted mechanism of H_2O_2 decomposition in acid homogeneous aqueous solution, involves the formation of hydroxyl peroxyl ($HO^{2\bullet}/O^{2-}$) and hydroxyl radicals HO•. The HO• radical mentioned before, once in solution attacks almost every organic compound. The metal regeneration can follow different paths. For Fe^{2+}, the most accepted scheme is described in the following equations *(Sychev and Isak, 1995)***.**

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^* \quad (1)$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^* + H^+ \quad (2)$$
$$Fe^{2+} + HO^* \rightarrow Fe^{2+} + HO^* \quad (3)$$
$$HO^* + H_2O_2 \rightarrow HO_2^* + H_2O \quad (4)$$
$$Fe^{3+} + HO_2^* \rightarrow Fe^{2+} + H^+ + O_2 \quad (5)$$
$$Fe^{3+} + O_2^* \rightarrow Fe^{3+} + O_2 \quad (6)$$
$$Fe^{2+} + HO^* \rightarrow Fe^{3+} + HO_2^- \quad (7)$$

Fenton reaction rates are strongly increased by irradiation with UV/visible light. During the reaction, Fe^{3+} ions are accumulated in the system and after Fe^{2+} ions are consumed, the reaction practically stops. Photochemical regeneration of ferrous ions (Fe^{2+}) by photoreduction of ferric ions (Fe^{3+}) is the proposed mechanism *(Faust and Hoigné, 1990).*

The new generated ferrous ions reacts with H_2O_2 generating a second HO• radical and ferric ion, and the cycle continues.

$$Fe^{3+} + H_2O \longrightarrow Fe^{2+} + HO^*$$

Fenton and photo-Fenton reaction depend not only on H_2O_2 concentration and iron added, but also on the operating pH value. *Chamarro et al. (2001)* used the Fenton process for the degradation of phenol, 4-chlorophenol, 2,4-dichlorophenol and nitrobenzene. The stoichiometric coefficient for the Fenton reaction was approximately 0.5 mol of organic compound/mol H_2O_2. The process was found to eliminate the toxic substances and increased the biodegradability of the treated water. Regarding DCDE has been confirmed that DCDE's biodegradability can be enhanced by modified Fenton's reagent. Some works about textile waters treatment by means of Fenton and photo-Fenton process have been published. Most of them showed their effectiveness for colour removal and COD reduction an improvement of photo assisted Fenton processes is the UV-vis/ferrioxalate/H_2O_2 system, which has been recently demonstrated to be more efficient than photo-Fenton for the abatement of organic pollutants. two new electrochemical procedures for the detoxification of acidic waste waters, the so-called electro-Fenton and photoelectron-Fenton processes, where H_2O_2 is electro generated, have been developed and have shown their good efficiencies for the mineralization of aniline , 4-chlorophenol and 2,4-D.

1.3.5 PHOTOCHEMICAL PROCESSES

For the oxidation of organic pollutants, a series of researchers have proposed direct photooxidation with ultraviolet light *(Petersen et al. 1988)***.** However, there are a number of limitations for its use. The first one being that the organic compound to be eliminated must absorb light in competition with other compounds of the effluent to be treated. The second one is that the organic compounds generate a wide variety of photochemical reactions that can produce products more complex for degradation. In addition, not all the radiation emitted by the source of radiation is fully exploited, only the radiation absorbed and only a part of this produces chemical changes which means that some reactions of photodegradation have very slow kinetics. The addition of energy as radiation to a chemical compound is the principle of the photochemical processes. The molecules absorb this energy and reach excited states the enough time to be able to carry out chemical reactions. A large amount of studies *(Legrini et al., 1993)* dealt with the degradation of chemicals in water using the Hg emission at 253.7 nm produced by low-pressure mercury lamps. However, results showed that 253.7nm irradiation alone could not be used as an effective procedure for the removal of organics from water: it may be useful for the degradation of substituted aromatic; however it is totally inefficient for effective removal of chlorinated aliphatics. It should, however, be noted that low-pressure Hg lamps are quite efficient for water disinfections purposes. Medium and high-pressure lamps, with a broader emission spectrum, have been more frequently used for the degradation of contaminants. Medium-pressure Hg lamps emit particularly strongly in the spectral region between 254 and 400 nm and are not only effective in generating hydroxyl radicals from e.g. hydrogen peroxide or ozone, but also by causing electronic transitions in a large number of organic molecules. In the photochemical hydroxyl radicals may be generated by water photolysis *(Cervera and Esplugas, 1983)*

$$H_2O + h\nu \rightarrow H\bullet + OH\bullet$$

Photolysis involves the interaction of light with molecules to bring about their dissociation into fragments. This reaction is a poor source of radicals, and in the reaction medium large quantity of reaction intermediates that absorb part of the radiation are generated, which decreases considerably the photooxidation kinetics of the contaminants. That fact makes the process valid only for effluents with low concentration of pollutants. The photochemical treatment, although partially solving the problem of the refractory compounds, has some negative aspects in its practical application, as the high cost of UV radiation production. Furthermore, not all the emitted radiation is used, only the absorbed radiation and only a fraction of this radiation produces chemical changes. This fact makes that some photo degradation reactions have a very low yields and slow kinetics. To accelerate the process, other oxidants like hydrogen peroxide and/or ozone, metallic salts or semiconductors like TiO_2 can be added, giving rise to the so-called Advanced Oxidation Processes. Instead of UV lamps, solar light could be used as radiation energy to degrade some compounds.

1.4 PARAMETERS INFLUENCING REMOVAL OF PRIORITY POLLUTANTS

There are several parameters can influence the removal of priority pollutants from waste water:

- **Hydraulic Retention Time (HRT):** this is the average time waste water remains in the reactors Increasing the HRT in an activated sludge plant has been reported in literature to contribute to improving pollutant removal (e.g. COD, BOD, xenobiotics etc.) *(Barr, 1996; and Rempel, 1992).* Higher HRT enable longer contact time between the degrading organisms and pollutants and also increase the pollutant sorption on to sludge.

- **Solids Retention Time (SRT):** this is the average time that sludge remains in the reactors. Depending on the pollutants to be removed, decrease change in SRT influences the sorption of pollutants to sludge and the adaptation and specialisation of micro-organisms. It was found in literature that long SRTs in biological treatment processes favour the biodegradation of many xenobiotic compounds but not all potentially hazardous organic substances *(Byrns, 2001; Clara et al., 2005; Jacobsen et al., 2004).*
- **Mixed Liquor Volatile Suspended Solids (MLVSS):** This is the microbial suspension in the aeration tank of an activated sludge wastewater treatment plant. MLVSS is the combination of influent waste water going into the reactor with the recycled sludge taken from the same reactor and from the secondary settling tank.
- **Airflow rate:** This is the injection of diffused air into the aeration vessel and strongly influences the volatilization of priority pollutants.

1.5 PHOTOCATALYSIS:

The word photocatalysis is composed of two parts:

1. The prefix *photo,* defined as "light",
2. *Catalysis* is the process where a substance participates in modifying the rate of a chemical transformation of the reactants without being altered in the end. This substance is known as the catalyst which increases the rate of a reaction by reducing the activation energy.

Hence, photocatalysis is a reaction which uses light to activate a substance which modifies the rate of a chemical reaction without being involved itself.

1.6 HISTORY OF PHOTOCATALYSIS

We are surrounded by photochemistry everyday; we see it in the green colour of grass and leave every summer day. However, the first mention of photo catalysis was by Plotnikov in the 1930's in his book entitled Allaemeine photochemie. The next major development followed in the 1950's when Markhani and Laidler performed a kinetic study of photo oxidation on the surface of zinc oxide in an aqueous suspension. By the 1970's researchers started to perform surface studies on photo catalysts like Zinc Oxide and Titanium dioxide.

Titanium Dioxide may come in the anatase or the rutile form. Degussa P25 Titanium Dioxide contains both the anatase and rutile form. Curiously, this mixture long stood as the standard in photo catalysis with high reactivity. In the 1970's solar energy was being studied due to a need for more available renewable resources and environmental concerns; photochemistry was looked upon for the storage and usage of solar energy. In *1972 Fujishima and Honda* had a breakthrough for the photolysis of water with a semiconductor electrode, which could also be a solar powered cell. The next big breakthrough in photochemistry occurred in 1976 when Carey and Oliver developed a method for measuring the variation in quantum efficiency with intensity .The interest in using titania as a photo catalyst has since been revived in the 1990.

In the 1980's and 1990's there came an increasing concern for environmental preservation and cleanup. As a result some environmental scientists have looked at photochemistry for air, water, and soil cleanup TiO_2 catalyzed photochemistry can accomplish the rnineralization, which is the degradation of organic compounds to H_2O and CO_2 and its inorganic substituants if the organic compound should have any**,** of many different organic compounds. During the last few years, semiconductor mediated photo catalysis has been reported as a promising route to destroy toxic and hazardous organic substances in industrial wastewater and drinking water. In most cases, a complete oxidative destruction of pollutants has been observed and the end products include CO_2, H_2O and inorganic ions. The harvest of sunlight for photo catalysis has been a tremendous boon to the process, on account of the economic feasibility, ease of large scale operation and process efficiency.

1.7 PRINCIPLE OF PHOTOCATALYSIS

Photocatalytic destruction of organic compounds is based on semiconductor photochemistry. The most effective photocatalyst for this purpose is titanium dioxide. This is a non-toxic, material that is a constituent of toothpastes and many cosmetics. In order to fully appreciate the characteristics of photocatalysis with this semiconductor it is necessary to understand the basic physics of semiconductor materials. The titania catalyst is illuminated by UV radiation with a wavelength sufficient to displace electrons from the valence band of the catalyst; for titanium dioxide this is below 387.5 nm. An electron/hole pair is produced on the semiconductor surface. The photo catalytic oxidation of an organic species often proceeds via adsorption of the pollutant on the surface of the catalyst, followed by direct subtraction of the pollutant’s electrons by positively charged holes. Another possible way is oxidation with OH radicals, generated from water of the aqueous environment, which takes place at the catalyst surface or in its vicinity.

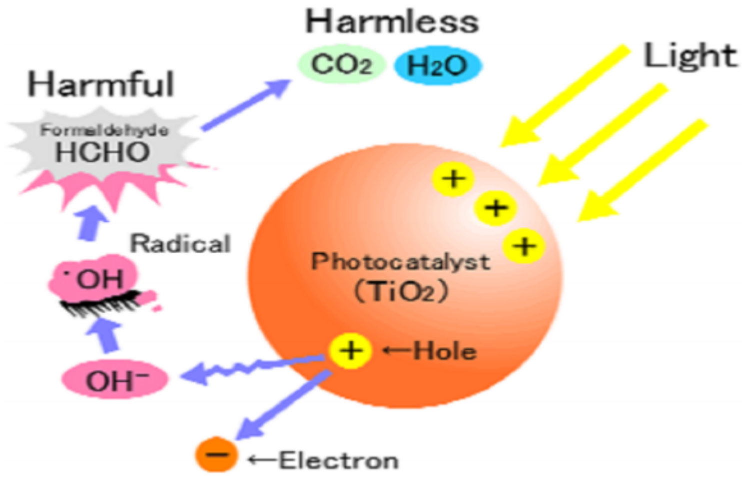


Fig- 1.4 Principle of photo catalysis

Both reactions may proceed simultaneously and which mechanism dominates depends on the chemical and adsorption properties of the pollutant. Figure 1.4 illustrates direct oxidation of an adsorbed species on the catalyst surface while the simple general reactions (R1) and (R2) give an idea of what occurs for the case of hydroxyl radical generation.

1.8 TiO_2 AS A CATALYST

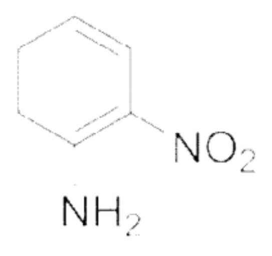
The element Titanium was discovered in 1791 by William Gregor, in England. Gregor spent much of his time studying mineralogy, which led him to his discovery. This happened when he discovered a sample of a black sandy substance in his neighbourhood. He studied this substance and after he was assured that it was a mineral, he called it menachanite. Four years later a man named Martin H. Klaproth, recognized that there was a new chemical element in this mineral, he later named it Titanium after the Titans, which were humongous monsters that ruled the world in Greek mythology. Martin H. Klaproth was not able to make the pure element of titanium however, he was only able to produce TiO_2, or Titanium Dioxide There are many types of catalyst, some act on very few substrates while some act on many substrates. The best way to cleanse a wastewater would be to use a photocatalysis process that can be effective on a multitude of contaminants or in other words a heterogeneous environment of contaminants. Metal oxides work well in this case. It is true that many oxides work well, WO_3, and ZnO but in scientific studies it has been proven that TiO_2 has an advantage over the others.

The reasons that TiO_2 does so well and is desired as an agent in remediation of wastewater are based on several factors. 1. The process occurs under ambient conditions. 2. The formation of photocyclized intermediate products, unlike direct photolysis techniques, is avoided. 3. Oxidation of the substrates to CO_2 is complete. 4. The photocatalyst is inexpensive and has a high turnover. 5. TiO_2 can be supported on suitable reactor substrates. 6. The process offers great potential as an industrial technology to detoxify .semiconductors are usually selected as photocatalysts, because semiconductors have a narrow gap between the valence and conduction bands. In order for photocatalysis to proceed, the semiconductors need to absorb energy equal to or more than its energy gap. This movement of electrons forms e^-/h^+ or negatively charged electron/positively charged hole pairs. The hole can oxidize donor molecules. Among the possible semiconductors, TiO_2, or Titanium Dioxide, (E_g = 3.2 eV) is most extensively used because it has many advantages. It is inert and resistant to corrosion, and it requires little post-processing, making it inexpensive. Finally, it can react under mild-operating conditions. However, it currently needs to use ultraviolet light for photo catalysis to occur.

1.9 2-NITROANILINE

2-Nitroaniline, also known an *ortho*-nitroaniline and *o*-nitroaniline, is aniline carrying a nitro functional group in position 2.It is present in the form of orange yellow crystals.

Table 1.4 Properties of 2-nitroaniline

PROPERTIES	
Molecular formula	$C_6H_6N_2O_2$
Molar mass	138.14 g/mol
Appearance	Solid
Boiling point	284°C
Melting point	71°C
Density	1.44 g/cm³
Solubility in water, g/100 ml at 25°C	0.126
Vapour pressure, Pa at 20°C	4
Flash point:	168°C
Auto-ignition temperature	521°C
Structure	

1.9.1 ACUTE HAZARDS AND SYMPTOMS

- **Fire:** Combustible. Many reactions may cause fire or explosion.
- **Explosion:** Finely dispersed particles form explosive mixtures in air.
- **Inhalation:** Blue lips or finger nails. Blue skin. Headache. Dizziness. Nausea. Confusion. Convulsions. Laboured breathing. Unconsciousness
- **Skin:** Mau be absorbed
- **Spillage disposal:** Sweep spilled substance into covered containers; if appropriate, moisten first to prevent dusting. Carefully collect remainder. (Extra personal

protection: P3 filter respirator for toxic particles.) Do NOT let this chemical enter the environment.

- **Physical danger:** Dust explosion possible if in powder or granular form, mixed with air.
- **Chemical danger:** On combustion forms a toxic fume of nitrogen oxides. Reacts with strong acids, strong oxidants and strong reducing agents. Reacts with organic materials in presence of moisture causing fire.
- **Routes of exposure:** The substance can be absorbed into the body by inhalation of its vapour, through the skin and by ingestion.
- **Inhalation risk:** No indication can be given about the rate in which a harmful concentration in the air is reached on evaporation of this substance at 20°C.
- **Effects of short-term exposure:** The substance may cause effects on the blood, resulting in formation of met haemoglobin. The effects may be delayed. Medical observation is indicated.
- **Effects of long-term or repeated exposure:** The substance may have effects on the blood, resulting in the formation of met haemoglobin

1.9.2 PREVENTION OF HAZARDOS

- NO open flames. NO contact with combustible substances
- Prevent deposition of dust; closed system, dust explosion-proof electrical equipment and lighting
- Local exhaust or breathing protection
- Protective gloves. Protective clothing.
- Face shield, or eye protection in combination with breathing protection
- Do not eat, drink, or smoke during work. Wash hands before eating
- Separated from strong acids, strong oxidants, combustible and reducing substances, food and feedstuffs

1.9.3 FIRST AID / FIRE FIGHTING

- Powder, water spray, foam, carbon dioxide.
- In case of fire: keep drums, etc., cool by spraying with water. Combat fire from a sheltered position.
- Fresh air, rest. Artificial respiration if indicated. Refer for medical attention.

- Remove contaminated clothes. Rinse skin with plenty of water or shower. Refer for medical attention.
- First rinse with plenty of water for several minutes (remove contact lenses if easily possible), then take to a doctor.
- Induce vomiting (ONLY IN CONSCIOUS PERSONS!). Refer for medical attention

1.10 OBJECTIVES OF PRESENT STUDY

Main objective of the study was to degrade a model compound 2-nitroaniline which is a persistent non biodegradable priority pollutant and cannot be treated by conventional treatment processes. The photocatalytic oxidation of 2-nitroaniline compound which is present in industrial wastewater is the subject of this research. The prime objective was to carry out the literature survey on the available lists of priority pollutants which are assigned by Environmental Protection Act (EPA). After the critical literature review, 2-nitroaniline was selected as a model compound for the degradation studies to be undertaken with photocatalysis since few scattered reports exist on the treatment of nitro-aniline with photocatalytic processes. Another objective is to optimize the photocatalytic process for different parameters such as pH, UV intensity, use of Solar light, catalyst dose (TiO_2), initial concentration, volume to area ratio etc. and to study their effect on the degradation and decolourization of 2-nitroaniline in terms of change in absorbance and COD of the resulting solution.

CHAPTER 2

LITERATURE REVIEW

Industrial development is pervasively connected with the disposal of number of toxic pollutants that are harmful to the environment & the human and are also not easily degraded in nature. Wastewater generated from industries which degrades local streams with bacteria and other pollutants, threatening human health, landmass fertility, and our environment. In order to meet international standards treatment of industrial water containing pollutants is mandatory. The removal of organic pollution from water supplies has traditionally been effected by adsorption with activated carbon. For this reason attention is being given to alternative photocatalytic oxidation processes for water treatment, frequently referred to as advanced oxidation processes. The object of destructive oxidation processes is to mineralize organic contaminants, i.e., convert them to carbon dioxide, water and the oxidised inorganic anions of any heteroatoms present. These processes frequently include the addition of oxidizing agents such as hydrogen peroxide and ozone in the presence of a Catalyst like Tio_2 or UV light. Hydroxyl radicals are known to be involved in most of these processes. Photo catalytic oxidation to water treatment is a comparatively recent development and it offers certain advantages over the oxidation processes. Photocatalytic oxidation and ozonation appear to be the most popular treatment technologies compared with other advanced oxidation processes (AOP’s) as shown by the large amount of information available in the literature. The principal mechanism of AOP’s function is the generation of highly reactive free radicals. Consequently, combination of two or more AOP’s expectedly enhances free radical generation, which eventually leads to higher oxidation rates.

2.1 PHOTOCATALYTIC TREATMENT OF PRIORITY POLLUTANTS

T.E. Agustina and H.M. Ang (2005) gave a synergistic effect of photocatalysis and ozonation for the treatment of wastewater that contain recalcitrant organic compounds, such as organo-halogens, organic pesticides, surfactants, and colouring matters, wastewater engineers are now required to develop advanced treatment processes. A promising way to perform the mineralization of this type of substance is the application of an advanced oxidation process (AOP’s).

Dhananjay S. Bhatkhande et al. (2003) show the Photocatalytic degradation of nitrobenzene (NB) using titanium dioxide (Degussa P-25) as photocatalyst and concentrated solar radiation has been studied. The effects of various factors, such as the presence of anions common in the industrial wastewater, the initial pH and the addition of $FeSO_4$, were investigated. The intermediates detected were *o, p, m*-nitrophenols and dihhydroxy derivatives and shows that degradation proceeds via √OH radicals.

Bekkouche et al. (2004) studied the adsorption of the micro pollutant on the photocatalyst, mainly the titanium oxide anatase form, is a determining stage in the process of photo degradation. An experimental study carries out the adsorption of phenol, chosen as the model pollutant, on a photocatalyst, titanium oxide anatase (Degussa P25). The aggregation effect of TiO_2 in aqueous solution had an optimal concentration of the catalyst for a concentration of phenol. The adsorption was optimal for a pH between 5 and 6 in the neighborhood of the isoelectric point of TiO_2.*Damien Gumy, (2006)* has been investigated the factors influencing photocatalytic drinking water detoxification and disinfection by suspended and fixed TiO_2.

Wide range of organic compounds in aqueous solutions is photocatalytically oxidized to carbon dioxide in the presence of titanium dioxide with artificial and solar light. The photocatalytic mineralization of the most important classes of pesticides in water by illuminated TiO_2 has been reviewed. The study focuses on the determination of the nature of the principal organic intermediates and the evolution of the mineralization as well as on the degradation pathways followed during the process *(Ioannis K. Konstantinou and Triantafyllos A. Albanis (2003))*.

The photocatalytic degradation and oxidation to carbon dioxide of aqueous phenol solutions have been studied *(R.W. Matthews and S.R. McEvoy (1992))* using natural sunlight in geometries simulating shallow ponds. The photo catalyst was titanium dioxide freely suspended in the solution or immobilized on sand or silica gel. Photo degradation rates were approximately three times faster with the free suspension than with the immobilized catalyst under the same conditions, and were dependent on the time of the year and the time of the day. The seasonal variation correlated roughly with seasonal solar irradiance tabulations for the UV component of the spectrum

N. Kometani et al. (2008) designed a fluidized-bed-type flow reactor available for the photocatalytic treatment of the suspension of model soil under high-temperature, high-pressure conditions. An aqueous suspension containing hydrogen peroxide (H_2O_2) as an oxidizer and inorganic oxides as a model soil, titania (TiO_2), silica (SiO_2), or kaoline was continuously fed into the reactor with the temperature and the pressure controlled to be T=20–400◦C and P = 30 MPa, respectively. The degradation of chlorobenzene (CB) in water was chosen as a model oxidation reaction. It appeared that most of the model soils are not so harmful to the SCWO treatment of CB in solutions. When the TiO_2 suspension containing H_2O_2 was irradiated with near-UV light, the promotion of the degradation caused by photocatalytic actions of TiO_2 was observed at all temperatures. Persistence of the photocatalytic activity in the oxidation reaction in high-temperature, high-pressure water would open up a possibility of the development of the hybrid process based on the combination of SCWO process and TiO_2 photocatalysis for the treatment of environmental pollutants in soil and water, which are difficult to handle by conventional SCWO process or catalytic SCWO process alone.

The mechanism of atrazine degradation in aqueous phase under sonolysis at 20 kHz, ozonation, photolysis at 254 nm and photocatalysis in the presence of TiO_2, employed either separately or in combination *(Claudia L. Bianchi et al. (2006))***.** Ozonation and photocatalysis induced atrazine de-alkylation, followed by slower de-chlorination, while direct photolysis at 254 nm produced very efficient de-chlorination. Simultaneous sonolysis had beneficial effects on ozonation and photocatalysis, especially by increasing the rate of photocatalytic de-alkylation, and no effect on the unimolecular photolytic de-chlorination of atrazine. Although complete atrazine mineralization could not be attained, because of the stability of the *s*-triazine ring toward oxidation, atrazine degradation and overall detoxification, as related to the disappearance of chlorinated by-products, proceeded at the highest rate when photolysis at 254 nm was combined with ozonation.

Several different pesticides (alachlor, atrazine, chlorfenvinphos, diuron, isoproturon and pentachlorophenol) considered PS (priority substances) by the European Commission and dissolved in water at 50 mg/L (or at maximum water solubility) have been degraded at pilot-plant scale using photo-Fenton and TiO_2 photocatalysis driven by solar energy. Two different iron concentrations (2 and 55 mg/L) and TiO_2 at 200 mg/L have been tested and discussed, using mainly TOC mineralisation for comparison of treatment effectiveness *(M. Hincapié et* *al. (2005)). Vibrio fischeri* toxicity assays were also employed for evaluating the photocatalytic treatments and comparison between these results and parent compound disappearance, TOC evolution and anion (or ammonia) release were discussed. Almost complete mineralisation and total detoxification were always attained. It has been demonstrated that evolution of chloride could be a key-parameter for predicting toxicity of chlorinated compounds.

Andjelka S. Topalov (2004) were investigated the kinetics and possible mechanism of the photocatalytic degradation of herbicide mecoprop, in UV illuminated aqueous colloids of synthesized nanosized TiO_2 were investigated. The rate of degradation was studied by ^1H NMR, UV spectrometry, as well as by potentiometric titrimetric determination of generated chloride. The catalyst dosage and effects of other kinetic factors on the photocatalytic degradation, such as initial substrate concentration, temperature and type of TiO_2 were investigated as well. The degradation rates were found to be strongly influenced by the above parameters. It was found that photocatalytic efficiency is lower and that a smaller number of observed organic intermediates (only 4-chloro-2-methylphenol and acetic acid) were detected than those observed in the presence of TiO_2 (Degussa P-25). Kinetics of the degradation was also monitored for direct photolysis, as well as for solar degradation in the presence and in the absence of $TiO_{2.}$

The combination of TiO_2-assisted photocatalysis and ozonation *(M. Mare et. al.1999)* in the degradation of nitrogen-containing substrates such as alkylamines, alkanolamines, heterocyclic and aromatic N-compounds has been investigated. A laboratory set-up was designed and the influence of the structure of the N-compound, the TiO_2 and ozone concentration on the formation of breakdown products was examined. The experimental results showed that a considerable increase in the degradation efficiency of the N-compounds is obtained by a combination of photocatalysis and ozonation as compared to either ozonation or photocatalysis only.

C. C. Wong and W. Chu (2002) has done the direct photolysis and photocatalytic degradations of alachlor, a widely used herbicide, were studied using three different monochromatic UV lamps (254, 300 and 350 nm) and two TiO_2 sources. Both the direct photolysis and photocatalytic degradations of alachlor follow pseudo-first-order decay kinetics. TiO_2-P25 was found to be an effective photocatalyst compared to TiO_2-BDH. The direct photolysis of alachlor was dominant at 254 nm even if TiO_2 was present in the solution. Among the three

UV wavelengths used, the highest photocatalysis quantum yield was obtained at 300 nm. The photocatalytic degradation rate of alachlor increased with the dosages of TiO_2, but an overdose of TiO_2 would retard the reaction due to light attenuation.

Photocatalytic degradation of 3-amino-2-chloropyridine, as a model compound for pyridine containing pesticides, in UV illuminated aqueous suspensions of TiO_2 were investigated *(Biljana F. Abramovi (2004))***.** It was found that mineralization to carbon dioxide, water, chloride, ammonia, and nitrate takes place during the process. The rate of degradation was studied by HPLC, ion chromatography and UV spectrometry, as well as by continuous potentiometric measurement of the rate of chloride generation and the pH change of the medium. It was found that the reaction in the investigated concentration range is of the zero-order in respect to 3-amino-2-chloropyridine degradation with the reaction rate constant 8.9×10^{-6} mol/(dm^3 min) and adsorption coefficient 1.2×10^4 dm^3/mol. HPLC analysis indicated that very few pyridine containing intermediates at low concentrations are formed during the process. Based on the obtained data a tentative reaction mechanism was proposed. Kinetics of the degradation was also monitored for direct photolysis, as well as for solar degradation in the presence and in the absence of TiO_2.

Tibiriçá G. Vasconcelos (2009) examines the results of the performance of photo-induced oxidation, heterogeneous photocatalysis, ozonation and peroxone in degrading the fluoroquinolone antimicrobial ciprofloxacin (CIP) in a hospital effluent. Both heterogeneous photocatalysis and peroxone led to almost complete CIP degradation after 60 min treatment. Ozonation showed the best performance: total degradation after 30 min treatment. This was an unexpected result in view of the greater capacity of the other two processes to generate hydroxyl radicals.

12 hybrid photocatalysts consisting of titania (TiO_2) and an adsorbent such as mordenite were investigated for the photocatalytic decomposition of toluene, a major indoor contaminant in indoor air. The highest decomposition rate was obtained with the use of mordenite and silicon dioxide (SiO_2) as additives to TiO_2. The photocatalytic activities of hybrid photocatalysts in decomposing toluene are 1.33 times as high as pure P25 at the net weight loading of 0.49 mg/cm^2 under the test condition. Scanning electron microscopy (SEM) images confirmed that the hybrid photocatalyst films were very porously distributed; TiO_2 was adsorbed on the surface of mordenite and SiO_2, increasing the reaction area of TiO_2. The

unimolecular Langmuir–Hishelwood model and mass-transfer-based (MTB) method were used to evaluate the reaction coefficients and adsorption equilibrium coefficients of hybrid photocatalysts. It is evidenced that the reaction areas of two hybrid photocatalysts were 1.52 and 1.64 times larger than that of P25, respectively, which is the major reason to make the high removal efficiency of toluene *(Jinhan Mo (2009))***.**

O.T. Woo et al. (2009) studied that polycyclic aromatic hydrocarbons (PAHs) are hydrophobic pollutants and their low water solubility limits their degradation in aqueous solution. They study the effects of acetone on the photocatalytic degradation efficiency and pathways of 5 selected PAHs, namely naphthalene (2 rings), acenaphthylene (3 rings), phenanthrene (3 rings), anthracene (3 rings) and benzo[a]anthracene (4 rings). The Microtox toxicity test was used to determine whether the PCO system can completely detoxify the parental PAHs and its intermediates. The addition of 16% acetone can greatly alter the degradation pathway of naphthalene and anthracene. Based on intermediates identified from degradation of the 5 PAHs, the location of parental PAHs attacked by reactive free radicals can be correlated with the localization energies of different positions of the compound. For toxicity analysis, irradiation by UV light was found to induce acute toxicity by generating intermediates degradation products from PAHs and possibly acetone. Lastly, all PAHs (10 mg l^{-1}) can be completely detoxified by titanium dioxide (100 mg l^{-1}) within 24 h under UVA irradiation (3.9 mW cm^{-2}).

Ren-Jang Wu et al. (2008) studied the photocatalytic degradation of terbufos in aqueous suspensions was investigated by using titanium dioxide (TiO_2) as a photocatalyst. About 99% of terbufos was degraded after UV irradiation for 90 min. Factors such as pH of the system, TiO_2 dosage, and presence of anions were found to influence the degradation rate. Photodegradation of terbufos by TiO_2/UV exhibited pseudo-first-order reaction kinetics, and a reaction quantum yield of 0.289. The electrical energy consumption per order of magnitude for photocatalytic degradation of terbufos was calculated and showed that a moderated efficiency (E_{EO} = 71 kWh/ (m^3 order)) was obtained in TiO_2/UV process. To obtain a better understanding of the mechanistic details of this TiO_2-assisted photodegradation of terbufos with UV irradiation, the intermediates of the processes were separated, identified, and characterized by the solid-phase microextraction (SPME) and gas chromatography/mass spectrometry (GC/MS) technique.

One of the commercial N-doped TiO_2 powders (Sumitomo Chemicals, TPS 201) was studied as a model material by photocatalytic and photoelectrochemical methods in order to evaluate the photoactivity of N-doped TiO_2 materials and the possibility of their applications in solar photocatalysis. The N-doped TiO_2 powder (TPS) was able to degrade and mineralize phenol under solar or visible light (VL) irradiation, and the degradation rate was strongly dependent on the suspension concentration *(Xintong Zhang et al. (2008))***.** Photoelectrochemical studies showed that the VL-irradiated TPS electrode was able to oxidize water, phenol, as well as maleic acid, an open-ring oxidized product of phenol, consistent with the results of photocatalytic studies. Calcining the TPS powder at/over 773 K was found to lower the absorption in the VL region and the photocatalytic activity under VL irradiation, but improve the photocatalytic activity under solar irradiation, suggesting that the mid-gap states introduced by nitrogen doping also worked as recombination centers. Deposition of Pt (0.2 wt%) on the TPS photocatalyst thus greatly increased the degradation rate of phenol under either solar or VL irradiation due to the suppression of charge recombination, and the degradation rate was found to be higher than a pristine TiO_2 photocatalyst (ST-01, anatase) either with or without loading of Pt. The potential application of the N-doped TiO_2 in solar photocatalysis was discussed on the basis of above-mentioned studies.

Photocatalytic degradation of the antibiotic sulfamethoxazole (SMX) by solar photo-Fenton at pilot plant scale in distilled water (DW) and in seawater (SW). Degradation and mineralization of SMX were strongly hindered in SW compared to DW. The influence of H_2O_2 and iron concentration on the efficiency of the photocatalytic process was evaluated. An increase in iron concentration from 2.6 to 10.4 mg L^{-1} showed only a slight improvement in SMX degradation and mineralization. However, an increase in H_2O_2 concentration up to 120 mg L^{-1} during photo-Fenton in DW decreased SMX solution toxicity from 85% to 20%, according to results of *Daphnia magna* bioassays. The same behaviour was not observed after photo-Fenton treatment in SW. Despite 45% mineralization in SW, toxicity increased from 16% to 86% as shown by *Vibrio fischeri* bioassays, which suggests that the intermediates generated in SW are different from those in DW. A SMX degradation pathway during the photo-Fenton treatment in DW is proposed *(Alam G. Trovo (2009)).*

Degradation products and pathway of chlorfenvinphos (CFVP) in water treated by photo-Fenton driven by solar irradiation were determined in a laboratory experimental setup.

Routine water sample analysis was done by standard laboratory wet chemistry procedures and the use of laboratory equipment such as HPLC–UV and ionic chromatography (IC). Solid-phase extraction (SPE) was used to extract analytes from an aqueous matrix, and GC–MS was used to identify intermediate degradation products. The use of an HPLC–TOF-MS provided more results on degradation products and more insight was gained into how degradation takes place. In all experiments, strong mineralisation and degradation of CFVP was observed. CFVP and its degradation products, like 2,4-dichlorophenol, 2,4-dichlorobenzoic acid and triethyl phosphate were decomposed into organic substances like acetate, formate, maleate, and inorganic ions like chloride and phosphate, within the detection limits (12.5 μg/L for CFVP in the GC–MS and 40 μg/L in HPLC–UV) of the equipment used. In fact, Cl^- emerges in nearly stoichiometric concentrations and PO_4^{3-} is precipitated as $FePO_4$. The remarkably complete absence of chlorinated aliphatic substances and chlorinated acids leads to the conclusion that chlorine is removed very quickly, and that residual DOC does not correspond to any chlorinated compound. *(Nikolaus Klamerth et al. (2008))*

Fang Han et al. (2009) studied that Organic dyes are one of the largest groups of pollutants released into wastewaters from textile and other industrial processes. Because of potential toxicity of the dyes and their visibility in surface waters, removal and degradation of organic dyes have been a matter of considerable interest. A wide range of methods have been developed, amongst which the heterogeneous photocatalysis involving titanium dioxide (TiO_2) appears to be the most promising technology. This paper presents a critical review of novel achievements in the modification of TiO_2photocatalytic systems aimed at: enhanced TiO_2 photocatalytic efficiency; complete mineralization of organic dyes; efficient utilization of visible and/or solar light; stability and reproducibility of the modified TiO_2; recycle and reuse in real wastewater treatment.

Wojciech Baran (2009) shown that the photocatalytic degradation of sulfanilamide, sulfacetamide, sulfathiazole, sulfamethoxazole and sulfadiazine in aqueous solutions was examined during their irradiation with UV-A (366 nm) with TiO_2, Fe salts and $TiO_2/FeCl_3$ catalysts. The study was carried out by HPLC-UV, HPLC/MS-EI and total organic carbon (TOC) methods. It was found that sulfonamides underwent photocatalytic degradation in the presence of TiO_2, $TiO_2/FeCl_3$ and Fe^{3+} salts, and the optimum catalyst for this process can be $FeCl_3$. Based on the identified intermediate products, a degradation pathway was proposed. Moreover, the rate of photocatalytic process carried out with $FeCl_3$ as well as the relationship between the pH of irradiated solutions, initial concentrations of sulfanilamide and $FeCl_3$ were stated.

Hilal S. Wahab and Andreas D. Koutselos (2009) investigated the adsorption and initial oxidation step for the photodegradation of aniline on anatase TiO_2 (1 0 0) surface. This surface has been chosen because it is present in TiO_2 powders used in the adsorption experiments. Molecular dynamics (MD) simulations for the adsorption behavior of aniline have revealed a planar orientation of the aromatic ring to the surface linked via amino nitrogen with the surface lattice titanium ion. With the intention of predicting the primary photochemical and photocatalytic $^{\bullet}OH$ initiated oxidation intermediates, two different theoretical approaches, frontier electron theory and Wheland localization theory, have been applied. Based on our results, all isomers, *para-*, *ortho-* and *meta-*hydroxyaminocyclohexadienyl radicals, could be present in the case of photochemical oxidation, but the *para-* and *ortho-*positions are energetically more favorable than *meta-*position. Whereas, for the photocatalytic oxidation, where the aniline is adsorbed onto the TiO_2 surface via amino group, the *para-* and *meta-*isomers are energetically more stable than the *ortho-*isomer, which is mainly influenced by steric hindrance.

n-Butyl benzyl phthalate (BBP) has been classified as endocrine disrupting compound and priority pollutant*(Xiang-Rong Xu et al. (2008))***.** The optimal TiO_2 dosage and pH value for the BBP degradation were 2.0 g L^{-1} and 7.0, respectively. The degradation rate of BBP by TiO_2/UV process could be fitted pseudo-first-order kinetics. The effects of co-existing substances on the degradation rate of BBP revealed that some anions (such as BrO_3^-, ClO_4^- and $Cr_2O_7^{2-}$) could enhance BBP degradation, and other anions would restrain BBP degradation. The sequence of inhibition was $PO_4^{3-} > CO_3^{2-} > NO_3^- > SO_4^{2-} > Cl^-$. The cations K^+, Na^+, Mg^{2+} and Ca^{2+} had the restrained effect on the BBP degradation, and the effect of Ca^{2+} was the strongest among four cations tested. The organic compounds acetone and methanol decreased the degradation rate of BBP. The major intermediates of BBP degradation were identified as mono-butyl phthalate, mono-benzyl phthalate and phthalic acid, and a primary degradation mechanism proposed.

Synthetic dyes are a major part of our life as they are found in the various products ranging from clothes to leather accessories to furniture *(M.A. Rauf et al. (2009))***.** Advanced oxidation processes (AOP’s) are the most widely used approach that is employed for dye degradation studies and found that photocatalysis used for dye degradations in aqueous suspensions using TiO_2 as a catalyst. And highlight the effect of a variety of conditions on TiO_2-photocatalysed decoloration of dyes, such as amount of catalyst, reaction pH, light intensity, concentration of organic dye, and the presence of additives such as ions. This review also summarizes the degradation pathways that azo dyes undergo, with some of the intermediates that are generated during their degradation. Finally, a survey is presented of the various classes of dyes and their relative ease of degradation by AOP's.

A kinetic model for the advanced oxidation of aromatic hydrocarbons in water is proposed and tested with experimental results of the oxidation of nitrobenzene and phenanthrene, two aromatic hydrocarbons of different reactivity with ozone. The kinetic model leads to good results in the case that the compound treated reacts exclusively with ozone, that is, without the contribution of hydroxyl radical oxidation as in the case of phenanthrene oxidation. In this case, it is not necessary to account for intermediate reactions to have good predictions of experimental remaining concentrations of ozonation processes. On the contrary, when the aromatic hydrocarbon is mainly removed by hydroxyl radicals (case of nitrobenzene), mole balance equations of intermediates have to be included for the experimental concentrations to be reproduced. For so doing, the kinetic parameters, such as rate constants of reactions between ozone and hydroxyl radical with intermediates and their corresponding quantum yields at 254 nm were also determined. The kinetic model, however, is unable to reproduce, with accuracy, the experimental results of the ozone−UV radiation oxidation system *(Fernando J. Beltrán et al.1999)***.**

Advanced oxidation processes (AOP's) are used for the treatment of wastewaters containing non-easily removable organic compounds *(Marc Pera-Titus et al. (2003)).* Chlorophenols (CPs) are a group of special interest due to their high toxicity and low biodegradability. Data concerning the degradation of CPs by means of AOP's reported during the period 1995–2002 are evaluated in this work. Among the AOP's, the following techniques are studied: processes based on hydrogen peroxide (H_2O_2+UV, Fenton, photo-Fenton and Fenton-like processes), photolysis, photocatalysis and processes based on ozone (O_3, O_3+UV and O_3+catalyst). Half-life times and kinetic constants for CP degradation are reviewed and the different mechanistic degradation pathways are taken into account.

The oxidation of phenol and two substituted species (4-nitrophenol and 4-chlorophenol) has been carried out by means of the AOP's *(Olga Gimeno et al. (2005)).* From UV–vis experiments, the quantum yield of these organics has been calculated (0.018, 0.005 and 0.017 mol per Einstein for phenol, 4-nitrophenol and 4-chlorophenol, respectively). Broadly speaking, the addition of titania powder results in a slight inhibition of the parent compound degradation rate, although a positive effect is experienced when measuring the chemical oxygen demand (COD) and total organic carbon (TOC) removals. Amongst the technologies investigated, those combining ozone and radiation show the best efficiency in terms of phenols elimination and also COD and TOC decay rates. A simple economy analysis of the processes illustrates how the combinations O_3 + UV–vis and O_3 + UV–vis + TiO_2 are the most attractive technologies, although some additional considerations have to be taken into account.

The heterogeneous photocatalytic degradation of 2-, 3- and 4-nitrophenol has been investigated in oxygenated aqueous suspensions containing TiO_2 *(A. Di Paola et al. (2002)).* The organic reaction intermediates have been determined by high performance liquid chromatography. The results indicate the complete mineralisation of the substrates and the formation of both nitrate and ammonium ions. The degradation pathways involve a rapid opening of the aromatic ring followed by a slower oxidation of the aliphatic compounds. The hydroxyl radicals are responsible for the primary attack of the nitrophenols with formation of dihydroxy nitrobenzenes. The ring hydroxylation occurs in the positions activated by the contemporaneous presence of phenolic and nitro groups. The presence of ammonium ions confirms that reduction pathways are also operating.

Margarita Hincapié Pérez et al.(2007) Alachlor, atrazine and diuron (pesticides)dissolved in water at 50, 25 and 30 mg/L, respectively were photo degraded by Fe^{2+}/H_2O_2, Fe^{3+}/H_2O_2, TiO_2 and $TiO_2/Na_2S_2O_{8(\text{solar AOP})}$ treatments driven by solar energy at pilot-plant scale using a compound parabolic collector (CPC) photoreactor. All the advanced oxidation processes (AOPs) employed mainly compared the TOC mineralisation rate to evaluate treatment effectiveness. Parent compound disappearance, anion release and oxidant consumption are discussed as a function of treatment time. The use of Fe^{2+} or Fe^{3+} showed no influence on the reaction rate under illumination and the reaction using 10 or 55 mg/L of iron was quite similar $TiO_2/Na_2S_2O_8$ showed a quicker reaction rate than TiO_2 and a similar rate compared to photo-Fenton. The main difference found was between $TiO_2/Na_2S_2O_8$ and photo-Fenton, detected during atrazine degradation, where pesticide transformation into cyanuric acid was confirmed only for $TiO_2/Na_2S_2O_8$.

Heterogeneous and homogeneous oxidative destruction of phenol, cyclohexanol (CyOH), and 4-nitroaniline (4-NA) in aqueous solution by the photo-Fenton reaction and TiO_2/UV-A is described and compared. The decomposition mechanisms were investigated by studying the intermediate products by HPLC and a photodiode array. The degradation of 4-NA was monitored by GC/MS to trace the decomposition products (nitrobenzene, p-benzoquinone, hydroquinone and resorcine). During the photochemical degradation of 4-NA nitrate ions were detected by an ion selective electrode *(W. Spacek et. al. (2002)).*

1.2 PHOTOCATALYTIC TREATMENT OF ANILINE AND NITROANILINE COMPOUNDS

Aniline degradation by combined photocatalysis and ozonation investigated by *Laura Sánchez et al.(2003)* From the experimental results obtained it is observed that the ozonation pretreatment followed by photocatalysis strongly increases the yield of TOC removal in comparison to either ozonation or photocatalysis carried out separately. The opposite sequence (photocatalysis pretreatment followed by ozonation) does not enhance the efficiency of aniline degradation. Nevertheless, the highest TOC removal was achieved by simultaneous ozonation and photocatalysis. A mechanism involving the formation of an ozonide anion radical previous to the generation of OH radicals is suggested to explain the synergic effect between ozone and TiO_2 under illumination.

Solar photooxidation of aniline on ZnO surfaces was done done and The photoformation of azobenzene by the oxidation of aniline on ZnO in ethanol with natural sunlight and UV irradiation (365 nm) was studied as a function of aniline catalyst loading, airflow rate, solvent composition, etc *C. Karunakaran et al.(2005)* The photocatalyst exhibits sustainable catalytic activity. The product formation is larger with illumination at 254 nm than at 365 nm. Electron donors like triphenyl phosphine, diphenylamine and hydroquinone enhance the photocatalysis. Singlet oxygen quencher azide ion does not suppress the catalysis. The photocatalysis occurs in protic and aprotic solvents.

Satyen Gautam,et al.(2005) studied the Photocatalytic degradation of 4-nitroaniline using solar and artificial UV radiation in the presence of TiO_2 suspensions in a batch and continuous annular reactor. Artificial and solar radiation was employed as sources of UV radiation. The effect of catalyst loading, pH, presence of anions and initial concentration on the rate of photocatalytic degradation was investigated. *P-Aminophenol*, *p*-benzoquinone and hydroquinone were identified as the intermediates during the degradation process.

Aniline degradation at pH 2 by Fenton and electro-Fenton processes were kinetically investigated *(Jin Anotai, et al. (2006))***.** Electro-Fenton process was found to be superior to ordinary Fenton process with the current impacts of 1.2 to 3.1 for removal efficiency and 1.2 to 5.8 for degradation rate depending on initial Fe^{2+} concentration. This is mainly due to the rapid electrochemical regeneration of $Fe^{2+.}$

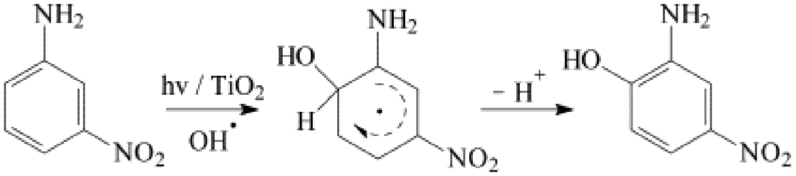
The mineralization of Aniline by AOP's like anodic oxidation, photocatalysis, electro-Fenton and photoelectro-Fenton processes and noticed aniline degradation in acidic medium of pH≈3 under photocatalytic and electrochemical conditions. The efficiency for substrate mineralization in each process has been comparatively analysed by the decrease in TOC of aniline solutions. Particular emphasis has been made on the role of Fe (II) ions and H_2O_2. The electrochemical experiments performed in the presence of both species (electro-Fenton conditions) leads to a fast aniline mineralization, which is notably increased by UVA irradiation (phooelectro-Fenton process). In photocatalysis with TiO_2 suspensions, the presence of H_2O_2 and Fe (II) ions in solution notably increases the aniline degradation rate at the initial stages of the process *Enric Brillas et al .(2006)).*

The degradation of *p*-nitroaniline (PNA) in water by solar photo-Fenton advanced oxidation process was investigated by *Jian-Hui Sun et al. (2008).* The effects of different reaction parameters including pH value of solutions, dosages of hydrogen peroxide and ferrous ion, initial PNA concentration and temperature on the degradation of PNA have been studied. The optimum conditions for the degradation of PNA in water were considered to be: the pH value at 3.0, 10 mmol L^{-1} H_2O_2, 0.05 mmol L^{-1} Fe^{2+}, 0.072–0.217 mmol L^{-1} PNA and temperature at 20 °C. Under the optimum conditions, the degradation efficiencies of PNA were more than 98% within 30 min reaction. The experimental results indicated solar photo-Fenton process has more advantages compared with classical Fenton process, such as higher oxidation power, wider working pH range, lower ferrous ion usage, etc. and also the present study showed the potential use of solar photo-Fenton process for PNA containing wastewater treatment.

Jian-Hui Sun et al. (2007) was developed a detailed kinetic model for the degradation of *p*-nitroaniline (PNA) by Fenton oxidation. Batch experiments were carried out to investigate the role of pH, hydrogen peroxide and Fe^{2+} levels, PNA concentration and the temperature. The kinetic rate constants, k_{ap}, for PNA degradation at different reaction conditions were determined. The test results show that the decomposition of PNA proceeded rapidly only at pH value of 3.0. Increasing the dosage of H_2O_2 and Fe^{2+} enhanced the k_{ap} of PNA degradation. However, higher levels of H_2O_2 also inhibited the reaction kinetics. The k_{ap} of PNA degradation decreased with the increase of initial PNA concentration, but increased with the increase of temperature. Based on the rate constants obtained at different temperatures, the empirical Arrhenius expression of PNA degradation was derived. The derived activation energy for PNA degradation by Fenton oxidation is 53.96 kJ mol^{-1}.

Transient and steady-state photolysis of p-nitroaniline in aqueous solution was performed by *Hui-Qin Guo and Yi-Fan Lee (2008)* and showed the kinetics and mechanisms of degradation of p-nitroaniline (p-NA) in aqueous solutions. Monophotonic photo-ionization of p-NA was characterized by 266 nm Laser Flash Photolysis (LFP). The quantum yield of e_{aq}^{-} was calculated. Radical cations and neutral radicals of p-NA were identified, respectively. The LFP of p-NA with H_2O_2 in aqueous solutions was investigated for the first time. For steady-state photo-degradation, degradation of p-NA was observed at diverse irradiation conditions under 254 nm UV light. Direct photo-degradation of p-NA by 254 nm UV light in aqueous solution was very difficult. Once H_2O_2 was added into the experimental system, degradation of p-NA was enhanced remarkably. In the absence of O_2, degradation rate increased rapidly along with the irradiation time and reached 80% at 10 min. p-NA could be totally removed after 15 min in UV/H_2O_2 process. In the presence of O_2 and H_2O_2, degradation rate increased linearly along with the irradiation time and reached 80% at 7.5 min. p-NA could be totally removed after 10 min. The mechanisms behind the photo-degradation of p-NA

The Photocatalysed reaction of few selected organic compounds such as 4-bromoaniline, 3-nitroaniline**,** pentachlorophenol, 1, 2, 3-trichlorobenzene, and diphenylamine has been investigated either in water or in acetonitrile/water mixture in the presence of titanium dioxide and molecular oxygen. GC–MS analysis of the irradiated mixture showed the formation of oxidative products. A probable pathway for the formation of products has been proposed involving $OH\text{-}$ and $O_2\text{-}^{-}$. *(M. Abu Tariq et al. (2006))*



The photocatalytic degradation of aniline was done in annular photoreactor, with 2×6 W (E_{max}=365 nm) UV lamp as light source, borosilicate glass as wave filter and titanium dioxide immobilized on porous nickel as catalysts. Parameters such as the initial concentration, flow rate, initial pH, dissolved oxygen, electrolyte, hydrogen peroxide addition, temperature and external potential bias affecting the degradation rate of aniline were studied. The results showed that photocatalysis is an effective process for the degradation of aniline. The activated energy for the photocatalytic degradation of aniline is 6.13 kJ mol^{-1}. The initial quantum yield is 1.89% for aniline 1.10×10^{-4} mol l^{-1}. Total mineralization requires a much longer illumination time than the disappearance of anilines. . The external potential bias can largely improve the efficiency of photocatalytic degradation of aniline *(Leng Wenhua et al. (2000))***.**

M. Canle L et al. (2005) gave the mechanism of TiO_2-photocatalyzed degradation of aniline derivatives Interaction between aromatic amines and TiO_2 takes place preferentially through the amino group when $pH > pK_a(BH^+)$ and, as a minor but mechanistically relevant mode, via a π-interaction if $pH < pK_a(BH^+)$. No significant direct photodegradation of aniline or *N*, *N*-dimethyl-aniline is detected in acidic medium using $\lambda > 290$ nm, but it is enhanced in alkaline medium. 2-Aminophenol and benzoquinone are the main photoproducts of direct irradiation of aniline**.** The main photoproducts of photocatalytic degradation of aniline at the pH of maximum adsorption are 2-aminophenol and phenol. Scavenging $HO^\bullet$ with *t*-BuOH shows that adsorbed aniline is oxidized by positive holes (h^+), with participation of the anilinium radical cation. In the case of *N*, *N*-dimethyl-aniline at the pH of maximum adsorption, *N*-methyl-aniline is the main photoproduct, formed also via the dimethyl anilinium radical cation. Photocatalytic degradation in acid medium is inhibited due to electrostatic repulsion between the positively charged surface and the protonated amines. Aniline is mainly transformed into phenol and 2-aminophenol, and *N*, *N*-dimethyl-aniline into aniline that undergoes hydroxylation to phenol. In alkaline medium the main photoproduct of degradation of aniline is nitrobenzene, formed with involvement of the anilinyl radical.

CHAPTER 3

MATERIAL AND METHODS

This chapter lays emphasis on the materials and methods used during this research, including the chemicals, glassware instrument like the UV photo reactor, pH adjustment and analysis by UV-Vis Spectrophotometer, COD digester, weighing machine and procedures used to treat the compound with the UV/TiO_2 catalysis and Solar/TiO_2. The compilation of the varying pH of solution, TiO_2 dosages and the varying UV and solar contact times for compound with varying concentrations.

3.1 MATERIALS

3.1.1 2-NITROANILINE

2-nitroaniline compound was purchased from sigma Aldrich(USA). 2-nitroaniline compound solution was used without further purification. Full scan of 2-nitroaniline was taken with the help of UV-vis spectrophotometer and maximum absorbance was observed at 282nm, 411nm and 223nm. Molecular structure of 2-nitroaniline is illustrated in Fig-3.1.1. It is present in the form of orange yellow crystals.. 2-nitroaniline solution was prepared with the help of single distilled water.

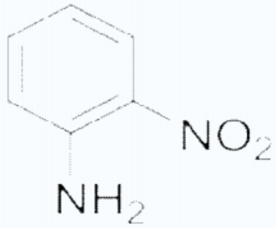


Fig 3.1 Structure of 2-nitroaniline

3.1.2 REAGENTS AND CHEMICALS USED

The photocatalyst TiO_2 (P25) was procured from Degussa Company. Hydrogen peroxide was used as an oxidant. Compound is characterized for pH, BOD, COD, Color etc. For the determination of BOD, phosphate buffer, Calcium chloride, Magnesium sulphate, Ferric chloride, Magneous sulphate, Potassium iodide, Sulphuric acid, Sodium thiosulphate and Strach as an indicator were used. COD of industrial effluent and treated sample was determined by using potassium dichromate solution (Containing Mercuric sulphate and Concentration Sulphuric acid), COD reagent (containing Silver sulphate and Conc. Sulphuric acid), ferrous ammonium sulphate solution (0.05 N) and Ferroin indicator. For all the experiments single distilled water were used. Different normality of (0.1, 1M) HCl and NaOH were used for adjustment of pH of compound solution.

3.2 INSTRUMENT USED

3.2.1 pH METER

pH of the solution was monitored by using a digital desktop, pH Meter (CP 901) from Century Instrument Company and pH was adjusted with the help of NaOH and HCl. Instrument was calibrated with freshly prepared buffer solutions (of pH 4 and 9) from time to time throughout the study.

3.2.2 MAGNETIC STIRRER

Magnetic stirrer was used during experimentation to solve the problem of mixing and titanium dioxide remains in suspension.

3.2.3 AIR SPARGER

Air is continuously supplied during experiments in UV reactor as well as solar experiments in order to oxidize the organic matter.

3.2.4 PHOTO REACTOR

Photocatalytic treatment of 2-nitroaniline was performed in batch experiments. For photocatalytic UV reactor was used which was rectangular having dimensions of 4.5 feet length, 3 feet width and 3.5 feet height and made up of iron. Roof of the reactor was made up of wooden; seven UV tubes (36 Watt each) were 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 photo catalytic reaction in slurry mode. Two different view of photoreactor are shown in Fig. - 3.2. and 3.3.

Fig-3.2 Outer view of photo reactor

Fig-3.3 Photo reactor at lab level during photo catalytic treatment

3.2.5 FILTRATION

After photo catalytic treatment by photo reactor dye and effluent sample were filtered through syringe filters having milipore filters of 0.45 um pore size.

3.2.6 COD DIGESTER

COD digester (Hatch) was used for the digestion of samples in the process of COD determination.

Fig-3.4 COD digester

Fig-3.5 pH meter

3.2.7 RADIOMETER

Intensity of UV and solar light was measured with Eppley radiometer.

3.2.8 REACTION VESSEL

Glass bowls were used for the photocatalytic reactions having a capacity of 1 L.

3.2.9 SPECTROPHOTOMETER

The spectrum was taken with UV-vis. Spectrophotometer (Hitachi V-500 UV/VIS (Japan) double-beam spectrophotometer).

Fig-3.6 Spectrophotometer

3.3 METHODS

3.3.1 PREPARATION OF SOLUTION

a) **2-Nitroaniline solution:** The solutions were prepared by adding a known amount of compound into a small amount of deionized water in a 1-liter Erlenmeyer flask and filling it to the mark with single distilled water. The flasks were covered with aluminum 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. For most of the experiments, compound solutions of 25 ppm concentration were prepared by dissolving 0.025g in single distilled water and make the solution quantity to1 L. (If 1 g is present in 1 L then solution is said to be 1000 ppm and 0.1 g in 1000 ml then it becomes 100 ppm.)

b) **Handling and Storage of 2-nitroaniline compound:** Keep container tightly closed. Keep it Separated from strong acids, strong oxidants, combustible and reducing substances, food and feedstuffs. Keep away from heat. Keep away from sources of ignition on combustion, forms toxic fumes of nitrogen oxides. Reacts with strong acids, strong oxidants and strong reducing agents. Reacts with organic materials in presence of moisture causing fire hazard. The substance can be absorbed into the body by inhalation of its vapour, through the skin and by ingestion have effects on the blood, resulting in the formation of methaemoglobin. Many reactions may cause fire or explosion. Finely dispersed particles form explosive mixtures in air. open flames and contact with combustible substances should be avoided. Prevent deposition of dust; closed system, dust explosion-proof electrical equipment and lighting Protective gloves, Protective clothing should be used.

3.3.2 ESTIMATION OF COD

COD was estimated as per the standard method No. 5220C, page No.5-14 from STANDARD METHODS for the examination of water and wastewater, 1989(17thedition).

3.3.3 ESTIMATION OF BOD

BOD was estimated as per standards method No. 5210 B, page No.5-4 from STANDARD METHODS for the examination water and wastewater, 1989(17th edition).BOD was estimated by BOD bottle method.

3.3.4 UV INTENSITY MEASUREMENT

UV intensity was measured in the UV reactor with the help of radiometer. Radiometer was placed at different places from top with variation in distance from UV tubes such as top of the reactor, bottom of the reactor and middle of the reactor. It has been observed that the maximum UV intensity was at the middle of the UV reactor which was measured to be 25 W/m^2.

3.3.5 ANALYSIS FOR DECOLORATION/DEGRADATION

The decolorisation/degradation studies were conducted by measuring absorbance in UV/VIS spectrophotometer, having a wavelength range from 190-1100nm using a 1 cm quartz cell. The measurement of absorbance was done in a 4 ml quartz couvette. 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.Full scan was taken after treatment for the 2-nitroaniline solution.

3.4 PHOTOCATALYTIC TREATMENT

Photocatalytic treatment was done for 2-nitroaniline compound solution. The compound solution was treated and the various parameters like pH, catalyst dose, concentration of oxidant, initial concentration of compound were varied and optimized.

3.4.1 DEGRADTION OF 2-NITROANILINE COMPOUND

2-nitroaniline solution of 25 ppm was prepared by the single distilled water. This type of reactions is also done in solar with same conditions. Single distilled water was used for the all dilutions. Initial pH of sample was checked and varied all the parameter to optimize the value of pH, catalyst dose, oxidant concentration and comparison of photocatalytic activity with solar light. 200 ml of sample taken in glass bowl (1000ml quantity) and bowl was covered with transparent thin foil; air is also supplied by the aerator during experiments. Compound sample was treated in the presence of UV light in photo reactor for about 5 or 6 hours. Sample was withdrawn in every 30 min. or 1 hour, filtered through the syringe filter and absorbance was taken in spectrophotometer. COD of samples was measured as per the standard methods. All tests were repeated for getting the reproducibility of results.

After the photocatalytic and solar photocatalytic treatment of wastewater (with optimized conditions), sample was filtered and it has been analyzed for BOD, COD, Colour, pH, etc.

CHAPTER 4

RESULT AND DISCUSSIONS

The photocatalytic treatment using TiO_2 catalyst was employed for the effective degradation of 2-nitroaniline solution. A matrix of experimental variables was developed in which the TiO_2 dose, pH, UV exposure time, solar exposure time, compound concentration and use of oxidant were varied and applied to compound solution.

4.1 DEGRADATION OF 2-NITROANILINE

The 2-nitroaniline compound solution was subjected to photocatalytic treatment and the efficiency of treatment was investigated by altering parameters like pH, catalyst dose, variation of conc. and effect of UV /Solar light, area/volume, and UV intensity.

4.1.1 UV –Vis SPECTRA OF 2-NITROANILINE

The photocatalytic experiments were conducted under both UV as well as solar light. The decolorization and degradation was recorded in term of change in intensity of characteristics peaks.2-nitroanilne solution (25ppm) shows the absorption peaks at 282 and 411 nm. Fig. 4.1 shows the UV-Vis. Spectra of 25 ppm of 2-nitroaniline solution. The rate of degradation was recorded with respect to change in intensity of absorption of peaks at 282 and 411nm.

Fig-4.1 Initial scan of 2-nitroaniline

4.1.2 INFLUENCE OF pH

2-nitroaniline compound solution in question has pH of 7.37. pH plays an important role in photocatalytic oxidation processes because pH affects the production of hydroxyl radical which is powerful oxidizing agent. So pH was varied from 2.0 to 12 at 4g/l of catalyst dose during experimentation and it was observed that the maximum degradation of 89.5% & 83% occured at pH 2 and 10 respectively at 282nm and 98.9% and 92% at 411nm was observed at pH 2. In UV in case of solar at pH 2 and 10 maximum degradation of 93% and 85% was observed at 282nm while 99.3% & 97.3% at 411nm was obtained. And the final pH after photo catalytic treatment was 7.36 which are suitable for biological treatment as well as discharge of wastewater into the water bodies. So on the basis of results obtained pH 2 was chosen to be best pH for photodegradtion.

Aniline degradation at pH 2 by Fenton and electro-Fenton processes were kinetically investigated *(Jin Anotai, et al. (2006))* but the mineralization of Aniline by AOP's like anodic oxidation, photocatalysis, electro-Fenton and photoelectro-Fenton processes and noticed aniline degradation in acidic medium of pH≈3 under photocatalytic and electrochemical conditions and also photocatalysis with TiO_2 suspensions notably increase the degradation rate(*Enric Brillas et al .(2006)).*

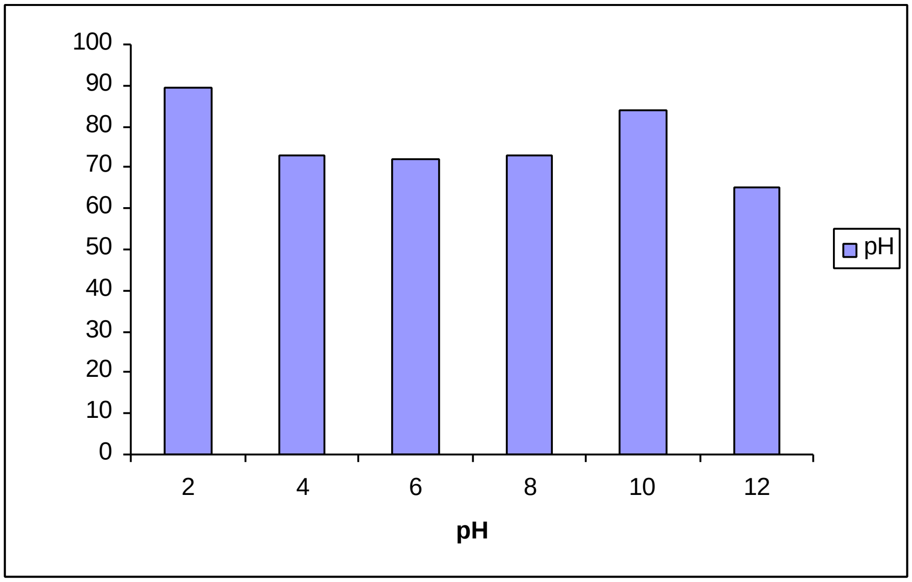


Fig-4.2 Effect of initial pH on photocatalytic degradation of 2-nitroaniline [Conc.] =25ppm, [wavelength] = 282nm, [Tio_2] =4g/L, [Time] =6hrs

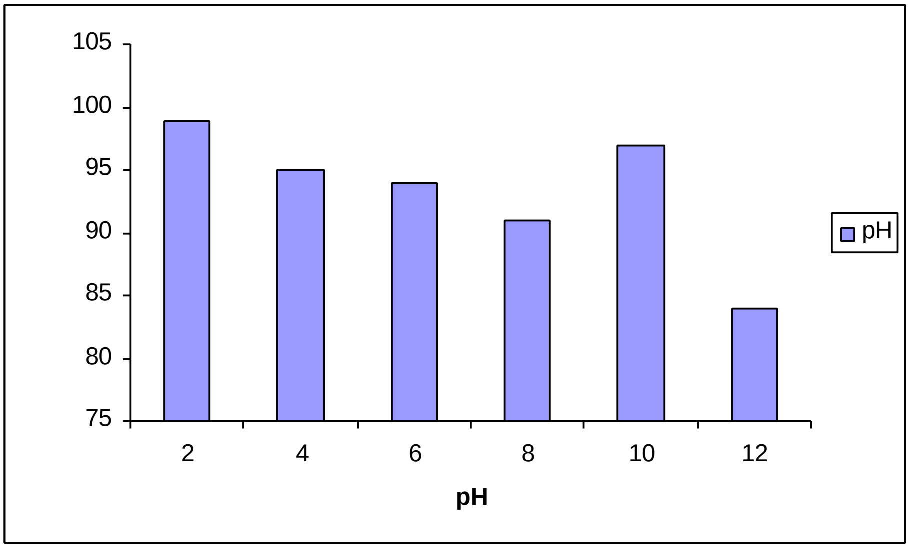


Fig-4.3 Effect of initial pH on decolourisation of 2-nitroaniline [Conc.] =25ppm, [wavelength] = 411nm, [Tio_2] =4g/L, [Time] =6hrs

4.1.3 EFFECT OF CATALYST DOSE

After optimizing pH, the catalyst dose is another important parameter which has strong influence on the degradation kinetics of 2-nitroaniline solution. Degussa P-25 TiO_2 catalyst was used in slurry mode. In order to determine the optimal amount of catalyst concentration, a series of experiments were carried out using different concentrations of TiO_2 catalyst varying from 2 to 5g/L at optimized pH of 2.0 with 25 ppm 2-nitoaniline solution. And it was observed that as the concentration of catalyst increases from 2g/L to 5g/L, the percentage degradation varies. So maximum degradation 89.5% and 98.9% has been observed at 282nm and 411nm respectively in UV and 93% and 99.3% has been observed at 282nm and 411nm respectively in solar with catalyst dose of 4g/L and it was considered as the optimum dose for the degradation of 2-nitroaniline solution (25 ppm) for subsequent analysis.

The increased degradation rate that follows the increase in the catalyst loading can be attributed to the fact that a larger amount of photons are adsorbed, thus accelerating the process. When all the compound solution molecules are adsorbed on TiO_2 no improvement is achieved by adding more catalyst. The decrease in efficiency, which is observed in the figure, may be due to an increasing opacity of the suspension and to an enhancement of the light reflectance, because of the excess of TiO_2 particles. Additionally, in the case of high catalyst loads we observed agglomeration and sedimentation of TiO_2 which makes a significant fraction of catalyst to be inaccessible to either absorbing the dye or absorbing the radiation, with consequent decrease in active sites available to the catalytic reaction.

Ren-Jang Wu et al. (2008) studied the photocatalytic degradation of terbufos in aqueous suspensions by using titanium dioxide (TiO_2) as a photocatalyst. About 99% of terbufos was degraded after UV irradiation for 270 min. Factors such as pH of the system, TiO_2 dosage, and presence of anions were found to influence the degradation rate.

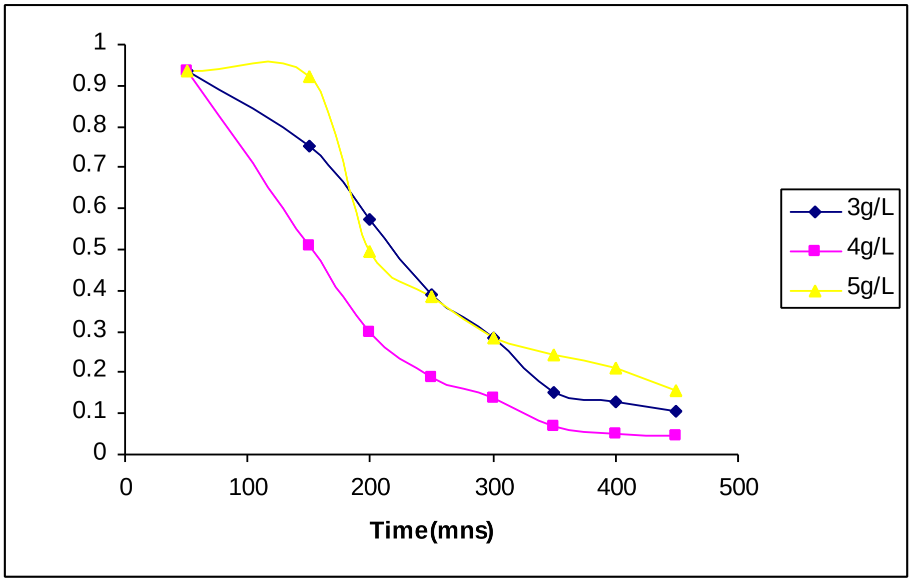


Fig-4.4 Effect of catalyst dose on photocatalytic degradation of 2-nitroaniline [pH] =2, [Conc.] =25ppm, [wavelength] = 282nm, [Time] =6hrs

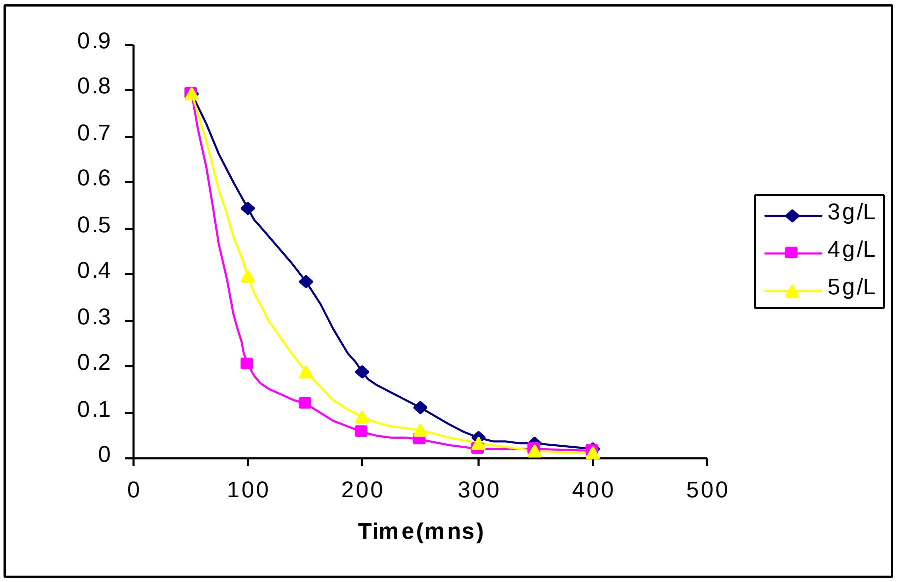


Fig-4.5 Effect of catalyst dose on decolourisation of 2-nitroaniline compound [pH] =2, [Conc.] =25ppm, [wavelength] = 411nm, [Time] =6hrs

4.1.4 EFFECT OF CATALYST ADDITION

The catalyst dose is important parameter which has strong influence on the degradation kinetics of 2-nitroaniline solution. Degussa P-25 TiO_2 catalyst was used in slurry mode. we carried out experiments in solar and UV with catalyst and without catalyst in order to determine the effect of catalyst presence or. It was observed that 63% and 80% degradation at 2pH and 44% and 55% at 10pH at 282nm and 411nm in UV and 53% and 56% at 2pH and 35% and 72% at 10 pH at 282 and 411nm was observed in solar without catalyst. The experiments with catalyst shows that 89.5% and 98.9% degradation at 2pH and 73% and 92% at 10pH at 282 and 411nm in UV and 93% and 99.3% at 2pH and 85% and 97.3% at 10 pH at 282 and 411nm was observed in solar. So on the basis of results; one can clearly say that better results were obtained in presence of catalyst in both UV as well as solar light.

The increased degradation rate that follows the increase in the catalyst loading can be attributed to the fact that a larger amount of photons are adsorbed, thus accelerating the process.

Hilal S. Wahab and Andreas D. Koutselos (2009) investigated the adsorption and initial oxidation step for the photodegradation of aniline on TiO_2 surface. Molecular dynamics (MD) simulations for the adsorption behaviour of aniline have revealed a planar orientation of the aromatic ring to the surface linked via amino nitrogen with the surface lattice titanium ion. Predicted the primary photochemical and photocatalytic $^{\bullet}OH$ initiated oxidation intermediates.

Faisal et. al., (2005) have documented the effect of catalyst dose on two dyes acridine orange and ethidium bromide and observed that the degradation rate for the decomposition of both the dyes in the presence of TiO_2 Degussa P25 increases with the increase in catalyst concentration and a further increase in catalyst concentration leads to a decrease in degradation rate.

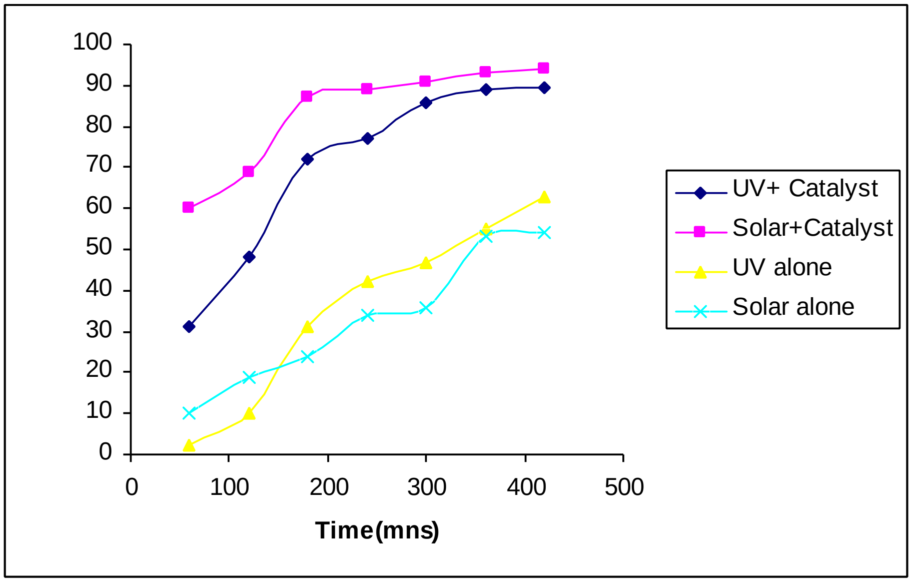


Fig-4.6 Effect of catalyst/without catalyst on photocatalytic degradation of 2-nitroaniline [pH] =2, [Conc.] =25ppm, [wavelength] = 282nm, [TiO_2] =4g/L

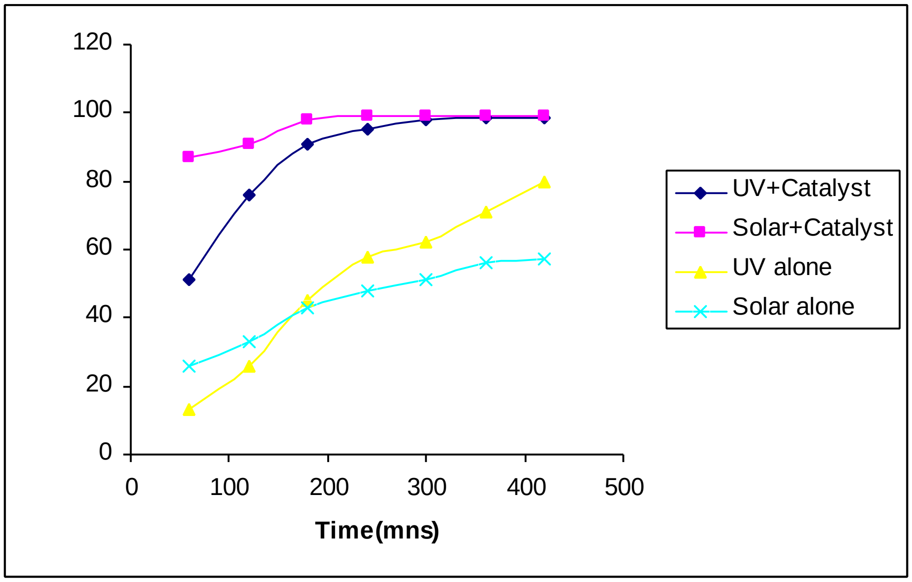


Fig-4.7 Effect of catalyst/without catalyst on decolourisation of 2-nitroaniline [pH] =2, [Conc.] =25ppm, [wavelength] =411nm, [Time] =6hrs

4.1.5 EFFECT OF INITIAL CONCENTRATION

The pollutant concentration is very important parameter. The influence of initial concentration of the 2-nitroaniline solution has been investigated on the photocatalytic degradation of compound after the optimization of pH and catalyst dose. In order to optimize the catalyst dose the initial compound concentrations was varied during the photo catalytic treatment from 25 to 100 ppm, at constant pH of 2.0 and catalyst dose of 4g/L. It has been observed from the graph (Fig- 4.1.5) that increasing concentration of compound solution from 25 to 100 ppm decreases the percentage degradation rate and it was found that at 25ppm concentration, degradation was 89.5% and 98.9% at 282nm and 411nm respectively. For 100 ppm compound concentration, percentage degradation was reduced to 54% and 74% at 282nm and 411nm respectively. The reason behind this behaviour may be due to the increase in the extent of adsorption on the catalytic surface at necessary compound concentration which reduces the catalytic activity of TiO_2. The increases in the 2-nitroaniline solution concentration also decrease the path length of photon entering into the dye solution. At high dye concentration a significant amount of UV-light may be absorbed by the dye molecule rather than the catalyst and this may also reduce the catalytic efficiency.

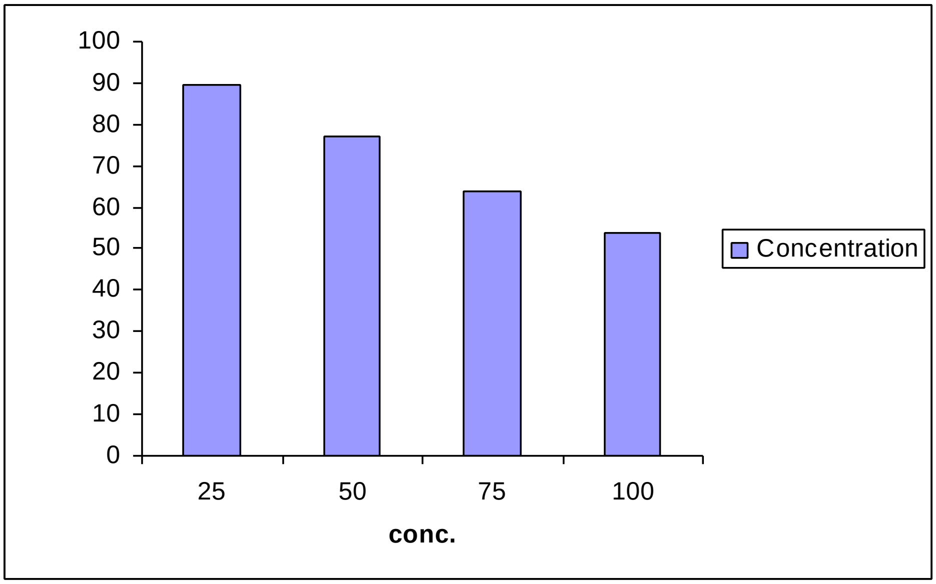


Fig-4.8 Effect of concentration on photocatalytic degradation of 2-nitroaniline [pH] =2, [wavelength] = 282nm, [TiO2] =4g/L, [Time] =6hrs

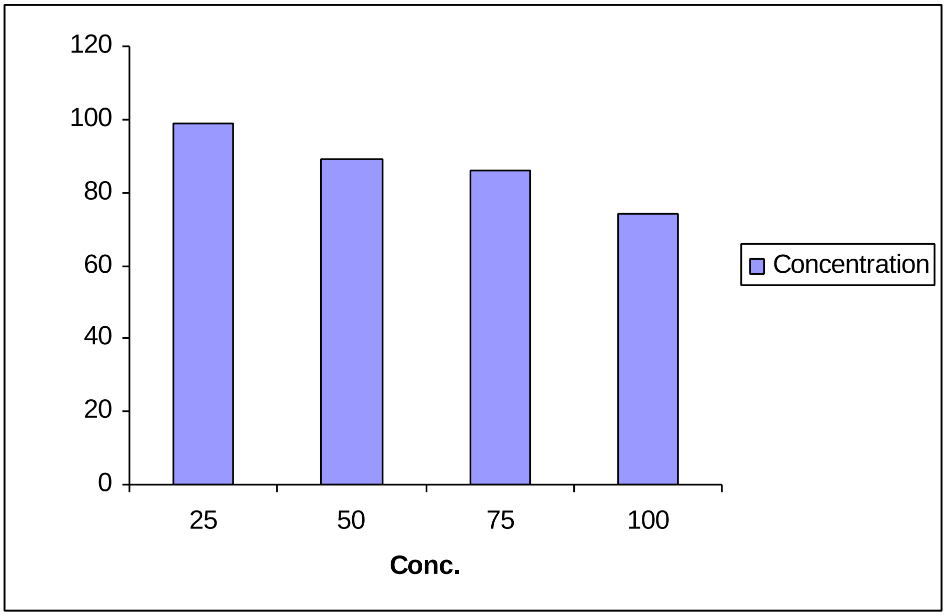


Fig-4.9 Effect of concentration on decolourisation of 2-nitroaniline
[pH] =2, [wavelength] = 411nm, [TiO_2] =4g/L, [Time] =6hrs

4.1.5 EFFECT OF UV INTENSITY

The influence of light intensity on the degradation efficiency has been examined at constant 2-nitroaniline concentration (25 ppm), at pH 2 and catalyst loading of 4g/L. It is evident from the results that the percentage degradation increases with increase in the light intensity. The UV irradiation generates the photons required for the electron transfer from the valence band to the conduction band of a semiconductor photo catalyst and the energy of a photon is related to its wavelength and the overall energy input to a photocatalytic process is dependent on light intensity. The rate of degradation increases when more radiations fall on the catalyst surface and hence more hydroxyl radicals are produced.

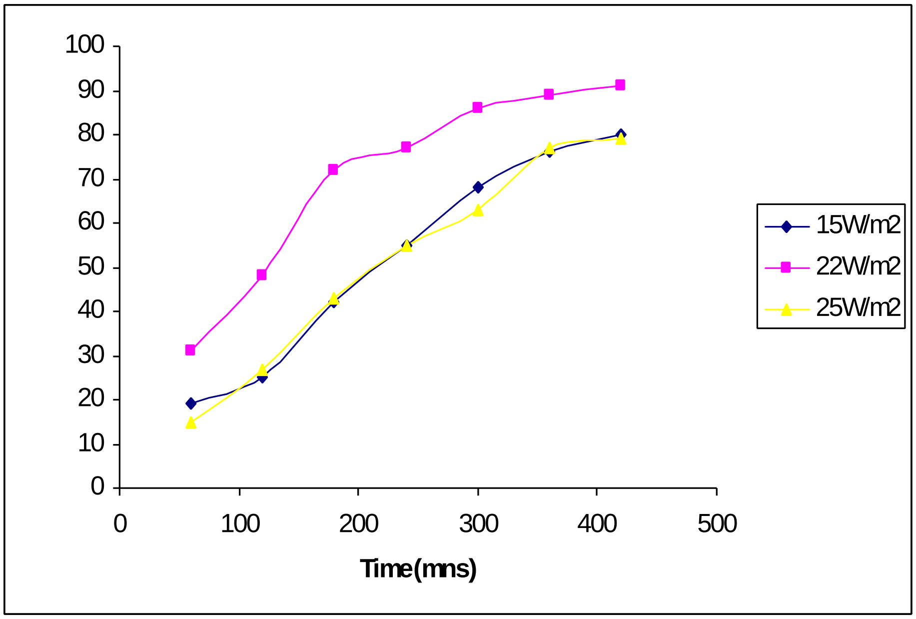


Fig-4.10 Effect of light intensity on photo catalytic degradation of 2-nitroaniline [pH] =2, [Conc.] =25ppm, [wavelength] = 282, [TiO_2] =4g/L, [Time] =6hrs

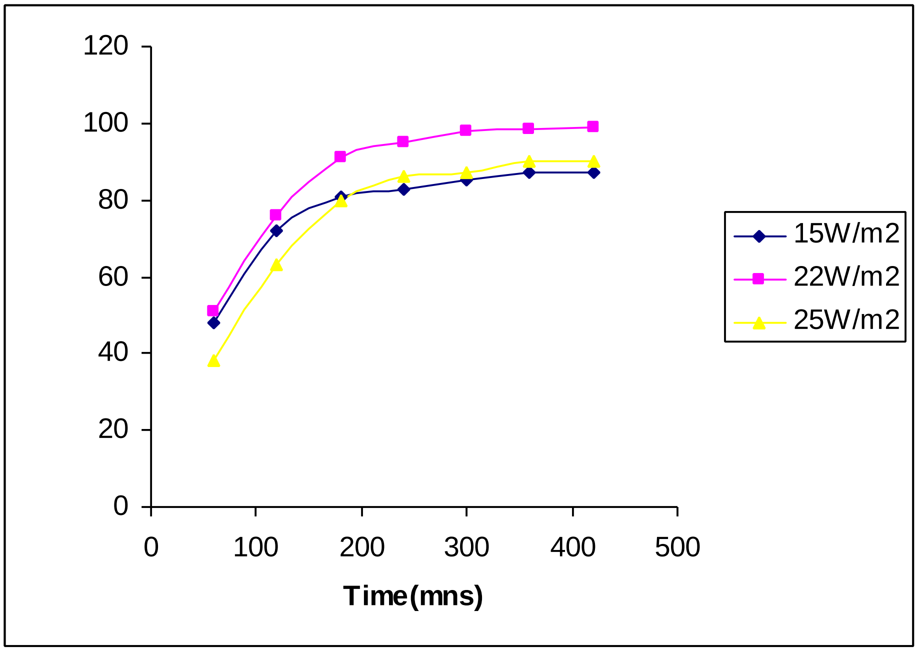


Fig-4.11 Effect of light intensity decolourisation of 2-nitroaniline [pH] =2, [Conc.] =25ppm, [wavelength] = 411, [TiO_2] =4g/L, [Time] =6hrs

4.1.6 COMPARISON OF UV/SOLAR LIGHT

The effect of UV light on the degradation of 2-nitroaniline compound solution by photocatalytic process has been investigated. The comparative study has been carried out for the degradation of compound solution in Solar/UV light. The aqueous suspensions of TiO_2 (4g/L) containing 2-nitroaniline compound solution (25 ppm) was exposed to Solar & UV at pH 2.0 and pH10. Fig shows the degradation rate as a function of irradiation time on illumination of an aqueous suspension of compound solution under sunlight, and UV light source, respectively. The rate of degradation was found to be slightly more in the solar light in comparison to UV light. After 3hrs of reaction time the percentage degradation was 98% in solar light and 91% in UV light at 411nm and 72% in UV and 87% in solar was observed after 3hrs at 282nm. It is evident from the graph that percentage degradation of UV is also close to solar light degradation so because of that there is not so much difference on degradation in UV light so solar light can be efficiently used for the photocatalytic degradation of wastewater or different type of priority pollutants. *Satyen Gautam,et al.(2005)* studied the Photocatalytic degradation of 4-nitroaniline using solar and artificial UV radiation in the presence of TiO_2 suspensions. Artificial and solar radiation was employed as sources of UV radiation. The effect of catalyst loading, pH, presence of anions and initial concentration on the rate of photocatalytic degradation was investigated. *P-Aminophenol*, *p*-benzoquinone and hydroquinone were identified as the intermediates during the degradation process.

The photocatalytic degradation and oxidation of aqueous phenol solutions have been studied *(R.W. Matthews and S.R. McEvoy (1992))* using natural sunlight and artificial light. The photo catalyst was titanium dioxide freely suspended in the solution or immobilized on sand or silica gel. Photo degradation rates were approximately three times faster with the solar light than with the artificial light under the same conditions, and were dependent on the time of the year and the time of the day. The seasonal variation correlated roughly with seasonal solar irradiance.

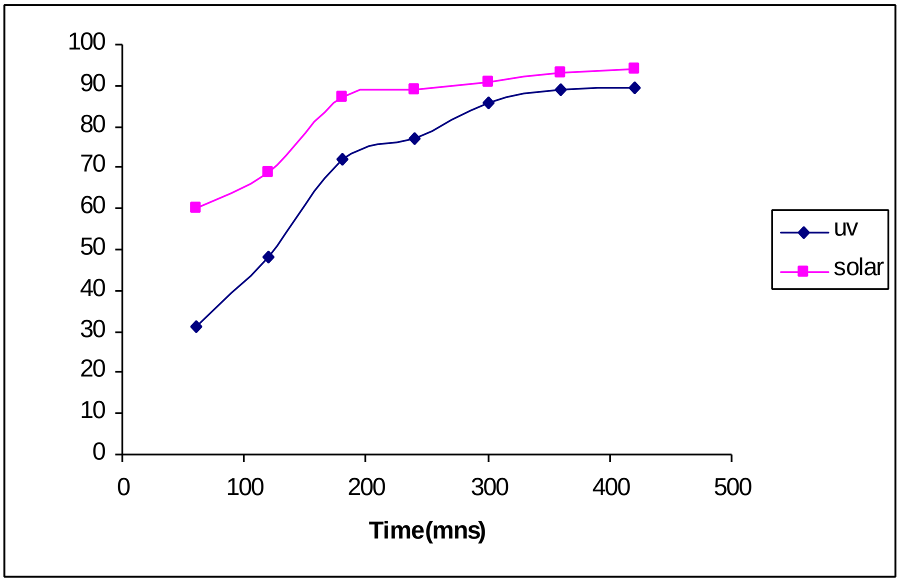


Fig-4.12 Effect of UV/Solar light on photo catalytic degradation of 2-nitroaniline [pH] =2, [Conc.] =25ppm, [wavelength] =282nm, [TiO$_2$] =4g/L, [Time] =6hrs

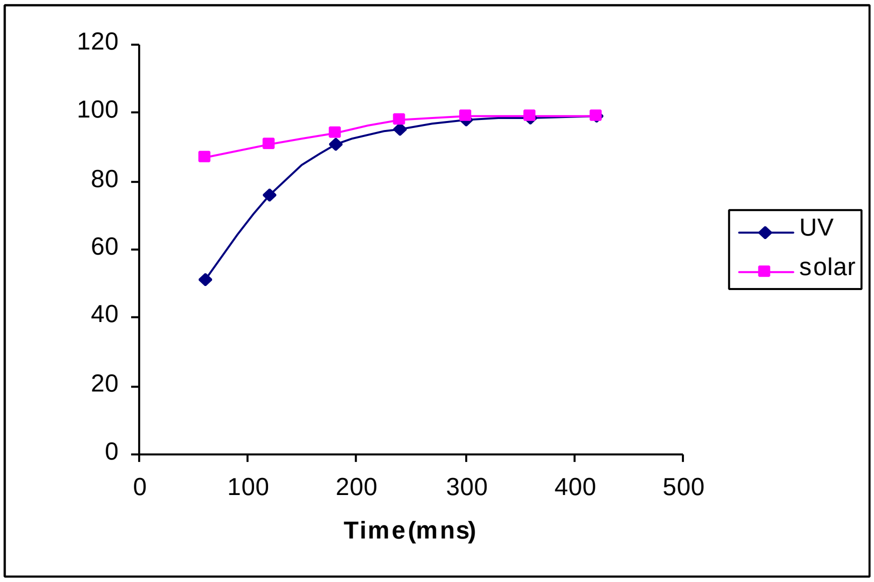


Fig-4.13 Effect of UV/Solar light on decolourisation of 2-nitroaniline [pH] =2, [Conc.] =25ppm, [wavelength] =411nm, [TiO$_2$] =4g/L, [Time] =6hrs

4.1.7 EFFECT OF AREA/VOLUME

The area and volume are again other two different parameters which affect the degradation of pollutants. If area is increased and the volume is decreased the there will be the more degradation as compared to if area is decreased and volume is increased its but obvious because if more is the area then more surface area will be available for light to come in contact with solution and if volume is decreased less amount of solution will be available for degradation because of that more degradation will occur. Here we keep the volume constant i.e. 200ml but varied the area in one case the diameter of bowl was 20cm and the other one diameter was 10cm and we found that area in first case was 314cm^2 then degradation was 89.5% and 98.9% at 282nm and 411nm and the area in second case was decreased to 78.5cm^2 then degradation observed was 75% and 85% at 282nm and 411nm.

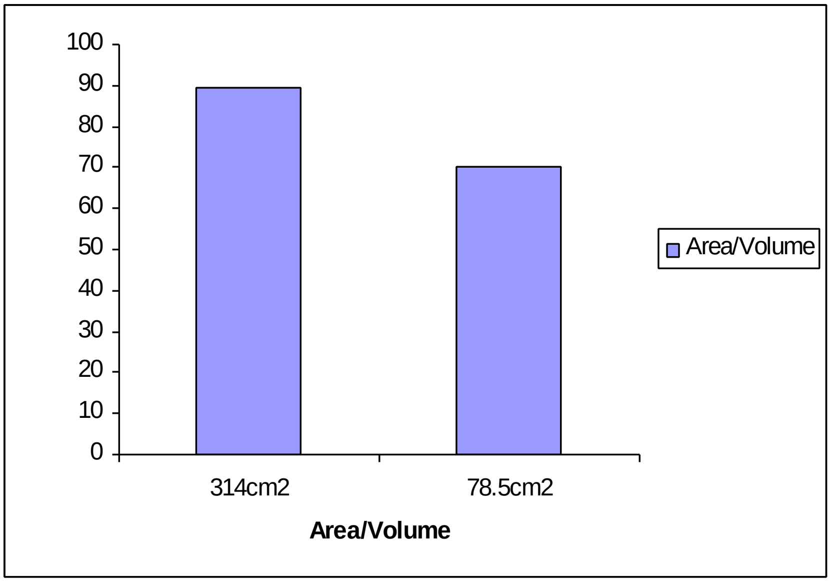


Fig-4.14 Effect of Area/Volume in UV on photo catalytic degradation of 2-nitroaniline [pH] =2, [wavelength] = 282nm, [Volume] =200ml, [TiO2] =4g/L, [Time] =6hrs

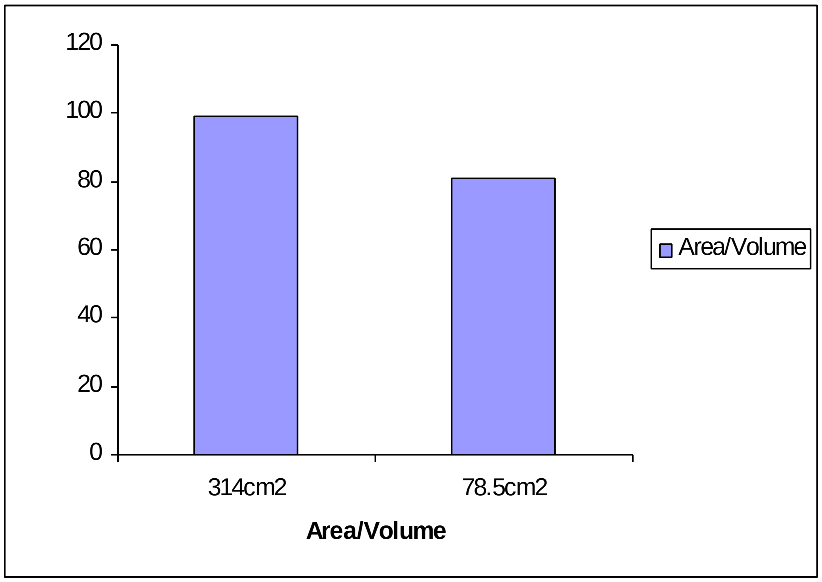


Fig-4.15 Effect of Area/Volume in UV on decolourisation of 2-nitroaniline [pH] =2, [wavelength] = 411nm, [Volume] =200ml, [TiO2] =4g/L, [Time] =6hrs

4.1.8 MINERALISATION OF 2-NITROANILINE

COD is again an important parameter to be analysed for any compound. Here COD from 80 to 8.4 mg/l in UV and 80 to 5.6mg/l in solar at 282nm and 60 to 2mg/l in UV and 60 to 1mg/l in solar at 411nm was observed.

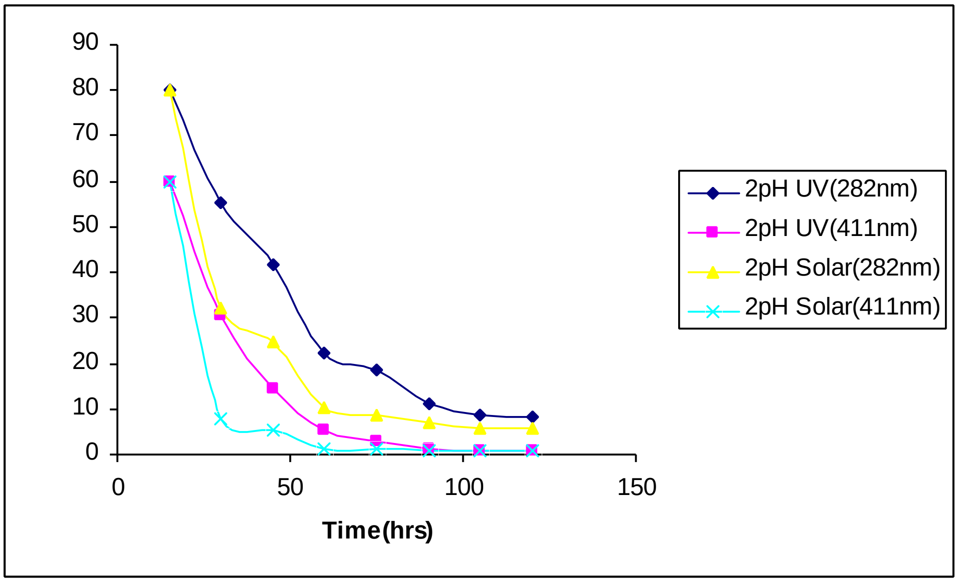


Fig-4.16 Effect of UV and Solar on COD of 2-nitroaniline [Ph] =2, [Conc.] =25ppm, [TiO_2] =4g/L, [Time] =6hrs

CHAPTER 5

CONCLUSION

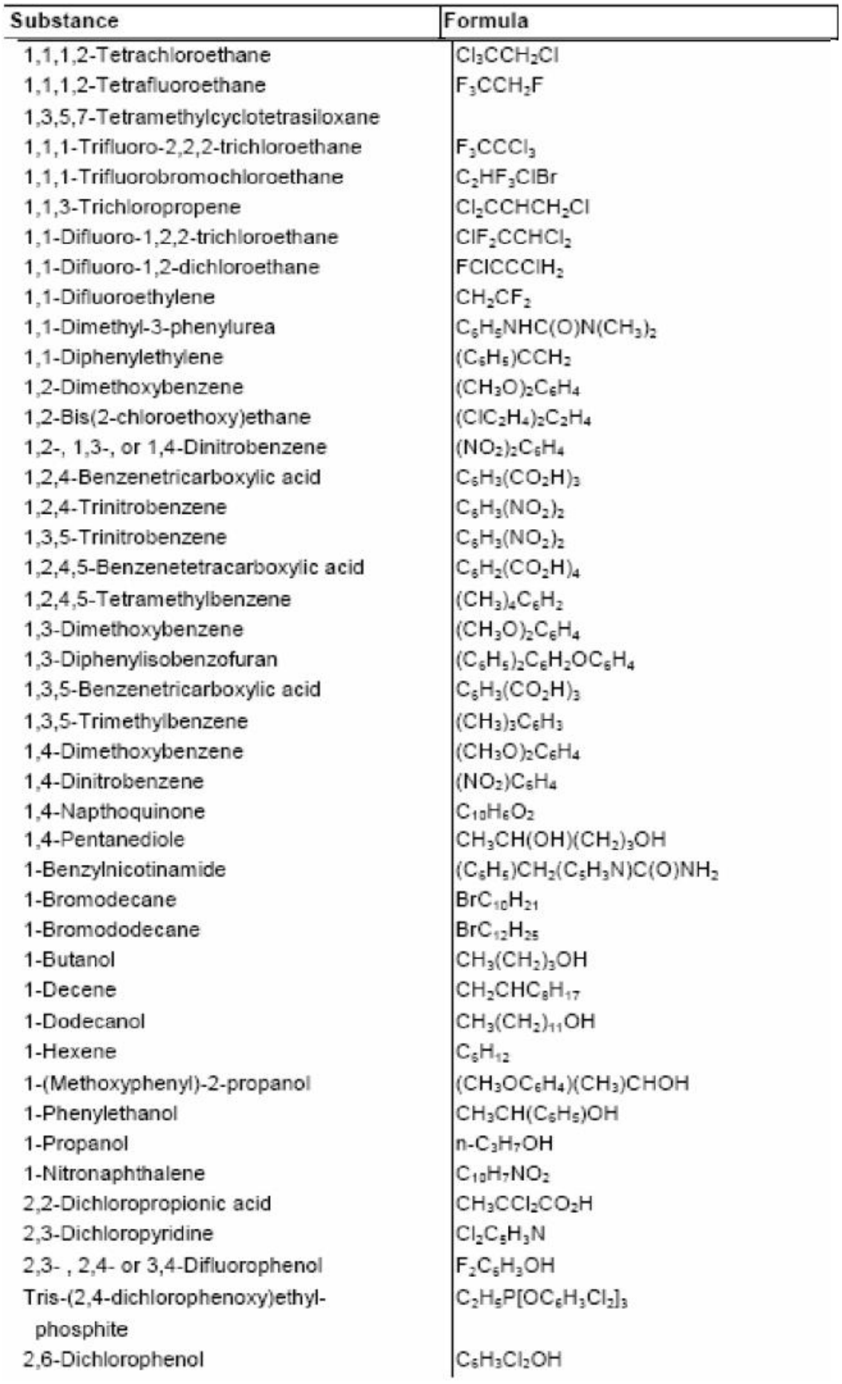
Photocatalysis is a promising technique, for the photodegradation of various hazardous chemicals that are present in industrial wastewater and it mineralize the organic contaminants, into final end product. Heterogeneous photocatalysis is eco-friendly way to reduce the pollutants load of wastewater. It has been found that results obtained in solar light are better than UV light so the solar light can be efficiently used for treatment of priority pollutants which will reduce cost of operation.

2-nitroaniline compound has been successfully degraded in the presence of TiO_2 photocatalyst. TiO_2 dose was optimized to be 4g/l, at operating pH of 2.0 with UV intensity of 25 W/m^2. In case of 2-nitroaniline, 89.5% and 98.9% degradation was achieved in UV at 282nm & 411nm and 93% and 99.3% degradation was achieved in solar light at 282nm & 411nm at the optimized parameter. It is evident from the results that solar light can be effectively used for the degradation and decolourization of compound solution. The diminishing of peaks in the UV and visible region of 2-nitroaniline compound solution during solar/UV photo catalytic treatment shows the complete degradation of organic compounds into simpler end products.

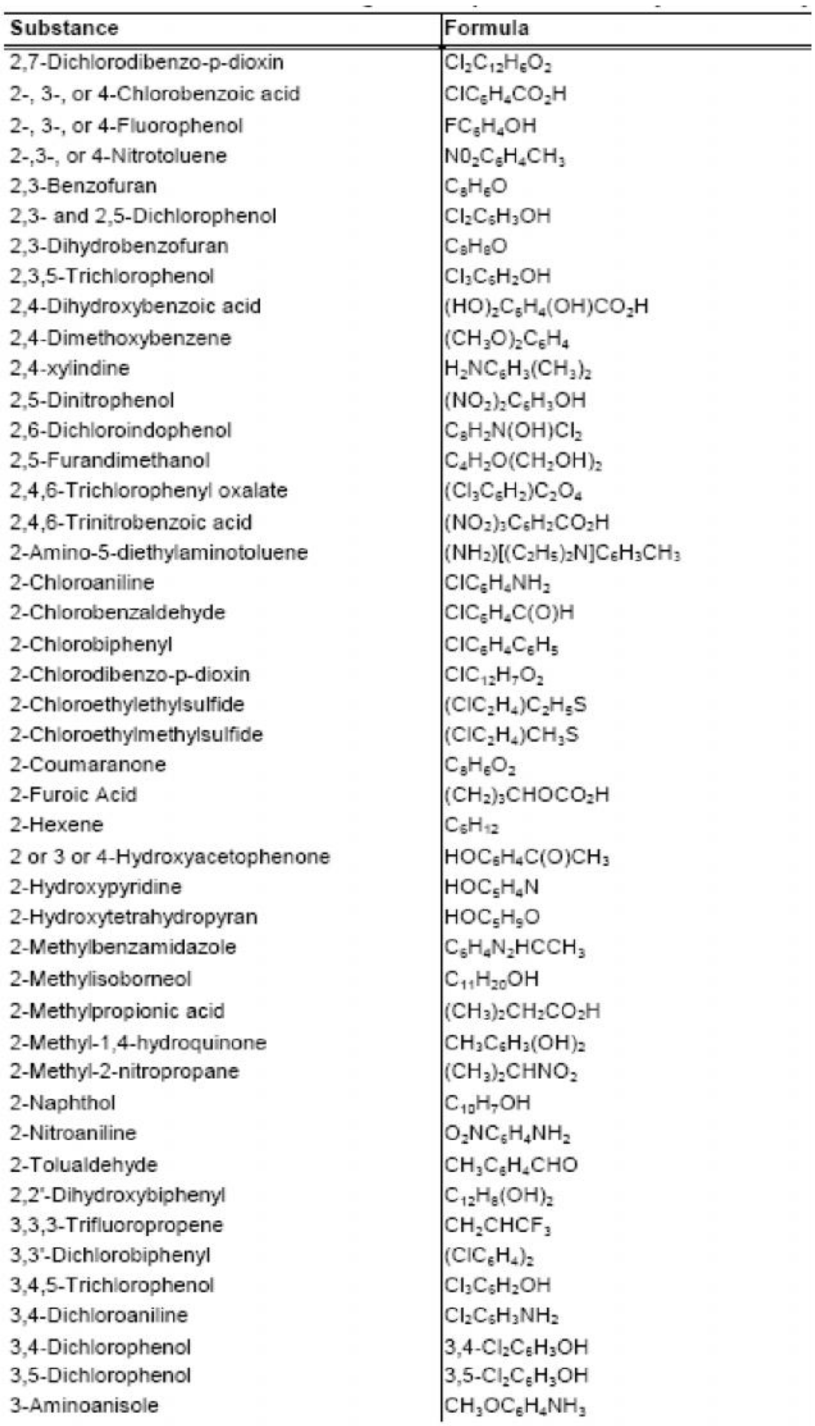
The important parameters like COD, pH and colour have been compared with the National Environmental Quality Standards (NEQS) and it is evident from the results that end pH was 7.36 which is near to neutral. At optimized process parameters, the COD of the treated sample in case of UV and solar photcatalysis has been found that there has been reduction from 80 to 8.4 mg/l in UV and 80mg/l to 5.6mg/l in solar at 282nm and 60mg/l to 2mg/l in UV and 60 to 1mg/l in solar at 411nm was observed. Hence, it can be concluded from the observations that solar photo catalysis can be suitably and cost effectively employed for the degradation of priority pollutants.

APPENDIX I:

List of some organic compound treated by photocatalytic process



Substance	Formula
1,1,1,2-Tetrachloroethane	Cl_3CCH_2Cl
1,1,1,2-Tetrafluoroethane	F_3CCH_2F
1,3,5,7-Tetramethylcyclotetrasiloxane	
1,1,1-Trifluoro-2,2,2-trichloroethane	F_3CCCl_3
1,1,1-Trifluorobromochloroethane	C_2HF_3ClBr
1,1,3-Trichloropropene	Cl_2CCHCH_2Cl
1,1-Difluoro-1,2,2-trichloroethane	ClF_2CCHCl_2
1,1-Difluoro-1,2-dichloroethane	$FClCCClH_2$
1,1-Difluoroethylene	CH_2CF_2
1,1-Dimethyl-3-phenylurea	$C_6H_5NHC(O)N(CH_3)_2$
1,1-Diphenylethylene	$(C_6H_5)CCH_2$
1,2-Dimethoxybenzene	$(CH_3O)_2C_6H_4$
1,2-Bis(2-chloroethoxy)ethane	$(ClC_2H_4)_2C_2H_4$
1,2-, 1,3-, or 1,4-Dinitrobenzene	$(NO_2)_2C_6H_4$
1,2,4-Benzenetricarboxylic acid	$C_6H_3(CO_2H)_3$
1,2,4-Trinitrobenzene	$C_6H_3(NO_2)_2$
1,3,5-Trinitrobenzene	$C_6H_3(NO_2)_2$
1,2,4,5-Benzenetetracarboxylic acid	$C_6H_2(CO_2H)_4$
1,2,4,5-Tetramethylbenzene	$(CH_3)_4C_6H_2$
1,3-Dimethoxybenzene	$(CH_3O)_2C_6H_4$
1,3-Diphenylisobenzofuran	$(C_6H_5)_2C_6H_2OC_6H_4$
1,3,5-Benzenetricarboxylic acid	$C_6H_3(CO_2H)_3$
1,3,5-Trimethylbenzene	$(CH_3)_3C_6H_3$
1,4-Dimethoxybenzene	$(CH_3O)_2C_6H_4$
1,4-Dinitrobenzene	$(NO_2)C_6H_4$
1,4-Napthoquinone	$C_{10}H_6O_2$
1,4-Pentanediole	$CH_3CH(OH)(CH_2)_3OH$
1-Benzylnicotinamide	$(C_6H_5)CH_2(C_5H_3N)C(O)NH_2$
1-Bromodecane	$BrC_{10}H_{21}$
1-Bromododecane	$BrC_{12}H_{25}$
1-Butanol	$CH_3(CH_2)_3OH$
1-Decene	$CH_2CHC_8H_{17}$
1-Dodecanol	$CH_3(CH_2)_{11}OH$
1-Hexene	C_6H_{12}
1-(Methoxyphenyl)-2-propanol	$(CH_3OC_6H_4)(CH_3)CHOH$
1-Phenylethanol	$CH_3CH(C_6H_5)OH$
1-Propanol	n-C_3H_7OH
1-Nitronaphthalene	$C_{10}H_7NO_2$
2,2-Dichloropropionic acid	$CH_3CCl_2CO_2H$
2,3-Dichloropyridine	$Cl_2C_5H_3N$
2,3- , 2,4- or 3,4-Difluorophenol	$F_2C_6H_3OH$
Tris-(2,4-dichlorophenoxy)ethyl-phosphite	$C_2H_5P[OC_6H_3Cl_2]_3$
2,6-Dichlorophenol	$C_6H_3Cl_2OH$

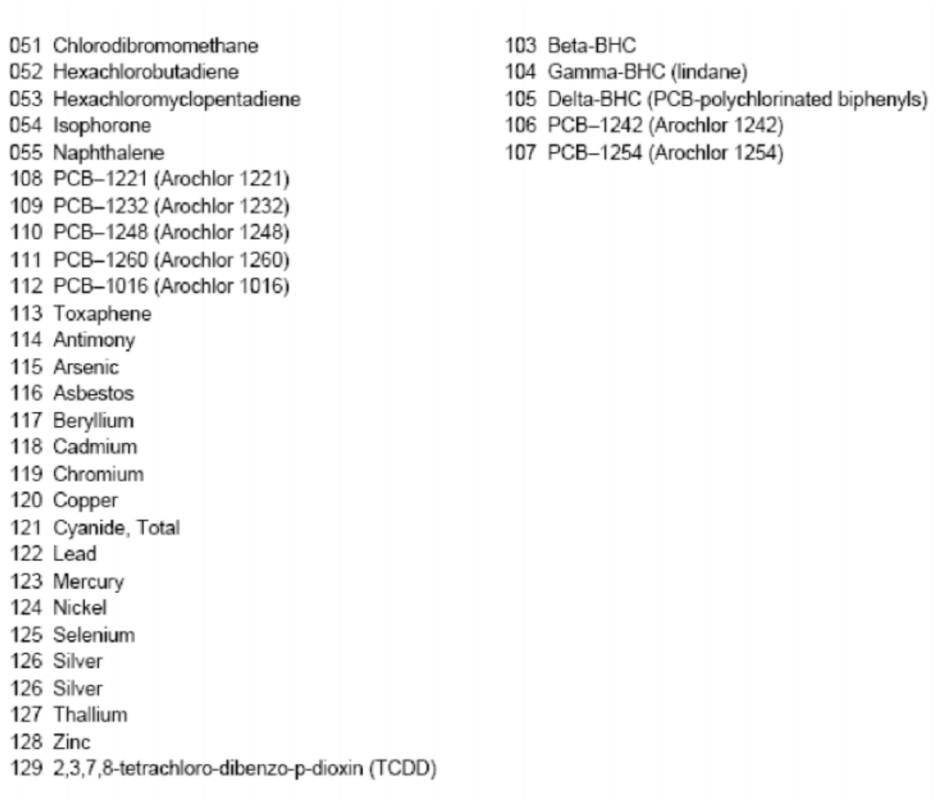


Substance	Formula
2,7-Dichlorodibenzo-p-dioxin	$Cl_2C_{12}H_6O_2$
2-, 3-, or 4-Chlorobenzoic acid	$ClC_6H_4CO_2H$
2-, 3-, or 4-Fluorophenol	FC_6H_4OH
2-,3-, or 4-Nitrotoluene	$N0_2C_6H_4CH_3$
2,3-Benzofuran	C_8H_6O
2,3- and 2,5-Dichlorophenol	$Cl_2C_6H_3OH$
2,3-Dihydrobenzofuran	C_8H_8O
2,3,5-Trichlorophenol	$Cl_3C_6H_2OH$
2,4-Dihydroxybenzoic acid	$(HO)_2C_6H_4(OH)CO_2H$
2,4-Dimethoxybenzene	$(CH_3O)_2C_6H_4$
2,4-xylindine	$H_2NC_6H_3(CH_3)_2$
2,5-Dinitrophenol	$(NO_2)_2C_6H_3OH$
2,6-Dichloroindophenol	$C_6H_2N(OH)Cl_2$
2,5-Furandimethanol	$C_4H_2O(CH_2OH)_2$
2,4,6-Trichlorophenyl oxalate	$(Cl_3C_6H_2)C_2O_4$
2,4,6-Trinitrobenzoic acid	$(NO_2)_3C_6H_2CO_2H$
2-Amino-5-diethylaminotoluene	$(NH_2)[(C_2H_5)_2N]C_6H_3CH_3$
2-Chloroaniline	$ClC_6H_4NH_2$
2-Chlorobenzaldehyde	$ClC_6H_4C(O)H$
2-Chlorobiphenyl	$ClC_6H_4C_6H_5$
2-Chlorodibenzo-p-dioxin	$ClC_{12}H_7O_2$
2-Chloroethylethylsulfide	$(ClC_2H_4)C_2H_5S$
2-Chloroethylmethylsulfide	$(ClC_2H_4)CH_3S$
2-Coumaranone	$C_8H_6O_2$
2-Furoic Acid	$(CH_2)_3CHOCO_2H$
2-Hexene	C_6H_{12}
2 or 3 or 4-Hydroxyacetophenone	$HOC_6H_4C(O)CH_3$
2-Hydroxypyridine	HOC_5H_4N
2-Hydroxytetrahydropyran	HOC_5H_9O
2-Methylbenzamidazole	$C_6H_4N_2HCCH_3$
2-Methylisoborneol	$C_{11}H_{20}OH$
2-Methylpropionic acid	$(CH_3)_2CH_2CO_2H$
2-Methyl-1,4-hydroquinone	$CH_3C_6H_3(OH)_2$
2-Methyl-2-nitropropane	$(CH_3)_2CHNO_2$
2-Naphthol	$C_{10}H_7OH$
2-Nitroaniline	$O_2NC_6H_4NH_2$
2-Tolualdehyde	$CH_3C_6H_4CHO$
2,2'-Dihydroxybiphenyl	$C_{12}H_8(OH)_2$
3,3,3-Trifluoropropene	CH_2CHCF_3
3,3'-Dichlorobiphenyl	$(ClC_6H_4)_2$
3,4,5-Trichlorophenol	$Cl_3C_6H_2OH$
3,4-Dichloroaniline	$Cl_2C_6H_3NH_2$
3,4-Dichlorophenol	$3,4\text{-}Cl_2C_6H_3OH$
3,5-Dichlorophenol	$3,5\text{-}Cl_2C_6H_3OH$
3-Aminoanisole	$CH_3OC_6H_4NH_3$

Substance	Formula
3-Chloroaniline	$CH_3OC_6H_4Cl$
3-Chloroanisole	$ClC_6H_4NH_2$
3-Chlorobenzaldehyde	$ClC_6H_4C(O)H$
3-Chlorophenol	$m\text{-}ClC_6H_4OH$
3-Chlorosalicylic acid	$C_7H_5ClO_3$
3-Chlorotoluene	$CH_3C_6H_4Cl$
3-Fluoroanisole	$CH_3OC_6H_4F$
3-Fluorotoluene	$CH_3C_6H_4F$
3-hydroxyanisole	$CH_3OC_6H_4OH$
3-Methyl-2-oxobutanoic acid	$(CH_3)CHC(O)CO_2H$
3-Nitroanisole	$CH_3OC_6H_4NO_2$
3-Nitrophenol	$O_2NC_6H_4OH$
3-Nitrotoluene	$CH_3C_6H_4NO_2$
3-Octanol	$CH_3CH_2CH(OH)(CH_2)_4CH_3$
3-Octanone	$CH_3CH_2C(O)(CH_2)_4CH_3$
4-Acetobenzaldehyde	$CH_3C(O)C_6H_4CHO$
4-Aminoanisole	$CH_3OC_6H_4NH_2$
4-Bromophenol	BrC_6H_4OH
4-t-Butyltoluene	$p\text{-}(t\text{-}C_4H_9)C_6H_4CH_3$
4-Chloroanisole	$CH_3OC_6H_4Cl$
4-Chlorobenzaldehyde	$ClC_6H_4C(O)H$
4-Chlorocatachol	$ClC_6H_3(OH)_2$
4-Chloro-3-nitro-benzotrifluoride	$C_6HCl(NO_2)F_3$
4-Chlorophenol	ClC_6H_4OH
4-Chlorophenoxyacetic acid	$ClC_6H_4CH_2CO_2H$
4-Chlorophenylisocyanate	ClC_6H_4NCO
4-Chlorotoluene	$CH_3C_6H_4Cl$
4-Fluoroanisole	$CH_3OC_6H_4F$
4-Fluorophenol	FC_6H_4OH
4-Fluorotoluene	$CH_3C_6H_4F$
4-Hydroxyanisole	$CH_3OC_6H_4OH$
4-Hydroxyacetophenone	$HOC_6H_4C(O)CH_3$
4-Hydroxybenzyl Alcohol	$p\text{-}HO(C_6H_4)CH_2OH$
4-Hydroxybiphenyl	$C_{12}H_9OH$
4-Iodophenol	IC_6H_4OH
4-Methoxybenzylalcohol	$CH_3OC_6H_4CH_2OH$
4-Methoxybenzyl(methyl) ether	$CH_3OC_6H_4CH_2OCH_3$
4-Methoxybenzyl(3-phenylpropyl)-ether	$CH_3OC_6H_4CH_2O(CH_2)_3C_6H_5$
4-Methoxybenzyl(t-buytyl) ether	$CH_3OC_6H_4CH_2OC(CH_3)_3$
4-Methoxybenzyl(phenyl)sulfide	$CH_3OC_6H_4CH_2SC_6H_5$
4-Methoxyphenol	$CH_3C_6H_4OH$
4-Nitroaniline	$NO_2C_6H_4NH_2$

APPENDIX 2:
US EPA List of priority pollutants

001 Acenaphthene
002 Acrolein
003 Acrylonitrile
004 Benzene
005 Benzidine
006 Carbon tetrachloride (tetrachloromethane)
007 Chlorobenzene
008 1,2,4-trichlorobenzene
009 Hexachlorobenzene
010 1,2-dichloroethane
011 1,1,1-trichloreothane
012 Hexachloroethane
013 1,1-dichloroethane
014 1,1,2-trichloroethane
015 1,1,2,2-tetrachloroethane
016 Chloroethane
018 Bis(2-chloroethyl) ether
019 2-chloroethyl vinyl ether (mixed)
020 2-chloronaphthalene
021 2,4, 6-trichlorophenol
022 Parachlorometa cresol
023 Chloroform (trichloromethane)
024 2-chlorophenol
025 1,2-dichlorobenzene
026 1,3-dichlorobenzene
027 1,4-dichlorobenzene
028 3,3-dichlorobenzidine
029 1,1-dichloroethylene
030 1,2-trans-dichloroethylene
031 2,4-dichlorophenol
032 1,2-dichloropropane
033 1,2-dichloropropylene (1,3-dichloropropene)
034 2,4-dimethylphenol
035 2,4-dinitrotoluene
036 2,6-dinitrotoluene
037 1,2-diphenylhydrazine
038 Ethylbenzene
039 Fluoranthene
040 4-chlorophenyl phenyl ether
041 4-bromophenyl phenyl ether
042 Bis(2-chloroisopropyl) ether
043 Bis(2-chloroethoxy) methane
044 Methylene chloride (dichloromethane)
045 Methyl chloride (dichloromethane)
046 Methyl bromide (bromomethane)
047 Bromoform (tribromomethane)
048 Dichlorobromomethane
056 Nitrobenzene
057 2-nitrophenol
058 4-nitrophenol
059 2,4-dinitrophenol
060 4,6-dinitro-o-cresol
061 N-nitrosodimethylamine
062 N-nitrosodiphenylamine
063 N-nitrosodi-n-propylamin
064 Pentachlorophenol
065 Phenol
066 Bis(2-ethylhexyl) phthalate
067 Butyl benzyl phthalate
068 Di-N-Butyl Phthalate
069 Di-n-octyl phthalate
070 Diethyl Phthalate
071 Dimethyl phthalate
072 1,2-benzanthracene (benzo(a) anthracene
073 Benzo(a)pyrene (3,4-benzo-pyrene)
074 3,4-Benzofluoranthene (benzo(b) fluoranthene)
075 11,12-benzofluoranthene (benzo(b) fluoranthene)
076 Chrysene
077 Acenaphthylene
078 Anthracene
079 1,12-benzoperylene (benzo(ghi) perylene)
080 Fluorene
081 Phenanthrene
082 1,2,5,6-dibenzanthracene (dibenzo(,h) anthracene)
083 Indeno (,1,2,3-cd) pyrene (2,3-o-pheynylene pyrene)
084 Pyrene
085 Tetrachloroethylene
086 Toluene
087 Trichloroethylene
088 Vinyl chloride (chloroethylene)
089 Aldrin
090 Dieldrin
091 Chlordane (technical mixture and metabolites)
092 4,4-DDT
093 4,4-DDE (p,p-DDX)
094 4,4-DDD (p,p-TDE)
095 Alpha-endosulfan
096 Beta-endosulfan
097 Endosulfan sulfate
098 Endrin
099 Endrin aldehyde
100 Heptachlor
101 Heptachlor epoxide (BHC-hexachlorocyclohexane)
102 Alpha-BHC


051 Chlorodibromomethane
052 Hexachlorobutadiene
053 Hexachloromyclopentadiene
054 Isophorone
055 Naphthalene
108 PCB–1221 (Arochlor 1221)
109 PCB–1232 (Arochlor 1232)
110 PCB–1248 (Arochlor 1248)
111 PCB–1260 (Arochlor 1260)
112 PCB–1016 (Arochlor 1016)
113 Toxaphene
114 Antimony
115 Arsenic
116 Asbestos
117 Beryllium
118 Cadmium
119 Chromium
120 Copper
121 Cyanide, Total
122 Lead
123 Mercury
124 Nickel
125 Selenium
126 Silver
126 Silver
127 Thallium
128 Zinc
129 2,3,7,8-tetrachloro-dibenzo-p-dioxin (TCDD)
103 Beta-BHC
104 Gamma-BHC (lindane)
105 Delta-BHC (PCB-polychlorinated biphenyls)
106 PCB–1242 (Arochlor 1242)
107 PCB–1254 (Arochlor 1254)

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