INVESTIGATIONS ON ADVANCED OXIDATION PROCESSES AS POTENTIAL ENVIRONMENT FRIENDLY TECHNIQUES FOR THE DEGRADATION OF PLASTIC POLLUTANTS

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By

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Investigations on Advanced Oxidation Processes as potential environment friendly techniques for the degradation of plastic pollutants

Ph.D. Thesis under the Faculty of Environmental Studies

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Certificate

This is to certify that this thesis entitled **"Investigations on Advanced Oxidation Processes as potential environment friendly techniques for the degradation of plastic pollutants"** is an authentic record of the research work carried out by **Smt. Phonsy P. D.**, Part-Time Research Scholar (Reg. No. 4262) under my guidance at the School of Environmental Studies, Cochin University of Science and Technology in partial fulfillment of the requirements for the award of the degree of Doctor of Philosophy in Environmental Technology and no part of this work has previously formed the basis for the award of any other degree, diploma, associateship, fellowship or any other similar title or recognition. All the relevant corrections and modifications suggested by the audience during the pre-synopsis seminar and recommended by the Doctoral committee have been incorporated in the thesis.

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July 2018

Dr. Suguna Yesodharan
(Supervising Guide)

Declaration

I do hereby declare that the work presented in the thesis entitled **"Investigations on Advanced Oxidation Processes as potential environment friendly techniques for the degradation of plastic pollutants"** is based on the authentic record of the original work done by me, for my Doctoral Degree under the guidance of **Dr. Suguna Yesodharan**, Professor (Emeritus), School of Environmental Studies, Cochin University of Science and Technology in partial fulfillment of the requirements for the award of the degree of Doctor of Philosophy in Environmental Technology and no part of this work has previously formed the basis for the award of any other degree, diploma, associateship, fellowship or any other similar title or recognition.

Kochi – 22 **Phonsy P. D.**
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Preface

Plastic and plastic materials are beneficial to mankind in a variety of ways. The versatility of plastic has made it an integral part of modern human life. However, the ‘white pollution’ caused by plastic wastes is a major environmental problem in today’s world. Disposal of plastic wastes is a serious environmental issue due to their recalcitrant nature.

In this context, an innovative treatment method based on Advanced Oxidation Process (AOP) is investigated as a safer technology for the disposal of plastic wastes. AOPs involve the formation and interaction of highly reactive hydroxyl radicals which are proven to be very efficient for the destruction and mineralization of recalcitrant organic pollutants. The radicals can non-selectively oxidize the organic pollutants to carbon dioxide (CO_2), water (H_2O) and inorganic mineral salts. Some of the major AOPs are wet-air oxidation, radiolysis, cavitation, photolysis, photocatalysis, sonocatalysis, Fenton oxidation, microwave catalysis and electrochemical oxidation. They can be used either independently or in combination with other techniques in order to enhance the efficacy, economy and safety of the process. The advantage of AOP is that it does not produce hazardous by-products or sludge which require further treatment. Reactive Oxygen Species (ROS) such as $^{\bullet}OH$, $HO_2^{\bullet}$, $O_2^{-\bullet}$ and H_2O_2 produced in the process interact with the pollutants and degrade them.

The main objective of the current study is to examine the suitability of AOPs based on photolysis and photocatalysis for the safe irreversible destruction of plastic wastes including plastic bags, pipes and other similar products of daily use.

In this context, the possibility of using photocatalysis mediated by TiO_2 and ZnO for the degradation of Low Density Polyethylene (LDPE) and Polyvinyl chloride (PVC) plastics is investigated under different conditions. The possibility of using solar energy as the source of activation is also examined and the results are encouraging.

As a precursor to this investigation, the qualitative and quantitative generation of waste plastic in a typical middle class community in the central part of Kerala State is evaluated by physical verification as well as questionnaire survey. It was alarming to note that, on an average ~ 1kg of plastic waste is generated per month per household. The quantity and quality of the waste plastic generated depend on the number of members, age group and the economic affluence of the family. The most common type of waste generated from the domestic sector belong to the Low Density Polyethylene (LDPE), High Density Polyethylene (HDPE) and Polyvinyl chloride (PVC) types. Semiconductor oxide mediated, persulphate assisted and UV/Visible light activated photolysis has been identified as an effective method for the irreversible destruction of the plastic waste. Relevant parameters have been identified and optimised. Fenton process and photofenton process also appear to be promising in this respect in view of the simplicity and inexpensive application characteristics. Approximately 12% of LDPE plastic is degraded under UV photolysis in presence of persulphate and TiO_2, in ~ 400 hr time which is one of the best efficiencies reported so far in this respect.

The thesis provides detailed report on the findings leading to the above conclusions and critical analysis of the observations.

The thesis is presented in seven chapters and four annexures as follows:

Chapter 1 Introduction: Background literature.

Chapter 2 Objectives of the study, materials used and plan of the thesis.

Chapter 3 Pattern of the use and disposal of plastic products in a typical village community in Kerala State, India: A case study

Chapter 4 Semiconductor oxide mediated photocatalytic degradation of Low Density Polyethylene plastic wastes

Chapter 5 Photolytic/Photocatalytic degradation of Polyvinyl chloride plastic wastes from the environment

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Chapter 1

INTRODUCTION: BACKGROUND LITERATURE

Contents

1.1 General

1.1.1 Plastic: History

The term “plastic’’ is derived from the Greek word “plastikos” meaning ‘fit for moulding’, and “plastos” meaning moulded. It refers to the malleability or plasticity of the material during manufacture, that allows it to be cast, pressed, or extruded into a variety of shapes - such as films, fibres, plates, tubes, bottles, boxes and much more. Parkesine is considered to be the first man-made plastic and it was patented by Alexander Parkes, in Birmingham, UK in 1857 [1].

Krische and Spitteler patented the manufacture of casein plastics [2]. This plastic was made in 1987 and is still in use in button industry. The formation process involves the reaction of casein and formaldehyde. The ability of formaldehyde to form resinous substances was observed by chemists as early as in the second half of the 19th century. First patent in the field of phenol-aldehyde resins for use as an ebonite substitute in electrical insulation was awarded to Arthur Smith in 1899 (Patent 16 274). In due course Leo Hendrik Baekeland discovered techniques of controlling and modifying the reactions so that more useful products could be made. The first of his 119 patents on phenol-aldehyde plastics was awarded in 1907 and the General Bakelite Company was formed in the United States in 1910. While celluloid was the first plastic material obtained by the chemical modification of a polymer, the phenolics were the first commercially successful fully synthetic resins [2].

The only plastic materials available by 1900 were shellac, gutta percha, ebonite and celluloid. The major growth period of the plastic industry has been since 1930. The decade 1930-1940 saw the initial industrial development of four major thermoplastics that are in use even today; ie polystyrene, polyvinylchloride, polyolefins and polymethylmethacrylate. Since all these materials can be formally considered as derivatives of ethylene, they have, in the past, been referred to as ethenoid plastics. However, the somewhat inaccurate term, vinyl plastics is usually preferred nowadays.

The discovery and development of polyethylene in 1931 by Fawcett and Gibson provides an excellent example of the importance of observation and follow up of any experimental result. Detailed investigation of the product showed that it is an excellent electrical insulator with very good chemical resistance. Nylon, developed as a fibre in the mid-1930s, by Carothers and his team of research workers for Du Pont was first used as a moulding material in 1941. Also, a patent was awarded to Kinetic Chemical Inc. in 1941 based on the discovery of polytetrafluoroethylene by R. J. Plunkett. Materials such as polyethylene and polystyrene, originally rather expensive special purpose materials, were produced in large tonnages at low cost during the first decade after world war II.

In the mid-1950s a number of new thermoplastics with very valuable properties became available. High-density polyethylenes produced by the Phillips process and the Ziegler process were marketed. These were shortly followed by the discovery and development of polypropylene which was the first genuinely new large tonnage thermoplastic material developed since World War II. This is arguably the most important episode in the history of polymer science [2].

Somewhat more specialised materials were the acetal resins, first introduced by Du Pont, and the polycarbonates, developed simultaneously but independently in the United States and Germany. Further developments in high-impact polystyrenes led to the discovery of acrylonitrile butadiene styrene (ABS) polymers. In 1943 Ziegler was able to grow long hydrocarbon chains by linking a series of ethylene molecules onto aluminum alkyls. The reaction rate increased in presence of titanium tetrachloride. This has also opened up the possibility of forming high molecular weight materials.

1.1.2 Raw materials for plastics

Today, the plastic industry is heavily integrated with the oil industry. In fact a popular view is that it would not be possible to produce plastics if oil were not available. Before World War II, the most important class of thermoplastics, the cellulosic, was produced from vegetable sources, cellulose being an important constituent of vegetable matter. The furane plastics were produced from waste oat husks. Nylons were also developed from this raw material. Henry Ford had experimented with soya bean plastics and several types of plastics had been derived from natural rubber. Early grades of polyethylene were obtained from sugar cane via molasses, ethyl alcohol and ethylene. Some of these processes are still in use but their relative significance has declined.

Until mid-1950s, the main raw material source for the European plastic industry was coal. Coal yields four products on destructive distillation: coal tar, coke, coal gas and ammonia. Coal is an important source of aromatic chemicals such as benzene, toluene, phenol, naphthalene and related products. From these materials, other chemicals such as adipic acid, hexamethylenediamine, caprolactam and phthalic anhydride could be produced eventually leading to such important plastics as the phenolic resins, polystyrene and the nylons. Reaction of coke with calcium oxide gives calcium carbide, which produces acetylene on treatment with water. Acetylene is an important starting point for the production of acrylonitrile, vinyl chloride, vinyl acetate and other vinyl monomers [2].

The development of the petrochemical industry is probably the greatest single contributing factor to the growth of the plastics industry. The two industries are having a remarkable degree of interdependence today. In the first instance, the growth potential of plastics stimulated research into the production of monomers and other intermediates from petroleum. As a result cheap and abundant intermediates became available and this in turn stimulated further growth of the plastics industry. This would not have been possible if the industry was dependent on coal alone.

Petrochemicals were also being used to produce ethylene dichloride, vinyl chloride, ethylene glycol, ethylene oxide and styrene. During World War II, the large synthetic rubber industry created in the United States used butadiene and styrene, the former entirely and the latter partly derived from petroleum. In the early days, polyethylene was produced from molasses via ethyl alcohol and ethylene. Today ethylene used for polymerisation as well as for other purposes, is obtained almost entirely from petroleum. With each succeeding year in the 1950s and 1960s there was a swing away from coal and vegetable sources towards petroleum for raw materials. Some such petroleum derived products include terephthalic acid, styrene, benzene, formaldehyde, vinyl acetate and acrylonitrile [2].

1.1.3 Chemistry, types, properties and uses of plastics

Plastics are organic polymers formed from thousands of small molecular units called monomers joining together by chemical bonds. The monomer units are usually from the petrochemical industry. In petroleum refinery, heavy crude oil is separated into lighter fractions by distillation process. Each fraction is a mixture of hydrocarbon chains, which differ in terms of size and structure of the molecules. The main fraction of oil that is used for plastic production is known as naphtha. In a polymerisation reaction, monomers like ethylene and propylene are linked together to form long polymer chains. These polymers differ in their properties, structure and size depending on the various types of basic monomers used.

There are two main methods for the manufacture of synthetic polymers. The first involves breaking the double bond in the original olefin by addition polymerization to form new carbon-carbon bonds, ie, the carbon-chain polymers. For example, the fabrication of polyolefins, such as polyethylene (eqn.1) and polypropylene, is based on this general reaction.

$$n[CH_2 = CH_2] \longrightarrow [-CH_2-CH_2-]_n \text{ .... (1)}$$

The second process is the elimination of water (or condensation) between a carboxylic acid and an alcohol or amine to form polyester (eqn. 2) or polyamide [3].

$$nCH_3COOH + nCH_3CH_2OH \longrightarrow [-CH_2COOCH_2CH_2-]_n\text{........... (2)}$$

$$HOOCC_6H_4COOH + H_2NC_6H_4NH_2\ [-OCC_6H_4CONHC_6H_4NH-]_n\text{......... (3)}$$

Broadly speaking, plastics are of two kinds; thermoplastics and thermosetting plastics. Thermoplastics are products of the first kind of general reaction mentioned above. Thermoplastics have either linear or branched chain structures and there are no cross links. Since different polymer chains of thermoplastics are held together by weak van der Waals' forces or dipole forces or hydrogen bonding, they soften on heating and stiffen again on cooling. Polyethylene (PE), Polyvinyl chloride (PVC), Polypropylene (PP), Polystyrene (PS) etc are examples. In thermoplastics, the backbone is solely built of carbon atoms which makes them resistant to degradation or hydrolytic cleavage of chemical bonds. Consequently, thermoplastics are considered as non-biodegradable plastics. Thermoset plastics are synthesized from the second kind of general reaction stated above. Thermosetting polymers have three dimensional cross linked structure and the neighbouring polymer chains are held together by strong covalent bonds. They are solidified after being melted (by heating). The process of changing from the liquid state to the solid state is irreversible [3]. Different from the linear structure of thermoplastics, thermoset plastics have a highly cross-linked structure [4-5]. Since the main chain of thermoset plastics is made of heteroatoms, they are potentially susceptible to be degraded by the hydrolytic cleavage of chemical bonds such as ester bonds or amide bonds [6]. Structures of the two types of plastics are given in figure 1.1.

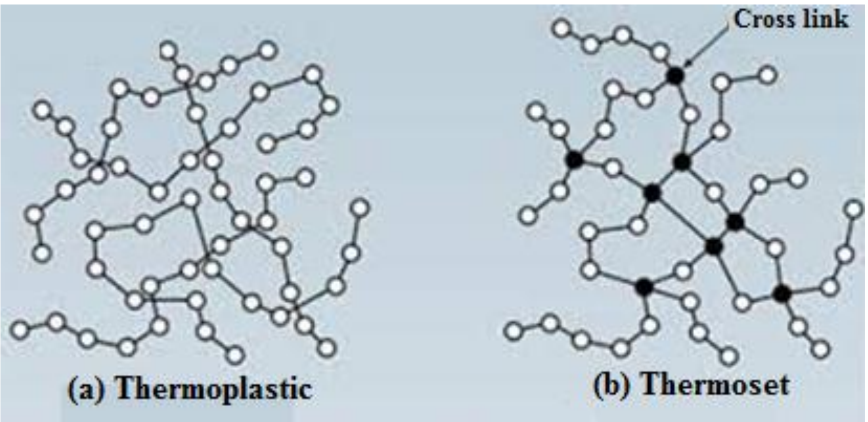


Figure 1.1: Structure of thermoplastics and thermosetting plastics

Some common types of plastics, their resin identification code and uses are given in table 1.1 below [7].

Table 1.1: Common plastics resin code, characteristics and applications

Plastic Identification Code	**Type of plastic polymer**	**Properties**	**Common Applications**
01 PET	Polyethylene terephthalate (PET)	Clarity, strength, toughness, barrier to gas and moisture.	Soft drink, water and salad dressing bottles; peanut butter and jam jars; small customer electronics.
02 PE-HD	High-density polyethylene (HDPE)	Stiffness, strength, toughness, resistance to moisture, permeability to gas.	Water pipes, hula hoop rings, five gallon buckets, milk, juice and water bottles; grocery bags, some shampoo/toiletry bottles.
03 PVC	Polyvinyl chloride (PVC)	Versatility, ease of blending, strength, toughness.	Blister packaging for non-food items; cling films for non-food use. May be used for food packaging with the addition of the plasticisers needed to make natively rigid PVC flexible . Non-packaging uses are electrical cable insulation; rigid piping; vinyl records.
04 PE-LD	Low-density polyethylene (LDPE)	Ease of processing, strength, toughness, flexibility, ease of sealing, barrier to moisture.	Frozen food bags; squeezable bottles, e.g. honey, mustard; cling films; flexible container lids.
05 PP	Polypropylene (PP)	Strength, toughness, resistance to heat, chemicals, grease and oil, versatile, barrier to moisture.	Reusable microwaveable ware; kitchenware; yogurt containers; margarine tubs; microwaveable disposable take-away containers; disposable cups; soft drink bottle caps; plates.
06 PS	Polystyrene (PS)	Versatility, clarity, easily formed	Egg cartons; packing peanuts; disposable cups, plates, trays and cutlery; disposable take-away containers.
07 O	Other (often polycarbonate or ABS)	Dependent on polymers or combination of polymers	Beverage bottles; baby milk bottles. Non-packaging uses for polycarbonate: compact discs; "unbreakable" glazing; electronic apparatus housings; lenses including sunglasses, prescription glasses, automotive headlamps, riot shields, instrument panels.

Plastic products have become absolutely necessary ingredients of modern living because of their properties like flexibility, toughness, durability, light weight, ease of fabrication, relatively low cost, ease of manufacture, versatility and imperviousness to water. Plastics are used in the manufacture of a wide range of products. Many traditional materials such as wood, stone, leather, paper, metal, glass, ceramic etc have been replaced by plastics. Applications of plastic to modern life are countless. It covers health, well being, shelter, transportation, sports, leisure activities etc. In developed countries, about one third of plastic is used in packaging and another one third in construction-related applications such as piping used in plumbing, vinyl sliding etc. Other uses include those in automobiles (up to 20% plastic), furniture and toys [3].

The energy requirement for the fabrication of plastic materials is comparatively less. The low density of plastic reduces the expenses for transportation and general handling. Complex parts can be moulded in one operation thereby work and material can be saved. Wide range of surface finish is possible for plastic goods. Good insulation property of plastics is useful for applications as thermal and electrical insulators [2].

The range of strengths, flexibilities, degrees of toughness as well as chemical and solvent resistances of plastic materials are wide and so are their range of applications. Many plastic materials posses photoconductivity, very low coefficient of friction to steel, high dielectric constant, high ultraviolet light transmission etc [2].

Worldwide production of different types of plastics during the period 1995-2010 is given in figure 1.2.

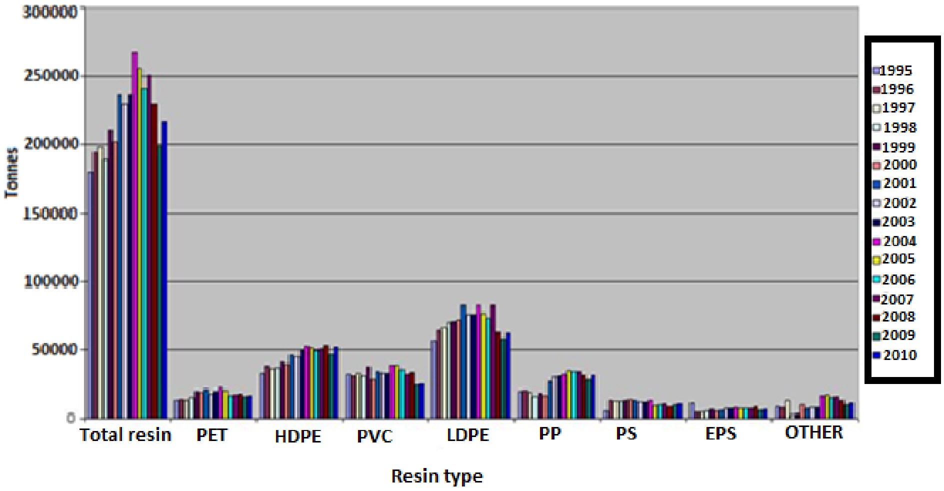
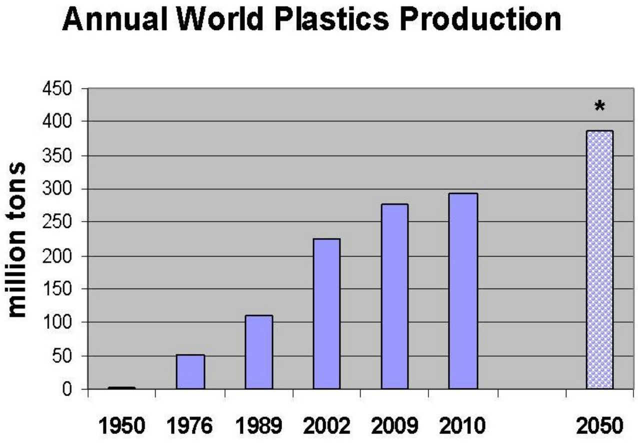


Figure 1.2: Statistics of the production of plastic from 1995-2010

The enormous quantity of plastics used world over is evident from figure 1.3 below:



Source: PlasticsEurope Market Research Group

Figure 1.3: The annual production of plastic worldwide

The per capita consumption of plastic in different geographical regions and its relation with the GNI is given in table 1.2.

Table 1.2: Plastic consumption worldwide

Main World Areas	KG/CAPITA	GNI/CAPITA
Europe W,C,E	90	18000
Eurasia, Russia, others	14	1600
North America	145	32000
Latin America	22	3500
Middle East, incl.TR	20	2500
Africa, North& South	13	2000
Other Africa	<1	300
China	14	800
India	4	450
Japan	90	3500
Other Asia Pacific, rest	11	600
Total World	25	5200

The approximate quantity of plastics used over the years in various sectors of application is given in table 1.3.

Table 1.3: Approximate quantity of different types of plastic used over the years (in ’000 tons)

Year	Adv. composites	Speciality	Engineering	Commodity
1979	1	60	950	8,000
1989	30	100	3,000	80,000
2000	90	300	6,500	90,000
2010	300	600	20,000	200,000
2020*	700	1000	40,000	700,000

*Estimated figures

The consumption pattern of plastics in various sectors of the Indian economy is shown in figure 1.4.

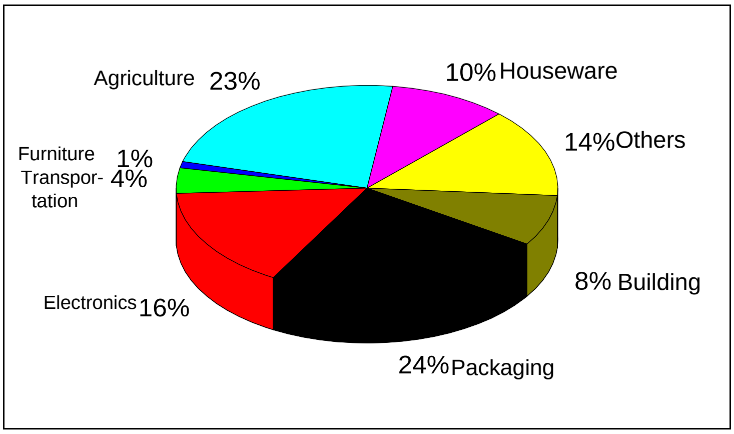


Figure 1.4: Plastic consumption pattern (India)

Being one of the fastest growing economies in the world, the production and consumption of plastic is growing very fast in India. Hence it is imperative that integrated measures are adopted to minimize the environmental hazards of plastics. These include, but are not limited to, minimization in the use of plastics and plastic products, recycling, reuse and safe disposal, education of the public on the hazards of plastics and the need for protecting the environment from plastics etc. In this context, investigations are in progress in many laboratories around the world on the development of appropriate technologies for the safe disposal of plastics [8-9]. In the current study, the application of Advanced Oxidation Processes (AOPs) and combination processes is examined in detail for the safe degradation and disposal of waste plastic materials.

1.1.4 Environmental issues related to plastics

The ‘white pollution’ caused by plastic wastes is a major environmental problem. Disposal of plastic wastes is a serious environmental issue due to their recalcitrant nature. The accumulation of plastic products in the environment adversely affects animals or/and humans and is called plastic pollution in general [10]. The main reason for the accumulation of plastic is its short-term and often single use. These wastes are not properly managed and are ultimately disposed off in unauthorized dumping sites or burnt in the open [11]. Evidences show that substantial quantities of plastic waste are polluting marine and other habitats [12]. This is a small component of the waste by weight but is huge in terms of volume due to the physical nature of the material.

Plastic pollutants are classified into micro- (between 2 μm and 5 mm), meso- (between 5mm and 20 mm), or macro-debris (larger than 20 mm) [13-14]. Yet another classification is as primary and secondary. Primary plastic pollutants are in the original form while the secondary plastics are resulting from the degradation of primary plastics [15]. Figure 1.5 is a typical unauthorized dumping site which is only a tip of the iceberg.

Figure 1.5: Accumulation of plastic wastes

The very same qualities that make plastic durable and attractive to manufacturers and consumers alike make it harmful to our health and environment. Plastic does not decompose biologically and this leads to a steady increase in the accumulation of plastic waste in our surroundings. These discarded non biodegradable wastes have become a major waste management challenge. Around 50% of non degradable materials are plastics or plastic related. It is estimated that a foam plastic cup will take 50 years, a plastic beverage holder will take 400 years, a disposable diaper will take 450 years and a fishing net will take 600 years [16] for complete degradation. When plastics are used, recycled or disposed off, harmful chemicals are released. More than 90% of the wastes found on the beaches around the world are plastic or plastic related.

Toxicity due to pure plastic as such is less since they are insoluble in water and are biochemically inert. Plastic products are blended with a variety of organics or additives, which serve as fillers, plasticisers, lubricants, anti-aging agents, flame retardants, pigments etc. Some of these added materials can be toxic. The amount of additives in plastic ranges from 0% (in polymers used to wrap foods) to more than 50% (for certain electronic applications). Many of the environmental issues associated with plastics are compounded by the additives [17]. For example adipates and phthalates are often added as plasticizers to brittle plastics like polyvinyl chloride [18]. Traces of these additives may leach out of the product leading to many health issues. Phthalates present in PVC can leach out of products as they are not chemically bound to the plastic matrix [19-20]. Bisphenol A(BPA) and phthalates are found in many plastic products including food packaging, perfumes, cosmetics, toys, flooring materials, computers and CDs. Phthalates and BPA are volatile in air and are detectable in the environment [21]. These chemicals can adversely affect animals and humans [18,22]. Additives such as phthalates, BPA, cadmium and lead have been shown to result in obesity and other health effects [23] in animal studies.

In some cases the finished plastic may be non-toxic (eg. PVC), but the monomers (eg. vinyl chloride) used in the manufacture of the corresponding polymers may be toxic. Some amount of these monomers can get trapped in the product unless the right processing is employed. The World Health Organization's International Agency for Research on Cancer (IARC) has identified vinyl chloride as a human carcinogen. Its exposure can cause angiosarcoma of the liver [24-25]. Debris composed of plastic, one of the world's most objectionable and visible kind of litter, affects our oceans and inland waterways. Plastic wastes found in the ocean includes food wrappers, fishing net, rope, diapers, beverage bottles, disposable plastic articles pellets etc [26].

Burning of plastic releases many pollutants. They get transported through the air to either short or long distances and then get deposited on land or in water bodies. These pollutants include some persistent organic pollutants (POPs) like mercury, PCBs, dioxins, furans etc and are also bioaccumulative. Bioaccumulation occurs usually indirectly through the contaminated food and water, especially through the consumption of fatty food items like milk [11] which may lead to many diseases like cancer, suppression of immune system, reproductive problems and developmental complications [27] to human beings and animals. Pollutants like dioxins are accidentally produced during the preparation of some chlorinated polymers like PVC [11].

Thousands of animals and birds are killed every year from plastic litter as they often mistake plastic waste for food . These plastic wastes stay in their stomach without digestion. The animals and birds are then unable to eat any real food and this situation ultimately kills them. A typical scene is shown in figure 1.6.

Figure 1.6: Animals eating plastic, mistaking for food.

Pollution due to plastic may directly or indirectly affect human health in many ways. The monsoon flooding in Mumbai city in the year 2005 was the indirect result of large accumulation of plastic bags in the gutters and drains leading to clogging. This blocked the rainwater flow through the underground systems leading to massive flood and death of thousands of people. Similar incidents are reported from Bangladesh and many other countries in the third world [28]. Education and outreach programs, stringent laws and policies, government and private enforcement etc are some of the major initiatives needed for successful prevention of plastic pollution [26].

1.2 Disposal methods

Disposal of plastic waste is an important environmental challenge. Unscientific disposal results in the formation of even more harmful chemical pollutants such as benzene, dioxins, etc which release harmful toxins into air and water bodies. Some of the disposal methods in use are shown in figure 1.7.

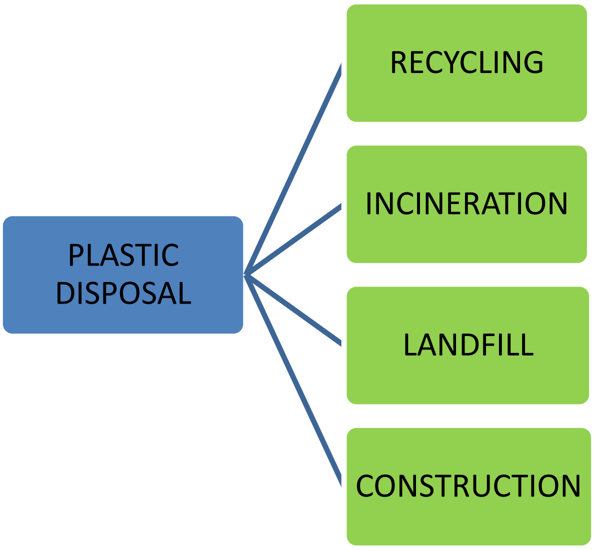


Figure 1.7: Commonly used disposal methods for plastics

1.2.1 Recycling

From the waste management perspective, the three R’s—reduce, reuse and recycle are widely advocated to manage the quantities of plastic, especially plastics packaging [29]. Plastic recycling is the process of recovering scrap or waste plastic and reprocessing the material into useful products, sometimes completely different in form from their original state. Recycling and reuse of plastics are gaining importance as a sustainable method for plastic waste disposal. Unfortunately, plastic is much more difficult to recycle than materials like glass, aluminum or paper. A common problem with recycling plastics is that they are often made up of more than one kind of polymer and/or there may be some sort of fibre added to it (a composite). Products made of a single polymer are easier and more efficient to be recycled than composite items, films and mixed wastes. As a consequence, it is not very easy to recycle a substantial proportion of the packaging plastics in a typical shopping basket using the currently available technology [29]. When plastic is melted during the recycling process, it breaks down and releases the chemicals used in the production process. Resulting air pollution causes skin and respiratory problems from exposure to and inhalation of toxic fumes, especially hydrocarbons and residues. The problem is more acute in the case of PVC. Heating and reheating of plastic for recycling also degrades it, resulting in downcycling. Plastic bottles, for example, are made into carpet, fleece, plastic lumber and other products that cannot be recycled again. Recycling and re-utilization of waste plastics lead to reduction of the use of virgin materials. This in turn results in lesser use of energy and thus reduction in carbon dioxide emissions.

Economically, in some cases, plastics recycling may be profitable. However, a number of factors can complicate the practice of plastics recycling, such as the collection of the plastics waste, separation of different types of plastics, cleaning of the waste and possible pollution from the recycling process. A further complicating factor is the low-value nature of most of the products that can be manufactured from recycled plastics. Reusing plastic is preferable to recycling as it uses less energy and fewer resources. At present our consumption of fossil fuels for plastic production is linear, from oil to waste via plastics. It is essential to take a more cyclical approach to material usage, though achieving this goal is complex [29].

Plastic polymers require complex processing to be recycled as each type melts at different temperatures and has different properties. Hence careful separation is necessary. Moreover, most plastics are not properly compatible with one another. Polyethlene terephthalate (PET) and high density polyethylene (HDPE) bottles have been proven to have high recyclability and are taken by most curb side and drop-off recycling programs. The growth of bottle recycling has been facilitated by the development of processing technologies that increase product purities and reduce operational costs. Recycled PET and HDPE have many uses and well-established markets. In contrast, the potential of recycling polyvinyl chloride (PVC) bottles and other materials is limited. A major problem in the recycling of PVC is the high chlorine content of raw PVC (around 56 percent of the polymer's weight) and the high levels of hazardous additives added to the polymer to achieve the desired material quality. As a result, PVC requires separation from other plastics before mechanical recycling.

We cannot escape from the toxins that are released when recycling takes place irrespective of the location, since toxins don't stay local. Once emitted into the environment, dioxins, for example, can travel vast distances via air and ocean currents which make them a global contaminant. In spite of many such disadvantages, ‘recycling’ option is viewed as the preferred route for plastic disposal because of its broad public appeal and comparatively less environmental hazards [11]. However, even the best technology available today for plastic recycling is not without harmful effects on human and environmental health. Hence reducing the use of plastics is the best option for our health and environment. The recycling message is simple; both industry and society need to regard end-of-life items, including plastics, as raw materials rather than waste.

1.2.2 Incineration

Incineration is a waste treatment process that involves the combustion of organic substances present in waste materials. Incineration and other high-temperature waste treatment systems are described as "thermal treatment". Incineration converts the waste into ash, flue gas, and heat. The ash is mostly formed by the inorganic constituents of the waste, and may take the form of solid lumps or particulates carried by the flue gas. The flue gases must be cleaned of gaseous and particulate pollutants before they are dispersed into the atmosphere. In some cases, the heat generated by incineration can be used to generate electric power.

When incinerated, plastic releases high amounts of fossil carbon into the atmosphere as CO_2. Burning plastic in incinerators releases toxic heavy metals and chemicals. They also produce a variety of toxic discharges to the air, water, and ground that are significant sources of powerful pollutants, including dioxin (common name for a group of ~ 25 chemicals) and other chlorinated organic compounds. Garbage incinerators and medical waste incinerators are two of the largest sources of dioxin according to the U.S. Environmental Protection Agency. It is a toxic waste product formed when waste containing chlorine is burned or when products containing chlorine are manufactured. Dioxins are among the most potent synthetic chemicals which can cause cancer and harm our immune and reproductive systems even at very low concentrations.

Many of these toxins enter the food supply and become more concentrated as they move up through the food chain. In addition to air and water emissions, incinerators create toxic ash—or slag—which contains heavy metals, dioxins, and other pollutants. This toxic ash must be landfilled and the pollutants present in the ash can then leach into groundwater.

Despite being an attractive technological option for waste management, combustion-based processes are subject of intense debate around the world. In the absence of effective controls, harmful pollutants may be emitted into the air, land and water which may adversely influence human health and environment [30].

1.2.3 Landfills

A large portion of the plastic waste is buried under ground, in landfills and some often end up littering streets and countryside via open dumping (quite unfortunately). In landfills, leachate is produced when water picks up toxins as it seeps through the trash. Although this toxic leachate is expected to be collected in landfills and to be safely disposed off, it also leaks into ground and surface water, releasing pollutants into the environment and causing health risks for humans and wildlife. It is often difficult to find adequate places to build landfills. Plastic products are not easily biodegradable and remain in landfills, without breaking down or changing composition. The buildup of plastic waste in landfills is simply not sustainable. Plastic wastes, including packaging, electrical equipment and scrap from old vehicles, are major components of both household and industrial wastes. Our capacity for disposal of waste in landfill is finite and in some locations landfills are at, or are rapidly approaching, capacity [14,31]. It has also been suggested that because of the longevity of plastics, disposal by landfill may simply be storing problems for the future [14,29]. For example, plasticizers and other additive chemicals have been shown to leach from landfills [32].

1.2.4 Construction of roads

The government has made it mandatory for road developers to use waste plastic along with bituminous mixes for road construction wherever possible to overcome the growing problem of disposal of plastic waste in India's urban centers. Road developers are encouraged to use waste plastic along with hot mixes for constructing bitumen roads within 50 km of periphery of any city that has a population of over five lakh. India generates ~5.6 million tonne of plastic waste annually. As per a study by the Central Pollution Control Board, 60 large cities in India generate over 15,000 tonne of plastic waste every day. Delhi generates close to 7,000 tonne of waste every day, of which over 10 per cent is pure plastic. This cannot be disposed of even through waste-to-energy plants because of environmental reasons [33].

The following types of waste plastic can be used in the construction of rural roads:

- Films (Carry Bags, Cups) thickness up to 60 micron (PE, PP and PS)
- Hard foams (PS) (any thickness).
- Soft Foams (PE and PP) (any thickness).
- Laminated plastics of thickness up to 60 micron (Aluminium coated also) such as packing materials used for biscuits, chocolates, etc.,
- Poly Vinyl Chloride (PVC) sheets or Flux sheets should not be used in any case.
- Plastic roads are presumed to have the following advantages.
- Strength of the road increased (Increased Marshall Stability Value)
- Better resistance to water and water stagnation
- No stripping and no potholes.
- Increased binding and better bonding of the mix.
- Increased load withstanding property
- Decrease in the overall consumption of bitumen.
- Reduction in pores in aggregate and hence less rutting and ravelling.
- Low maintenance cost.
- Increased road life period.
- No leaching of plastics [34].

Disadvantages of plastic roads are:

1) Toxics present in the co-mingled plastic waste would start leaching during the road laying process. In the presence of chlorine containing plastics, noxious HCl gas will be released.
2) After the road laying the first rain may trigger leaching, as the plastics will merely form a sticky layer (mechanical abrasion).
3) The components of the road, once it has been laid, are not inert.

The use of plastic waste for road construction seems to be a good solution for the environmental issues caused by plastic. The advantages and disadvantages of the method has been widely discussed. But still a comprehensive final view on the environmental effects of using plastic waste for road construction is not available. The main reason is that the effects were studied only for a limited period of time. Effects of such trials will be clear only after a long time period. To be used in the construction process, the plastics waste (bags, cups etc) made out of PE, PP and PS must be cut into a size between 2.36mm and 4.75mm using shredding machine. Converting plastic into small particles can cause major environmental issues in future because the natural degradation of plastic will take more than thousand years. The plastic particles may slowly get into the environment and will remain in the air/water/soil. Inhaling of this contaminated air can cause serious allergic issues and may lead to skin diseases and even cancer.

1.3 Degradation of Plastics

Irreversible degradation has been proposed by various investigators as viable option to reduce the environmental issues caused by plastic. Major degradation methods are:

- Thermal degradation
- Ozone-induced degradation
- Biodegradation
- Advanced Oxidation Processes

1.3.1 Thermal Degradation

Under normal conditions, photochemical and thermal degradations are similar and are classified as oxidative degradation. Thermal reactions occur throughout the bulk of the polymer sample, whereas photochemical reactions occur only on the surface [35]. The depolymerization reaction in thermal degradation need not be initiated at terminal end of the macromolecule. Instead, imperfections in the chain structure (initiator fragment or a peroxide or ether link) form a weak link from where depolymerization starts. A large number of addition polymers depolymerize at elevated temperature. Thermal degradation above 200^0 C leads to chain scission and largely depends on impurities like unsaturation sites, head-to-head units, etc. [36]. Polyolefins are known to be sensitive to thermal oxidation, due to the impurities generated during their manufacture at high temperatures [37].

Thermal degradation of polymers consists of two distinct reactions, which occur simultaneously. One is a random scission of links, causing a molecular weight reduction of the raw polymer, and the other is a chain-end scission of C-C bonds, generating volatile products [38-40]. Thermal degradation of the polymers follows either chain end degradation (Eqs. 4 and 5) or random degradation route (Eq. 6) as shown below:

$$M_n \longrightarrow M_{n-1} + M \quad \text{.......} (4)$$

$$M_{n-1} \longrightarrow M_{n-2} + M \quad \text{.......} (5)$$

$$M_n \longrightarrow M_x + M_y \quad \text{.......} (6)$$

$n = x + y$

where M represents the monomer.

The chain end degradation starts from the end of the chain and successively releases the monomer units. This type of degradation route is also known as depolymerization reaction. Such reactions are the opposite of the propagation step in addition polymerization and occur through free radical mechanism. Random degradation occurs at any random point along the polymer chain. This is reverse to polycondensation process where the polymer degrades to lower molecular weight fragments but practically no monomer is liberated. For random degradation to occur, the polymer chain does not necessarily require to have any active site [41]. The addition of a catalyst lowers the temperature of decomposition, improves the quality of products obtained from pyrolysis of plastic wastes and also enable a given selectivity to a certain product to be achieved. Solid acid catalysts, such as zeolites, favour hydrogen transfer reactions due to the presence of many acid sites. The access of molecules to reactive sites on the catalyst is limited to the pore size as well as the growth of end products inside the pores. Therefore, zeolite catalysts may produce molecular sieving and shape selectivity [42]. Garforth et al [43] have investigated catalytic degradation of polyolefins using TGA as a potential method for screening catalysts and have found that the presence of catalyst led to a decrease in the apparent activation energy. For polymer degradation, different types of catalysts have been reported in the literature [44-45]. These include Pt-Co and Pt-Mo supported over SiO_2 [46], zeolite catalysts and non-zeolite catalysts, transition metal catalysts (Cr, Ni, Mo, Co, Fe) on supports such as Al_2O_3 , SiO_2, zeolite etc.

1.3.2 Ozone-induced degradation

The presence of ozone in the air, even in very small concentrations, markedly accelerates the aging of polymeric materials [47]. This process in saturated polymers is accompanied by the intensive formation of oxygen-containing compounds, by impairment of the mechanical and electrical properties of the specimens [48]. Exposure of polymers to ozone results in the rapid and consistent formation of a variety of carbonyl and unsaturated carbonyl products based on aliphatic esters, ketones, and lactones as well as aromatic carbonyl associated with the styrene phase. This follows a more gradual formation of ether, hydroxyl and terminal vinyl groups with time and concentration [49]. The reactions of ozone with polymers occur with main chains containing C-C bonds, aromatic rings or saturated hydrocarbon links. The reaction proceeds through unstable intermediates such as the bipolar ion or peroxy radicals, which can isomerize, degrade or cause decomposition of macromolecules [50]. Ozone normally attacks the unsaturation in the unsaturated polymers and this reaction generally occurs in three principal steps. The first step is a cycloaddition of ozone to the olefin double bond to form ozone-olefin adduct referred to as the ‘primary ozonide’. This is an unstable species because it contains two very weak O-O bonds. The second step is the decomposition of the primary ozonide to carbonyl compounds and a carbonyl oxide. The carbonyl oxide is considered to be the key intermediate in the C-C bond ozonolysis mechanism. The third step is the fate of the carbonyl oxide, which depends on its source, as well as the environment [51-54].

The effects of ozone (O_3) gas exposure at various concentrations and treatment times on structural, mechanical and barrier properties of polyethylene and polyamide films were investigated by Ozen et al [55]. The results showed that O_3 treatment caused formation of oxygen-containing functional groups and degradation of polymeric chains in polyethylene films and significantly increased the –C-N- stretch observed at 1125 cm^{-1} in the FT-IR spectra in polyamide films.

Ozen et al [55] have studied the effect of ozone exposure on structural and mechanical properties of packaging films. The study showed that ozone treatment has affected the PE and polyamide films in different ways. Formation of oxygen-containing functional groups are responsible for the degradation of polymeric chains in PE films and increase in the -C-N- stretching in polyamide.

1.3.3 Biodegradation

Biodegradation is biochemical transformation of compounds by microorganisms. According to ASTM standard D-5488-94d biodegradation is defined as ‘‘process which is capable of decomposition of materials into carbon dioxide, methane, water, inorganic compounds, or biomass in which the predominant mechanism is the enzymatic action of microorganisms”.

Mineralization of organic compounds yields carbon dioxide and water under aerobic conditions, and methane and carbon dioxide under anaerobic conditions. Abiotic hydrolysis, photo-oxidation and physical disintegration of polymers may enhance biodegradation of polymers by increasing their surface area for microbial colonization or by reducing molecular weight [56].

Biological degradation is chemical in nature but the source of the reacting chemicals is from microorganisms. These chemicals are of catalytic nature e.g. enzymes. The susceptibility of the polymers to microbial attack generally depends on enzyme availability, availability of a site in the polymers for enzyme attack, enzyme specificity for that polymer and the presence of coenzyme if required [57].

Biodegradation of polymers occurs through four different mechanisms: solubilization, charge formation followed by dissolution, hydrolysis and enzyme-catalyzed degradation [58-59].

A good review about the degradation of plastics by microorganisms was done by Gnanavel et al [60]. Plastics are biodegraded, (a) in wild nature under aerobic conditions (CO_2, water are produced), (b) in sediments & landfills under anaerobic conditions (CO_2, water, methane are produced) and (c) in composts and soil under partial aerobic & anaerobic conditions. The plastics which were studied are polyethylenes, polyvinyl chloride, polyesters, polylcaprolactone, polylactic acid, polyurethane, polyvinyl alcohol, nylon, polyester-polyurethane etc. Bacterial and fungal species are used widely for degradation. Many strains of *Pseudomonas spp* are reported in this respect. The organisms which degrade the hydrocarbon in plastics and use them as carbon source can be employed.

Review by Leja et al [61] covers polymer biodegradation and biodegradable polymers. Biodegradation processes of xenobiotics such as aromatic compounds, plastics (PVA, polyesters, polyethylene, and nylon), and polymer blends (Starch/Polyethylene, Starch/Polyester, and Starch/ PVA) are described. Information about biodegradable polymers such as mixtures of synthetic polymers and substances that are easily digestible by microorganisms (chemically modified starch, starch-polymer composites, thermoplastic starch, and biodegradable packing materials), synthetic materials with groups susceptible to hydrolytic microbial attack (polycaprolactone) and biopolyesters (poly-β-hydroxyalkanoates) is also provided. This review has covered many major aspects about the natural and synthetic polymers, their types, uses and degradability.

Zheng et al [62] reviewed the technological advancement made in the development of more easily biodegradable plastics and the biodegradation of conventional plastics by microorganisms. Additives, such as pro-oxidants and starch, are incorporated in plastics to make them biodegradable. Recent research has shown that thermoplastics derived from polyolefins, which were generally resistant to biodegradation in ambient environment, are biodegraded following photo-degradation and chemical degradation. Thermoset plastics, such as aliphatic polyester and polyester polyurethane, are easily attacked by microorganisms directly because of the potential hydrolytic cleavage of ester or urethane bonds in their structures. Synthetic polyolefins are inert because their backbones consist of only long carbon chains [63] which are non-susceptible to degradation by microorganisms.

Yoon et al [64] isolated mesophilic bacterium capable of biodegradation of low-molecular-weight polyethylene (LMWPE). This rod-shaped gram negative bacterium was identified as *Pseudomonas sp. E4*. The biodegradability decreased with increase in molecular weight.

Sangale et al [65] consolidated most of the available literature on the biodegradation of polythene and considered that the cheapest, eco-friendly and acceptable method is microbial degradation. The microbes release extracellular enzymes such as lignin peroxidase and manganese peroxidase which degrade the polythene.

Bhardwaj et al [66] also reviewed the literature on microbial degradation of polymers and concluded that microbial enzymes provide one of the most powerful tools for the degradation of plastics.

Mülleret et al [67] tested the decay characteristics of three common types of shopping bag polymers in sea turtle gastrointestinal fluids (GIF): standard, degradable and biodegradable plastic. The biodegradable bags showed mass losses between 3 and 9% in 49 days.

Biodegradation studies on polyethylene and polypropylene plastic showed that pre-treated polymers degrade more easily than untreated polymers [68]. Degradation is more facile with starch and cellulose blended polymers. Study on cell surface hydrophobicity and the effect of addition of surfactants showed an important role for surface film formation which is a prerequisite for biodegradation.

Evaluation of the biodegradability of natural and synthetic polyethylene done by Nanda et al [69] with three different *Pseudomonas* sp. demonstrated that natural polyethylene plastic bags containing 6% vegetable starch, biodegraded faster compared to the synthetic ones. Best degradation was observed with *Pseudomonas* sp. from sewage sludge dump. *Pseudomonas* sp. isolated from textile effluents drainage site was less effective and the lowest activity was shown by *Pseudomonas* sp. from household garbage dump.

1.3.4 Advanced Oxidation Processes (AOPs)

Advanced oxidation processes (AOPs), are a set of processes designed to remove contaminants in water and waste water by oxidation through reactions involving highly reactive hydroxyl radicals (•OH) [70]. AOPs under appropriate conditions can reduce high concentration of contaminants to minute quantities and thus significantly bring COD and TOC down. AOPs are called the water treatment processes of the 21st century [71]. Usually AOPs involve a specific subset of processes that involve O_3, H_2O_2, and/or UV light. Reactive free radical in particular •OH, are generated by irradiation with different high energy sources. These reactive oxygen species (ROS) are the strongest oxidants that can be applied in water and can virtually oxidize any compound present in the water matrix, often at a diffusion controlled reaction speed. Once formed, •OH reacts nonselectively with the contaminants which will be quickly and efficiently fragmented and converted into small inorganic molecules.

•OH is the second strongest oxidizing species after fluorine with a relative oxidation power of 2.8 eV. This nonselective primary oxidant is capable of readily attacking or degrading almost all recalcitrant organic compounds and converting them to less harmful intermediates and end products [72].

Figure 1.8 illustrates some special characteristics of ·OH that make AOP a powerful method for the removal of refractory compounds.

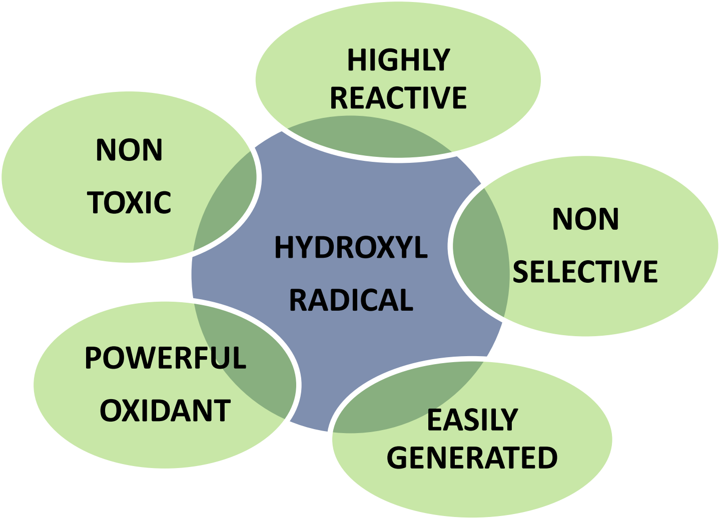


Figure 1.8: Special characteristics of $^{\bullet}$OH

AOPs are generally classified as homogeneous or heterogeneous based on the nature of the medium in which the process takes place. Homogeneous processes are further subdivided into processes that use energy and that do not use energy (see figure 1.9).

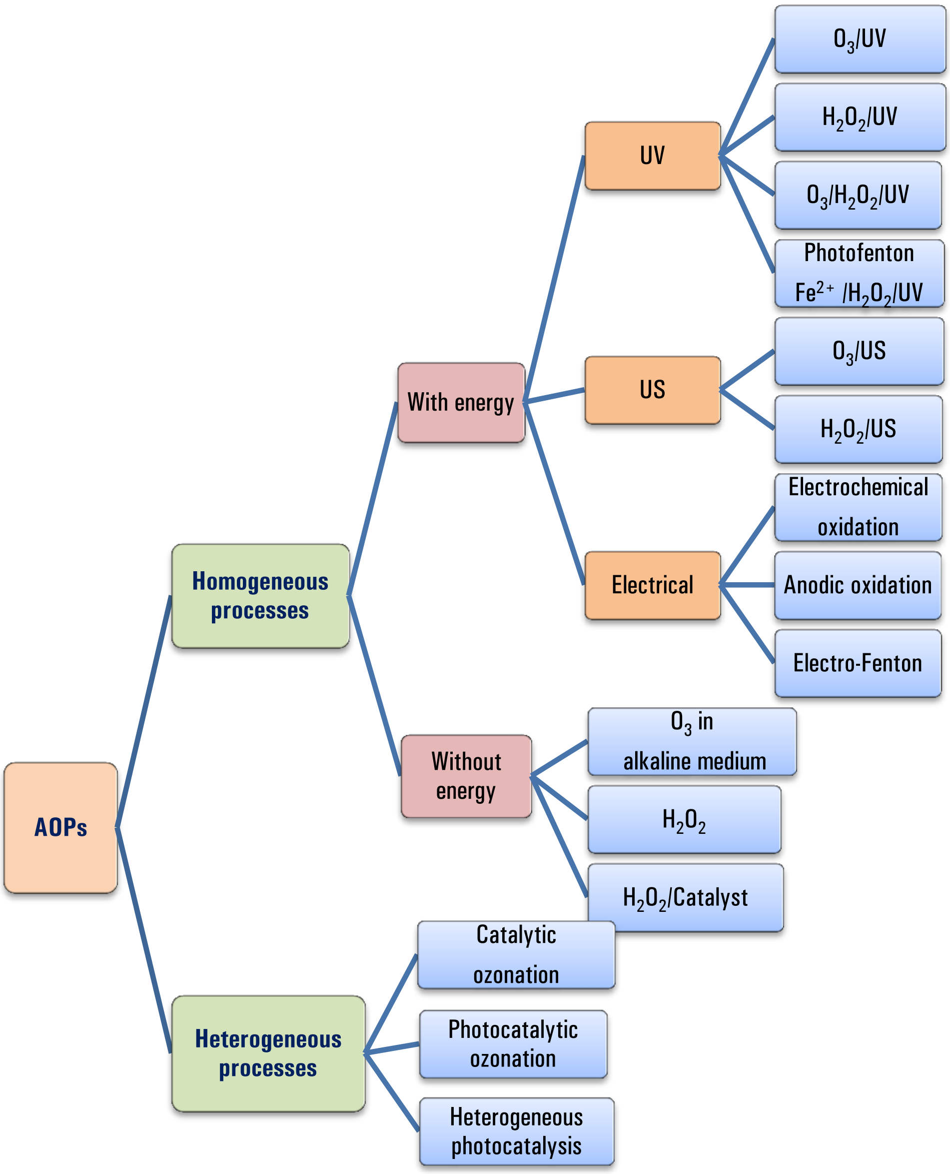


Figure 1.9: Classification of Advanced Oxidation Processes

1.3.4.1 Homogeneous AOPs

Homogeneous AOPs generally employ Ultraviolet (UV) radiation, Ultrasound (US), electrical energy etc for the degradation of compounds. Processes based on this include $O_3/H_2O_2/UV$, UV/H_2O_2, O_3/UV, Photo-Fenton, O_3/US, H_2O_2/US, Electro-Fenton etc and their combinations.

1.3.4.2 Heterogeneous AOPs

In Heterogeneous AOPs, catalysts are employed for the enhancement of the degradation of compounds. Here the contaminants are present in the aqueous phase, while the catalyst is in the solid phase. The catalyst accelerates the degradation process through the formation of electron-hole pairs on irradiation with an appropriate energy source. The photo-generated holes and electrons are responsible for the oxidation and reduction processes, respectively. Relevant details are discussed later in this chapter.

1.3.4.3 General mechanism of AOP

Oxidation is defined as the transfer of one or more electrons from an electron donor (reductant) to an electron acceptor (oxidant), which has a higher affinity for electrons. These electron transfers result in the chemical transformation of both the oxidant and the reductant, in some cases producing chemical species with an odd number of valence electrons. These species, known as radicals, tend to be highly unstable and, therefore, highly reactive because one of their electrons is unpaired. Oxidation reactions that produce radicals tend to be followed by additional oxidation reactions between the radical oxidants and other reactants (both organic and inorganic) until thermodynamically stable oxidation products are formed.

The ability of an oxidant to initiate chemical reactions is measured in terms of its oxidation potential. The most powerful oxidants are fluorine, hydroxyl radicals ($^{\bullet}$OH), ozone, nascent oxygen etc. The oxidation potential of some of the common oxidants are given in table 1.4.

Table 1.4: Oxidation potential of common oxidizing agents.

Sl. No.	Oxidation species	Oxidation potential, eV
1	Fluorine	3.06
2	Hydroxyl radical	2.80
3	Sulphate radical	2.60
4	Atomic oxygen	2.42
5	Nascent oxygen	2.42
6	Ozone	2.07
7	Persulphate	2.01
8	Hydrogen peroxide	1.77
9	Perhydroxyl radical	1.70
10	Permanganate	1.68
11	Hypobromous acid	1.59
12	Hypochlorous Acid	1.49
13	Hypochlorite	1.49
14	Hypoiodous acid	1.45
15	Chlorine	1.36
16	Chlorine dioxide	1.27
17	Oxygen(molecular)	1.23
18	Bromine	1.09
19	Iodine	0.54

The end products of complete oxidation (ie, mineralization) of organic compounds are carbon dioxide (CO_2),water (H_2O) and salts.

These reactive species are generated through ozonation [73], Fenton process, Fenton-like process [74-76], photochemical oxidation, electrochemical oxidation [77-78], H_2O_2/UV, UV/O_3 [79-80], photocatalytic oxidation [81-82], sonolysis etc. Precise, pre-programmed dosages, sequences and combinations of these reagents are used under appropriate reaction conditions in order to obtain a maximum yield of reactive free radicals, in particular •OH. The mechanism of AOPs essentially consists of three parts:

1) Formation of $^{\bullet}OH$
2) Initial attacks on target molecules by $^{\bullet}OH$ and their breakdown to fragments
3) Subsequent attacks by $^{\bullet}OH$ until ultimate mineralization

The hydroxyl radicals attack organic chemicals by radical addition, hydrogen abstraction and electron transfer as follows (R represents the reacting organic compound):

$R + {}^{\bullet}OH \rightarrow ROH$: Addition ....(7)

$R + {}^{\bullet}OH \rightarrow R^{\bullet} + H_2O$: Abstraction ....(8)

$R + {}^{\bullet}OH \rightarrow R^{+} + OH^{-}$: Electron transfer ....(9)

Subsequent steps involving $^{\bullet}OH$ as well as ROS formed during the course of the reaction, lead to further reaction and eventual mineralisation.

The AOPs have both advantages and disadvantages which have to be taken into consideration while selecting the process for specific type of pollutants. The advantages include:

- Effective removal of contaminants that are resistant to conventional treatment and the complete mineralization of organic compounds into H_2O and CO_2.
- Low selectivity and wider application potential.
- High reaction rate.
- Major disadvantages include:
- High consumption of reagents, especially H_2O_2 wherever it is a reagent.
- Homogeneous Fenton-based AOPs generate contaminated intermediate products which require secondary treatment.
- Radical scavenging by interfering compounds reduces effectiveness of AOP.
- The most widely investigated AOP in environmental decontamination is photocatalysis, in particular due to the possibility of using sunlight as the source of irradiation. Hence the technique is discussed in detail below.

1.3.4.4 Photocatalysis

In photocatalysis light is used to activate the catalyst which can modify the rate of a chemical reaction without itself getting consumed in the chemical transformation. The wavelength at which the reaction takes place depends on the nature of the processes and photochemical characteristics of components. The wavelength range of various photoprocesses are shown in figure1.10.

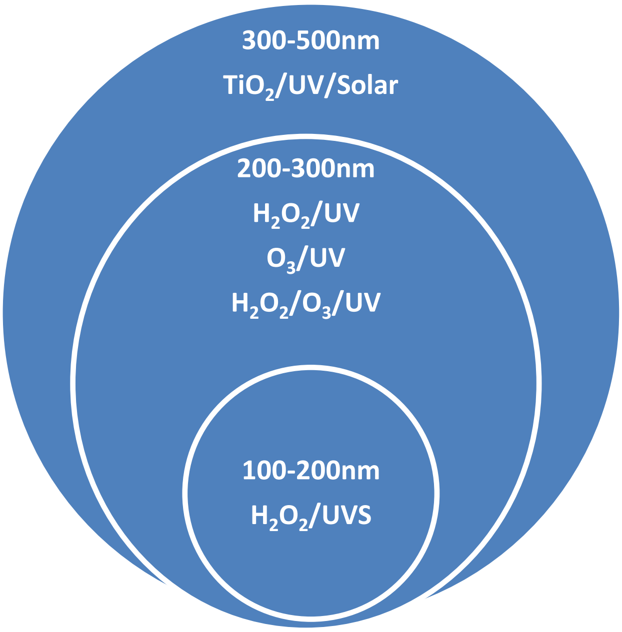


Figure 1.10: Wave length range of various photoprocesses

Depending on whether the catalyst is dissolved in the reaction system or remain suspended, photocatalysis can be classified into homogeneous and heterogeneous processes.

1.3.4.4.1 *Homogeneous Photocatalysis*

In homogeneous photocatalysis, the catalysts are in the same phase as the reactants and they are uniformly distributed within the reaction medium. Therefore, the reaction takes place within the liquid. Homogenous photoprocesses for pollutant degradation include O_3/UV, H_2O_2/UV, O_3/H_2O_2/UV, Fenton and Photo-Fenton [83-84]. The most widely used transition metals as homogeneous catalysts in Fenton and O_3-based AOPs are Fe^{2+}, Fe^{3+}, Zn^{2+}, Mn^{2+}, Mn^{3+}, Mn^{4+}, Ti^{4+}, Cr^{3+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+} etc [83-92]. Some of the major homogeneous catalytic processes are shown in table 1.5.

Table 1.5: Summary of the major homogeneous photocatalytic processes.

AOP Technology	Brief Description	Major Reactions
O_3/UV	Hydroxyl radicals are generated when UV light is applied to ozonated water. Destruction of organic compound occurs by hydroxyl radical reactions, coupled with direct photolysis and oxidation by molecular ozone.	$O_3 + H_2O + h\nu \rightarrow H_2O_2 + O_2$ $2O_3 + H_2O \rightarrow 2^{\bullet}OH + 3O_2$ $^{\bullet}OH$ + Pollutants → Oxidation By-products
H_2O_2/UV	This process involves the formation of hydroxyl radicals by the photolysis of H_2O_2 and subsequent propagation reactions. The photolysis of hydrogen peroxide occurs when UV radiation (hν) with wavelength less than 400 nm is applied. The process requires relatively high dose of H_2O_2 and longer UV-exposure time.	$H_2O_2 + h\nu \rightarrow 2^{\bullet}OH$ $H_2O_2 \rightarrow H_2O + ½O_2$ $^{\bullet}OH + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O$ $HO_2^{\bullet} + H_2O_2 \rightarrow {}^{\bullet}OH + H_2O + O_2$ $HO_2^{\bullet} + HO_2^{-} \rightarrow {}^{\bullet}OH + HO^{-} + O_2$ $2^{\bullet}OH \rightarrow H_2O_2$
O_3/H_2O_2/UV	When O_3 and H_2O_2 are simultaneously present in water, they react to form hydroxyl radicals. These hydroxyl radicals can oxidize most dissolved organic matter to form various intermediates. In the presence of UV, more hydroxyl radicals are generated leading to the mineralization and effective destruction of contaminants.	$H_2O_2 + H_2O \rightarrow H_3O^{+} + HO_2^{-}$ $O_3 + H_2O_2 + h\nu \rightarrow O_2 + {}^{\bullet}OH + HO_2^{\bullet}$ $O_3 + HO_2^{-} \rightarrow {}^{\bullet}OH + {}^{\bullet}O_2^{-} + O_2$ $O_3 + {}^{\bullet}O_2^{-} \rightarrow {}^{\bullet}O_3^{-} + O_2$ $^{\bullet}O_3^{-} + H_2O \rightarrow {}^{\bullet}OH + OH^{-} + O_2$
Photo Fenton	Fenton reagent is a mixture of ferrous iron (catalyst) and hydrogen peroxide. The photo Fenton process ($H_2O_2/Fe^{2+/}UV$) involves the $HO^{\bullet}$ formation through photolysis of hydrogen peroxide (H_2O_2/UV) and Fenton reagent (H_2O_2/Fe^{2+}). In the presence of UV irradiation, the ferric ions (Fe^{3+}) formed are photocatalytically converted back to ferrous ions (Fe^{2+}), with formation of an additional equivalent of hydroxyl radicals. The hydroxyl radicals formed react with organic species, promoting their oxidation.	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{-} + {}^{\bullet}OH$ $Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + .O_2^{-} + 2H^{+}$ $Fe^{3+} + .O_2^{-} \rightarrow Fe^{2+} + O_2$ $^{\bullet}OH$ + pollutants → oxidation product

1.3.4.4.2 *Heterogeneous photocatalysis*

Here the catalyst and reactants are in different phases. Heterogeneous photocatalysis appears to be a promising solution for the degradation of pollutants in water [93]. This treatment nonselectively degrades pollutants in the presence of catalysts (mostly semiconductor material) and UV radiation (wavelength ranging from 320 to 400 nm), visible light or solar radiation [94-99].

Most common heterogeneous photocatalysts are transition metal oxides and semiconductors which have unique characteristics. TiO_2, ZnO, ZrO_2, CdS, MoS_2, Fe_2O_3, WO_3 and ZnS are among the semiconductors used as heterogeneous photocatalysts for environmental waste treatment [94,100-104]. Among them, ZnO and TiO_2 have been widely investigated because they offer several advantages, such as effectiveness under ambient conditions, low cost, commercial availability, low toxicity and photochemical stability compared to others. Besides, the morphology of TiO_2 allows easy electron transfer and stabilizes charge separation. As a result, the recombination of photogenerated carriers is prevented. Based on literature, it can be concluded that heterogeneous systems are highly influenced by types and characteristics of catalysts, pH of the treatment system, light intensity, type of pollutant, concentration of oxidants, presence of ionic species and type of intermediates.

Hydroxyl radicals are produced with the help of one or more primary oxidants (e.g. ozone, hydrogen peroxide, oxygen) and/or energy sources (e.g. ultraviolet light) and/or catalysts (e.g. titanium dioxide). The photocatalytic procedure is particularly useful for removing biologically toxic or non-degradable materials such as aromatics, pesticides, petroleum constituents and volatile organic compounds in waste water [105].

1.3.4.4.2.1 *Semiconductors as Photocatalysts*

Semiconductors are crystalline or amorphous solids which behave as insulators at absolute zero but conduct electricity at normal temperatures. According to band theory there is only a small gap between the filled valence band (VB) of electrons and empty conduction band (CB) of semiconductor materials. At absolute zero since the electrons occupy their lowest possible energy level, the conduction band will be empty and the semiconductors will behave as perfect insulators. Since the energy gap is small in semiconductors at normal temperatures excitation of some electrons from the VB to CB can take place and electricity is conducted. This thermal excitation of electrons at normal temperature depends on the energy gap between VB and CB. Conductivity of semiconductors increases with increase in temperature. Si and Ge are the most commercially used semiconductors. Figure 1.11 shows the band structure of insulators, conductors (metals) and semiconductors.

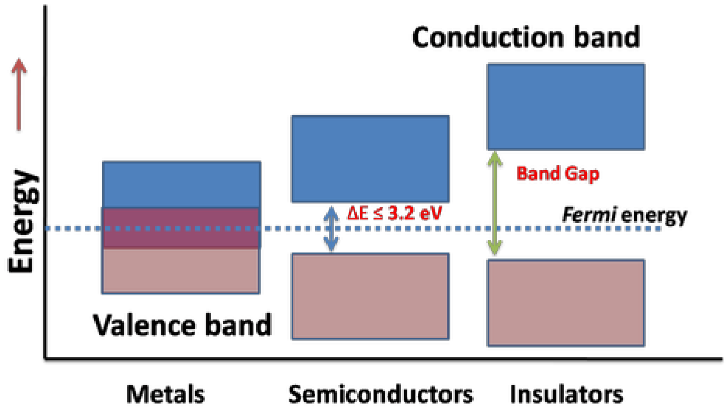


Figure 1.11: Energy bands of insulators, conductors and semiconductors

Semiconductors are of two types; intrinsic and extrinsic semiconductors. Intrinsic semiconductors are pure semiconductors having small energy gap between filled valence band and empty conduction band. Extrinsic semiconductors are obtained by adding proper trivalent impurities like Ga, Al, B etc or by adding pentavalent impurities like P, As etc to the intrinsic semiconductors. This process called doping improves the conductivity of semiconductors. Figure 1.12 shows the band structure of undoped and doped semiconductors [106].

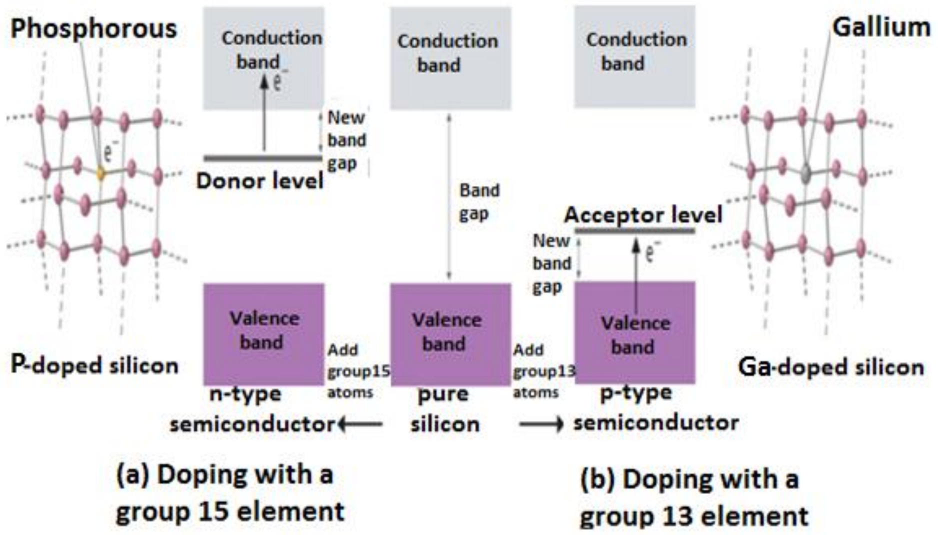


Figure 1.12: Energy bands of pure, n-type and p-type semiconductors

Many metal oxides such as TiO_2, ZnO, ZrO_2, Fe_2O_3, WO_3 etc and sulphides such as CdS and MoS_2 can act as semiconductor materials and are suitable for photocatalysis for the degradation of organic and inorganic pollutants [107-110]. These semiconductors posses characteristics such as suitable band-gap energies, stability towards photo-corrosion, nontoxic nature, low cost, and physical characteristics that enable them to act as catalysts. Figure 1.13 lists the energy levels of some semiconductor materials, which are used for photocatalytic reactions [111].

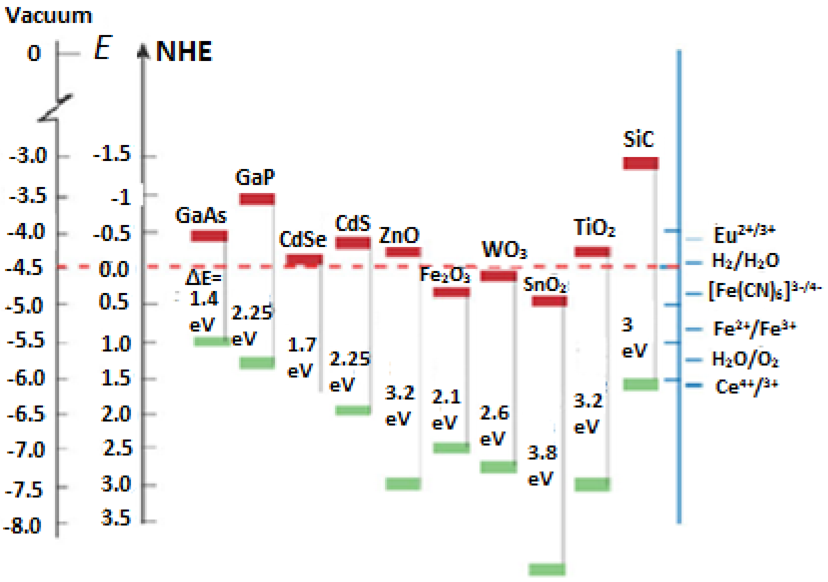


Figure 1.13: Energy level diagram for typical semiconductors

When a semiconductor is irradiated with photons of energy equal to or greater than its band gap energy (3.2eV in the case of TiO_2 as well as ZnO) the photons are absorbed and electron-hole pairs are created [92,112]. These electrons and holes can either recombine or migrate towards the surface participating in several redox reactions eventually leading to the formation of Reactive Oxygen Species (ROS) such as $^{\cdot}OH$ radicals and H_2O_2. These transitory ROS can initiate and promote a number of reactions which end up in complete mineralisation of the pollutants into harmless products such as CO_2, water and salts. The principle of semiconductor photocatalysis can be represented as in figure 1.14.

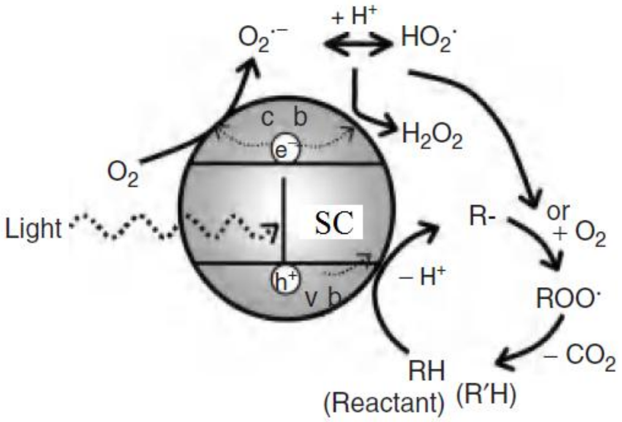


Figure 1.14: Schematic diagram illustrating the principle of Semiconductor photocatalysis

The basic reactions taking place are:

SC (Semiconductor) + $h\nu \rightarrow h^+ + e^-$ .... (10)

$h^+ + e^- \rightarrow$ Heat (Recombination) .... (11)

$h^+ + OH^- \rightarrow {}^{\bullet}OH$ ....(12)

$h^+ + H_2O \rightarrow {}^{\bullet}OH + H^+$ ....(13)

Scavenging of conduction band electrons

$e^- + O_2 \rightarrow O_2^{\cdot -}$ ....(14)

Formation of multiple peroxide species

$H^+ + O_2^{\cdot -} \rightarrow HO_2^{\cdot}$ ....(15)

$HO_2^{\cdot} + e^- + H^+ \rightarrow H_2O_2$ .... (16)

Pollutant + ROS (H_2O_2, $O_2^{\cdot -}$, $HO_2^{\cdot}$, ${}^{\bullet}OH$ etc) →

Intermediates → H_2O + CO_2 + Salts ....(17)

1.3.4.4.2.2 *Typical photocatalytic studies on plastic materials*

Numerous studies have been reported on the application of photocatalysis for the removal of chemical and bacterial pollutants from water. These are summarised in many excellent reviews. Detailed account of these findings is beyond the scope of this chapter and is hence not reviewed here. Studies on the application of photocatalysis for the degradation and removal of plastic and plastic products are very few. Some of the important studies in this context are summarised below.

A good review on mechanistic implications of plastic degradation was done by Singh et al [113]. This review covers studies on the degradation of different types of plastics, including photo-oxidative degradation, thermal degradation, ozone-induced degradation, mechanochemical degradation, catalytic degradation and biodegradation along with relevant mechanisms.

Zhao et al [114] studied solid-phase photocatalytic degradation of polyethylene plastic under UV and solar light radiation by measuring the weight loss. The weight loss rate was much higher for PE-TiO_2 samples than for pure PE. The study concluded that CO_2 and water are the main products of photocatalytic degradation of PE plastic.

Studies on the solid-phase photocatalytic degradation of polystyrene (PS) plastic with TiO_2 as photocatalyst in the ambient air under ultraviolet light irradiation showed that the weight loss rate was much higher for the PS-TiO_2 (TiO_2 incorporated in PS) than for pure PS sample [115]. The solid-phase photocatalytic oxidation of PS was initiated by reactive oxygen species generated on irradiation on TiO_2 surface.

Asghar et al [116] studied comparative photocatalytic degradation of polythene films with undoped and metal (Fe, Ag, and Fe/Ag mix) doped TiO_2 nanoparticles under different environments such as UV radiation, artificial light, and darkness. About 14% of weight loss is reported under UV irradiation with Fe/Ag mix doped TiO_2 nanoparticles. Similar results were observed under artificial light [household energy saver bulb of TORNADO 24 watt] with Ag doped TiO_2 nanoparticles in 300 hrs. Weight reduction was not observed under darkness. Results showed that polythene-TiO_2 compositing with metal doping is capable of enhancing the degradion of polythene plastic under light irradiation.

Photocatalytic degradation of TiO_2 incorporated polyethylene film exposed to visible white light and ultraviolet light has been investigated by Nair et al [117]. They observed that photodegradation of PE depended on the size of TiO_2 particles. PE film containing TiO_2 nanoparticles had more weight loss than that containing industrial TiO_2 in UV light while reverse is the case under sunlight. This is attributed to the composition of TiO_2; ie industrial TiO_2 was mostly anatase while nano TiO_2 was a mixture of anatase and rutile.

Ohtani et al [118] also conducted similar studies. They observed that, during photodegradation the transparent film of 'TiO_2 incorporated' PE turned white together with decrease in weight. The tensile strength also was reduced after irradiation. The study shows that the effect of photoirradiation is more in the amorphous region of the film which resulted in photooxidation to produce small voids. These voids result in decrease of light transmission in the visible region.

Solid phase photocatalytic degradation of polyethylene plastic with copper phthalocyanine (CuPc) modified TiO_2 photocatalyst was investigated by Zhao et al [119]. The study shows that the weight loss in the case of PE-(TiO_2/CuPc) samples is much higher than PE-TiO_2 samples. This is because in the case of PE-TiO_2, the photo degradation of PE mainly happens on the surface whereas in the case of embedded TiO_2/ CuPc enough $^{\cdot}OH$ is generated in the interior also to photo degrade more of the PE.

Solid phase photocatalytic degradation of PS plastic over copper phthalocyanine (CuPc) sensitized TiO_2 was investigated under fluorescent light radiation in the air by Shang et al [120] . The system has shown better photocatalytic degradation than PS over TiO_2. Higher charge separation efficiency of TiO_2/CuPc catalyst results in the generation of more ROS and that in turn leads to better degradation of PS.

Solid-phase photocatalytic degradation of polyethylene–goethite composite film under Ultra Violet (UV)-light irradiation was investigated by Liu [8]. The polyethylene–goethite (PE–goethite) composite film was prepared by embedding the goethite into commercial polyethylene. The photodegradation of the modified PE plastic was determined by monitoring its weight loss, Scanning Electron Microscopic (SEM) analysis and FT-IR spectroscopy. The weight of PE–goethite sample steadily decreased and led to a total 16% reduction in 300hrs under UV-light intensity of $1mW/cm^2$.

Solid phase photocatalytic degradation of polyethylene (PE) plastic with goethite modified by boron(B) under UV-Vis light irradiation was investigated by Liu et al [121]. Under UV light the PE-B-Goethite combination gave better degradation than in visible light.

Solid-Phase photocatalytic degradation of a Poly(vinyl chloride)-TiO_2 nano composite Film with Bismuth Oxyiodide (BiOI) as catalyst was investigated in ambient air at room temperature under UV light irradiation by Yang et al [122] .The degradation was monitored by weight loss, SEM and FT-IR spectroscopy. The PVC-BiOI/TiO_2 nanocomposite film exhibited higher photocatalytic degradation activity compared to the PVC-TiO_2 nanocomposite film, the PVC-BiOI nano- composite film or the pure PVC film. Due to the interaction between *p*-type BiOI and *n*-type TiO_2 in the BiOI/TiO_2 composite, the PVC-BiOI/TiO_2 nanocomposite film has shown higher photocatalytic degradation activity.

Another novel idea is the preparation of photocatalytically degradable nanohybrid hyperbranched poly(3-caprolactone)-TiO_2 (HPCL–TiO_2) by integrating the polymer with TiO_2 nanoparticles [123]. The composite is found to degrade faster under irradiation by UV light.

The solid-phase photocatalytic degradation of polyvinyl chloride (PVC) films by tungstophosphoric acid (HPW) was investigated by Zhang et al [124] based on the unique redox property of the heteropolyacid. PVC films doped with HPW (1.5, 2.0 wt.%) were prepared and their photocatalytic degradation was carried out under irradiation with UV light of wavelength 254nm and visible light above 300nm. The photocatalytic activity was determined by weight loss monitoring and SEM analysis. HPW-doped PVC showed highly enhanced photodegradation. Comparison of the photodegradation of PVC by boric acid and such acid catalysts implied that the high photocatalytic activity of HPW-doped PVC film was due to the unique redox property of HPW, rather than its acidity.

Li et al [125] carried out the photocatalytic degradation of polyethylene (PE) plastic directly under sunlight irradiation with polypyrrole (PPy), TiO_2 and (PPy/TiO_2) nanocomposite as photocatalysts, prepared by sol-gel and emulsion polymerization methods. The degradation efficiency was determined by weight loss monitoring, Gel Permeation Chromatography (GPC), Atomic Force Microscopy (AFM) and FT-IR analysis. It was reported that PPy/TiO_2 exhibited much higher reactivity than TiO_2 or PPy, ie, 35.4% weight loss for PPy/TiO_2 versus 11.7% for PPy and 3.2% for TiO_2 in 240 hr.

Degradation of PVC by Fenton reaction followed by biological decomposition was investigated by Mackulak et al [126]. Low molecular weight fragments like trans-1,2-dichloroethene, cis-1,2-dichloroethene, trichlororoethene, tetrachloroethene etc are formed by the Fenton pretreatment. Digestion of these fragments by anaerobic microorganisms, resulted in slow mineralisation.

Photo assisted Fenton degradation was found to efficiently mineralize polystyrene and sulfonated polystyrene materials [127]. Sulfonate groups were capable of rapidly binding the cationic Fe(III) catalyst.

Some of the most important studies reported in literature on the application of photocatalysis for the degradation of plastic wastes are summarised above. Most of the studies are on developing biodegradable plastic for the future by incorporating special materials in the plastic matrix. However, the equally important issue of safe disposal of plastic waste getting accumulated today is not seriously addressed. The present study is an attempt to explore the potential of heterogeneous semiconductor oxide mediated photocatalysis for the degradation of plastic waste littered around us. The possibility of using the relatively simple technique of Fenton reaction and its combination with light for the degradation of different types of plastics is also examined. The quantity of waste plastics generated in a typical lower middle class village community in central Kerala is also verified by physical survey as an eye opener to the gravity of the plastic menace.

* * *

Chapter 2

OBJECTIVES OF THE STUDY, MATERIALS USED AND PLAN OF THE THESIS

Contents

As mentioned in Chapter 1, Advanced Oxidation Processes (AOPs) are promising techniques for the degradation/mineralisation of a variety of pollutant molecules in water. AOPs are based on the generation of highly reactive $^{\bullet}OH$ radicals which attack the target molecules, degrade them and eventually mineralise them into harmless CO_2, water and salts. Eventhough a good number of studies have been reported on the application of photocatalysis for the removal of chemical and bacterial pollutants from water, studies on the application of AOPs for the degradation and removal of plastic pollutants are comparatively less. The current study is a modest attempt to fill this gap using polyethylene (PE) and polyvinylchloride (PVC) based plastics as test materials.

2.1 Objectives

The main objective of the current study is to examine the suitability of AOPs based on Fenton chemistry, photolysis and photocatalysis for the removal of plastic wastes including plastic bags, pipes and other similar products of daily use from the environment. Two widely used plastic types, ie low density polyethylene (LDPE) and polyvinyl chloride (PVC) are used as the test materials in the study.

Specific aims under this objective and the appropriate activities undertaken to achieve them are as follows:

1) Comparative assessment of two of the widely investigated semiconductor oxides, ie, ZnO and TiO_2 as photocatalysts for the degradation of plastic pollutants under UV light and sunlight.
2) Optimizing the relevant reaction parameters such as pH, catalyst dosage, concentration of oxidants, presence of natural salts, recycling of catalyst etc, under photocatalysis and photolysis as applicable for the degradation of the selected plastic pollutants.
3) Evaluating the effect of oxidants such as peroxydisulphate, peroxide and Fenton reagent on the efficiency of AOPs for the mineralization of the plastic pollutants.
4) Evaluating the physicochemical changes in the plastic pollutants when subjected to AOP treatment.
5) Identification of changes if any to the catalysts after their use in AOPs.
6) Evaluating the effect of water from different sources as the plastic suspension matrix on the degradation of respective plastics.
7) Elucidation of an appropriate mechanism for the photolytic and photocatalytic degradation of plastic pollutants.

2.2 Materials used

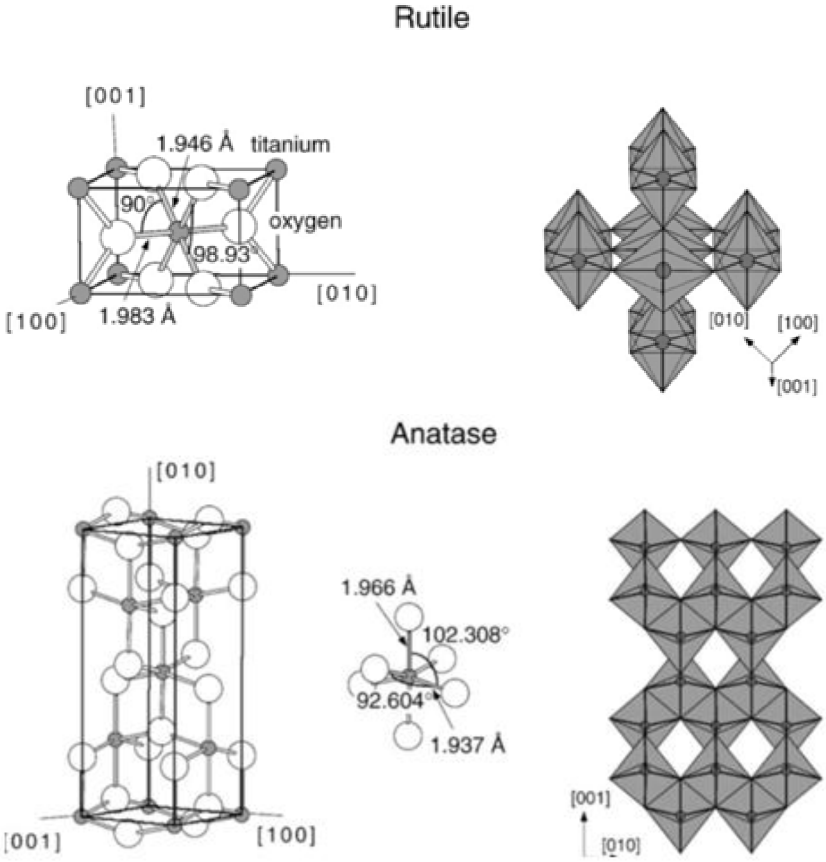
The catalysts used for the study are TiO_2 and ZnO. Of these, TiO_2 is selected as the catalyst for detailed study on the degradation of the plastic pollutants. The pollutants chosen are polyethylene plastic (PEP) and polyvinyl chloride (PVC) based materials (bags, pipes etc). The major oxidants used are potassium peroxydisulphate (PDS), H_2O_2 and Fenton reagent. The salts/anions/cations used are NO_3^-, SO_4^{2-}, $C_2O_4^{2-}$, CH_3COO^-, PO_4^{3-}, CO_3^{2-}, HCO_3^-, N_3^-, HPO_4^{2-}, S^{2-}, IO_3^-, SO_3^{2-}, F^-, Cl^-, Br^- and I^- (anions) and Na^+, K^+, Ba^{2+}, Ca^{2+} and Al^{3+} (cations). All the materials used are of AnalaR grade or equivalent unless indicated otherwise. Details of other miscellaneous chemicals/materials used are provided in the respective chapters.

2.2.1 Titanium dioxide (TiO_2)

TiO_2 is the most widely used and the best understood photocatalyst for the removal of organic pollutants from water because of its abundance, non toxicity, stability, high refractive index and relatively lower cost. It is white in colour, inexpensive, chemically stable, harmless and has no absorption in the visible region. In photocatalysis, the activity of TiO_2 in suspension depends on its physical properties such as crystal structure, surface area, surface hydroxyls, particle size etc and operating conditions such as light intensity, presence of oxygen, initial concentration of the target chemical, amount of $TiO_{2,}$ pH value etc.

Titanium dioxide crystallizes in three forms: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). Thermodynamically, the most stable structure is rutile. Anatase and brookite forms are metastable and transform to rutile on heating. The brookite form occurs rarely compared to the anatase form and exhibits no significant photocatalytic activity under daylight irradiation. Rutile, with a band gap of 3.0 eV (corresponding to a cut-off wavelength 413 nm) and anatase, with a band gap of 3.2 eV (cut-off wavelength 388 nm) have more industrial applications. Both band gaps are close to the limiting wavelength between UV-A light (320–400 nm) and visible light (400–700 nm). Anatase and rutile forms find application in most cases.

The structures of rutile and anatase TiO_2 are shown in figure 2.1.



Rutile

Anatase

Figure 2.1: **S**tructures of Rutile and Anatase TiO_2 [128]

The structures of rutile and anatase can be described in terms of chain of TiO_6 octahedra. The crystal structures of the two differ by the distortion of each octahedron and by the assembly pattern of the octahedral chain. Each Ti^{4+} ion is surrounded by an octahedron of six O^{2-} ions. The octahedron in rutile is not regular, showing a slight orthorhombic distortion. The octahedron in anatase is significantly distorted so that its symmetry is lower than orthorhombic. In rutile structure each octahedron is in contact with 10 neighbouring octahedra (two sharing edge oxygen pairs and eight sharing corner oxygen atoms) while in the anatase structure, each octahedron is in contact with eight neighbours (four sharing an edge and four sharing a corner). Of the two crystalline phases, anatase is believed to possess better photocatalytic and photoelectrochemical conversion performance probably because of its open structure compared to rutile [128-130].

Major properties of TiO_2 are summarized in table 2.1.

Table 2.1: Properties of TiO_2

Chemical Formula	**TiO_2**
Molecular mass	79.865 g/mol
Crystal structure	Rutile, anatase and brookite
Density	3.7 to 4.2g/cm³
Melting point	1,843 °C (3,349 °F; 2,116 K)
Boiling point	2,972 °C (5,382 °F; 3,245 K)
Solubility in water	Less than 1 g/L at 68° F
Magnetic susceptibility	$+5.9 \cdot 10^{-6}$ cm^3/mol
Energy gap	Rutile: 3.0 eV Anatase: 3.2 eV
Static dielectric constant	10-85
Refractive index	2.488 (anatase) 2.583 (brookite) 2.609 (rutile)

Titanium dioxide is used in photocatalysis due to its oxidative and hydrolysis properties.

TiO_2 is mainly used as a white powder pigment because of its brightness and very high refractive index. One of the major advantages for titanium dioxide is its resistance to discolouration under ultraviolet (UV) light in exposed applications. It is used in products such as paints and coatings, including glazes and enamels, plastics, paper, inks, fibres, foods, pharmaceuticals and cosmetics. Applications also include light-emitting diodes, liquid crystal displays (LCDs) and electrodes for plasma displays. Under exposure to UV light, it becomes increasingly hydrophilic and can be used for anti-fogging coatings and self-cleaning windows. The disinfecting properties of TiO_2 make it suitable for applications such as medical devices, food preparation surfaces, air conditioning filters and sanitary ware surfaces.

2.2.2 Zinc oxide (ZnO)

Zinc oxide is an inorganic compound with the formula ZnO. It usually appears as a white powder, nearly insoluble in water. It crystallizes in three forms: hexagonal wurtzite, cubic zinc blende and the rarely observed cubic rock salt. The wurtzite structure is the most stable at ambient pressure and temperature and thus the most common. Zinc blende form can be stabilized by growing ZnO on substances with cubic lattice structure. In both cases, the zinc and oxide centers are tetrahedral; each Zn ion is surrounded by a tetrahedron of O ions and vice-versa. This tetrahedral coordination gives rise to polar symmetry along the hexagonal axis. This polarity is responsible for a number of properties of ZnO. The wurtzite structure is shown in figure 2.2. The black spheres represent Zn atoms and grey spheres represent O atoms.

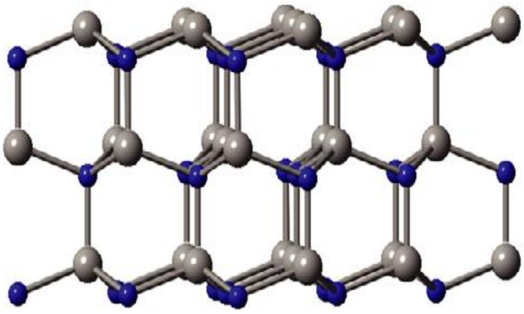


Figure 2.2: Structure of ZnO wurtzite [4]

ZnO is an inexpensive, moisture stable, reusable and commercially available catalyst [131-135]. The powder is widely used as an additive for numerous materials and products including plastics, ceramics, glass, cement, rubber (e.g. car tyres), lubricants, paints, ointments, adhesives, sealants, pigments, foods (sources of Zn nutrient), batteries, ferrites, fire retardants, first-aid tapes etc. ZnO is present in the earth crust as zincates. However, commercial ZnO is produced synthetically.

ZnO is often called II-VI semiconductor because zinc and oxygen belong to the 2nd and 6th groups of the periodic table, respectively. It has several favourable properties like good transparency, high electron mobility, wide band gap, strong room-temperature luminescence, etc., which are important in photocatalysis. The biggest advantage of ZnO is that it can absorb a relatively larger fraction of solar spectrum compared to TiO_2. Other favorable factors include; stability, non-toxicity, high catalytic efficiency, low cost and abundance in nature [136-141].

ZnO has a band gap of E_g= 3.4 eV at low temperature and 3.37 eV at room temperature and a large free-exciton binding energy (60 mV at room temperature). Hence, excitonic emission processes can persist at or even above room temperature. Advantages associated with large band gap include higher breakdown voltages, ability to sustain large electric fields, lower electronic noise, high-temperature and high-power operations. The band gap of ZnO can further be tuned from ~3–4 eV by its alloying with magnesium oxide or cadmium oxide. Mostly ZnO has n-type character, even in the absence of intentional doping. Controllable n-type doping is easily achieved by substituting Zn with group-III elements such as Al, Ga, In or by substituting oxygen with group-VII elements like chlorine or iodine. These facts make ZnO a promising alternative to TiO_2 in photocatalysis. In many cases photodegradation mechanism is also similar in the case of ZnO and TiO_2, though, at acidic pH range ZnO is considered to be less efficient due to its corrosion. The photocatalytic activity also depends upon the crystallinity, surface area and particle morphology, which in turn depend on the method of preparation. Some of the physical, chemical and electronic properties of ZnO are listed in table 2.2.

Table 2.2: Properties of Zinc oxide

Crystal structure	**Quartzite**
Lattice parameters at 300K a_0 c_0	 0.32495 nm 0.52069 nm
Density	5.606 g/cm^3
Melting point	1975^{0}C
Boiling point	2360^{0}C
Refractive index	2.0041
Energy gap	3.4 eV
Photoluminescence	375 nm
High electron mobility	>100cm^2/Vs
Exciton binding energy	60meV
Electron effective mass	0.24
Solubility in water	0.16 mg/100mL (20^{0}C)
Hole effective mass	0.59

Crystalline zinc oxide is thermochromic, changing from white to yellow when heated and reverting to white on cooling in air. This color change is caused by a very small loss of oxygen at high temperatures to form the non-stoichiometric, $Zn_{1+x}O$, where, x= 0.00007 at 800°C. Zinc oxide is an amphoteric oxide. It is nearly insoluble in water and alcohol, but is soluble in most acids, such as hydrochloric acid:

$ZnO + 2\ HCl \rightarrow ZnCl_2 + H_2O$ ....(18)

Bases also degrade ZnO to give soluble zincates:

$ZnO + 2\ NaOH + H_2O \rightarrow Na_2\,(Zn\,(OH)_4)$ ....(19)

It reacts with hydrogen sulphide to give the zinc sulphide.

$ZnO + H_2S \rightarrow ZnS + H_2O$ ....(20)

This reaction is used commercially for removing H_2S using ZnO powder as a deodorant.

2.2.3 Potassium peroxydisulphate

Potassium peroxydisulfate (PDS) or Potassium persulfate is an inorganic compound with the formula $K_2S_2O_8$. It is a white solid and is highly soluble in water. PDS is a powerful oxidant, and is commonly used to initiate polymerizations. Major properties of $K_2S_2O_8$ are summarized in table 2.3.

Table 2.3: Properties of $K_2S_2O_8$

Chemical Formula	**$K_2S_2O_8$**
Molecular mass	270.322 g/mol
Crystal structure	Triclinic
Density	2.477 g/cm^3
Melting point	< 100 °C (212 °F; 373 K) (decomposes)
Solubility in water	1.75 g/100 mL (0 °C) 4.49 g/100 ml (20 °C)
Refractive index (n_D)	1.467

Chemical structure of $K_2S_2O_8$ is shown in figure 2.3.

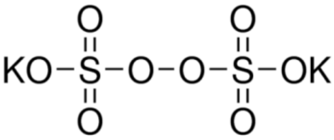


Figure 2.3: Structure of $K_2S_2O_8$

2.2.4 Hydrogen peroxide (H_2O_2)

H_2O_2 is a colourless liquid with viscosity slightly greater than that of water. It is a powerful oxidant and also acts as a bleaching agent and a disinfectant. Structure of H_2O_2 is shown in figure 2.4.

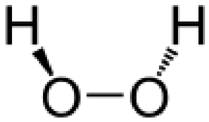


Figure 2.4: Structure of H_2O_2

Aqueous solution of H_2O_2 differs in its properties from pure H_2O_2 due to the presence of hydrogen bonding. It is thermodynamically unstable and decompose into water and oxygen which makes it environment-friendly.

$H_2O_2 \longrightarrow H_2O + 1/2\ O_2$ ....(21)

Major properties of H_2O_2 are summarized in table 2.4.

Table 2.4: Properties of H_2O_2

Molecular formula	**H_2O_2**
Molecular mass	34.0147 g/mol
Density	1.1 g/cm^3
Melting point	-0.43^{0}C
Boiling point	150.2^{0}C
Solubility in water	Miscible
Acidity (pKa)	11.75

2.2.5 Fenton reagent

Fenton reagent (FR) is a solution of hydrogen peroxide with ferrous iron as the catalyst and is used as a good oxidising agent. Iron(II) is oxidized by hydrogen peroxide to iron(III), forming a hydroxyl radical and a hydroxide ion in the process. Iron(III) is then reduced back to iron(II) by another molecule of hydrogen peroxide, forming a hydroperoxyl radical ($HO_2^{\cdot}$) and a proton. The net effect is a disproportionation of hydrogen peroxide to create two different oxygen-radical species, with water ($H^+ + OH^-$) as a by-product.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH \quad \text{...}(22)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO^{\cdot} + H^+ \quad \text{..}(23)$$

The free radicals generated by this process participate in secondary reactions subsequently. Oxidation of an organic compound by Fenton's reagent is rapid and exothermic and results in the oxidation of contaminants to primarily carbon dioxide and water.

2.2.6 Polyethylene (PE) plastic

Polyethylene is a thermoplastic polymer composed of the single monomer ethylene ($CH_2{=}CH_2$). Polyethylene is commonly categorized into several major compounds of which the most common include LDPE, LLDPE, HDPE and UHMWPE as follows.

- **Low Density Polyethylene (LDPE)** is a very flexible material with very unique flow properties that makes it particularly suitable for plastic film applications like shopping bags. LDPE has high ductility but low tensile strength which is evident in the real world by its propensity to stretch when strained.

- **Linear Low Density Polyethylene (LLDPE)** is very similar to LDPE with the added advantage that the properties (of LLDPE) can be altered by adjusting the formulation constituents and that the overall production process is typically less energy intensive (than LDPE).
- **High Density Polyethylene (HDPE)** is a strong, high density, moderately stiff plastic with a highly crystalline structure. It is frequently used as plastic for milk cartons, laundry detergent containers, garbage bins and cutting boards.
- **Ultra High Molecular Weight Polyethylene (UHMWPE)** is an extremely dense version of polyethylene with molecular weights typically an order of magnitude greater than HDPE. It can be spun into threads with tensile strengths many times greater than steel and is frequently incorporated into high performance equipment like bulletproof vests.

2.2.7 Polyvinyl chloride (PVC)

PVC is a homopolymer formed by the linking together of the monomer vinyl chloride molecules. PVC is a chemically stable, neutral and non-toxic substance containing chlorine (around 57 per cent by weight) as well as carbon and hydrogen. The presence of chlorine in the molecule makes PVC particularly versatile and flame retardant. PVC formulations can be shaped by a variety of techniques and made into the final product using very little energy. PVC formulations have a wide range of applications including the most sensitive, such as medical equipment, rigid piping, automotive, electrical cabling etc. Structure of PVC is shown in figure 2.5.

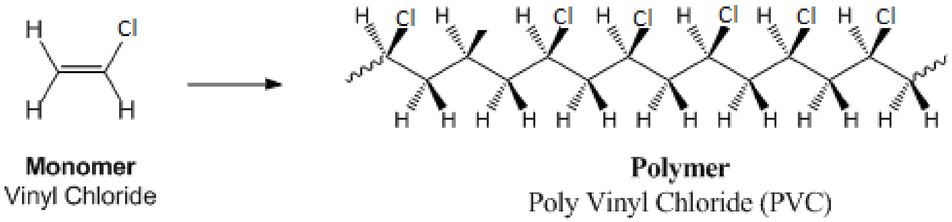


Figure 2.5: Structure of PVC

2.3 Miscellaneous materials

Details of various other materials used in the study and their characteristics are provided in the respective chapters.

2.4 Experimental set up and Analytical procedures

The experimental set up and the procedures used in the study including analyses are described in the respective chapters.

2.5 Plan of the thesis

The current thesis is divided into seven chapters. Specific objectives, experimental procedures, results, discussion, conclusions etc are provided in respective chapters.

Chapter 1 entitled “**Introduction: Background literature**” gives an overview of the recent relevant literature and discussion on various types of AOPs with special focus on the hazards of plastic pollution and the application of photocatalysis in pollution control and water treatment.

Chapter 2 entitled, "**Objectives of the study, materials used and plan of the thesis**", describes the main objective of the study, specific activities undertaken to accomplish the objective and plan of the thesis. Characteristics of the major materials used in the study; ZnO, TiO_2, $K_2S_2O_8$, H_2O_2, Fenton reagent, Polyethylene, PVC etc are also briefly discussed.

Chapter 3 entitled, "**Pattern of the use and disposal of plastic products in a typical village community in Kerala State, India: A case study**", presents the findings from a survey of the quantity and types of plastic wastes generated in different households in a typical rural/semiurban community in central Kerala. The pattern of use is correlated with the income, age distribution and size of the households.

Chapter 4 entitled, "**Semiconductor oxide mediated photocatalytic degradation of Low Density Polyethylene plastic wastes**", deals with the findings from the studies on the photocatalytic degradation of LDPE plastic in presence of TiO_2 catalyst under different conditions. Detailed experimental procedures followed, reaction details, analytical procedures etc. are also provided. This chapter describes the effect of pH, oxidants, Fenton reagent, anions, cations, oxygen, recycling of catalyst etc on the photocatalytic degradation of LDPE plastic and proposes a mechanism for the degradation.

Chapter 5 entitled, "**Photolytic/Photocatalytic degradation of Polyvinylchloride plastic wastes from the environment**", deals with the studies on the degradation of PVC plastic using AOPs under different conditions. Detailed experimental procedures followed, reaction details, analytical procedures etc. are also provided. The effect of various reaction parameters such as pH, oxidants, Fenton reagent, anions, cations etc on the photocatalytic degradation of PVC plastic also is experimentally verified. The results are discussed in detail.

Chapter 6 entitled, "**Solar photolysis and other Advanced Oxidation Processes for the degradation of Polyethylene and Polyvinyl chloride plastics**", describes the investigations on the degradation of both PE and PVC plastics using sunlight as the energy source and TiO_2 as the catalyst. The effect of relevant parameters such as catalyst dosage, presence of oxidisers, light intensity, temperature, time of irradiation, thickness of plastic sheet, colour of the plastic, presence of anions and cations etc is also investigated and discussed in detail.

Chapters 7 entitled, "**Summary and Conclusions**", summarizes the findings of the study and highlights the conclusions drawn.

Annexure I lists the abbreviations used in the thesis. (Expansions of respective abbreviations are also provided in the first place where they appear in the thesis.)

Annexure II	gives the questionnaire used for the survey described in Chapter 3.
Annexure III	gives the list of research papers published/presented in conferences, based on the results of the work.
Annexure IV	provides reprints of the research papers based on the investigations, published in various peer-reviewed journals.
Annexure V	lists Awards/Recognitions conferred based on the current study

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Chapter 3

PATTERN OF THE USE AND DISPOSAL OF PLASTIC PRODUCTS IN A TYPICAL VILLAGE COMMUNITY IN KERALA STATE, INDIA: A CASE STUDY

Contents

3.1 Introduction

Plastic and plastic materials, as mentioned in Chapter 1, are advantageous and beneficial to mankind in a variety of ways. Plastic combines the advantages of lightness, strength, toughness, resistance to corrosion, durability, excellent thermal and electrical insulation properties etc. Plastic products are also convenient, water proof, less expensive, odorless and can be made in different exquisite shapes and colors. The versatility of plastic has made it an integral part of many kinds of industries which include packaging, construction, electronics, aeronautics etc [2,113]. It won’t be an exaggeration to say the life of modern man would be almost unimaginable without the use of plastic in one form or the other. However, the downside of the extensive use of plastic in day to day life is the accumulation of plastic waste in the environment, partially due to the absence of any economic, environment-friendly technology and partially due to laxity in the implementation of the available technology.

Plastic waste is a severe health hazard as it can contaminate the earth in different ways. Unscientific burying of plastic clogs up the land making it unfit for cultivation or for any other productive utility. They can collect water and become breeding grounds for mosquitoes and other harmful insects. Plastic carry bags that get into water can cause severe hazard to marine creatures and also the fish wealth of the area. Burning of plastic will liberate dioxins and other toxic chemicals which are very harmful to all living organisms. So it is very essential to dispose of plastic waste in a safe scientific manner to prevent contamination and resulting hazardous consequences. Plastic which may look innocent and utilitarian is actually very hazardous if not handled and disposed of properly. Prevention is always better than cure. Hence first and foremost priority must be to reduce the use of plastic products. Implementation of a reasonable levi will help to reduce the avoidable usage. The Irish government in 2002 has introduced a levy of € 0.15 per plastic bag which resulted in fall in usage by more than 90% [142]. Plastic wastes which are thrown out from households do not decompose biologically and ultimately result in accumulation in the environment. This has been a major waste management challenge in recent years.

Recycling and reuse of plastics is gaining importance as a sustainable method for plastic waste disposal. The advantages include reduction in the use of virgin materials, savings in related energy consumption and thus reduction of carbon dioxide emissions.

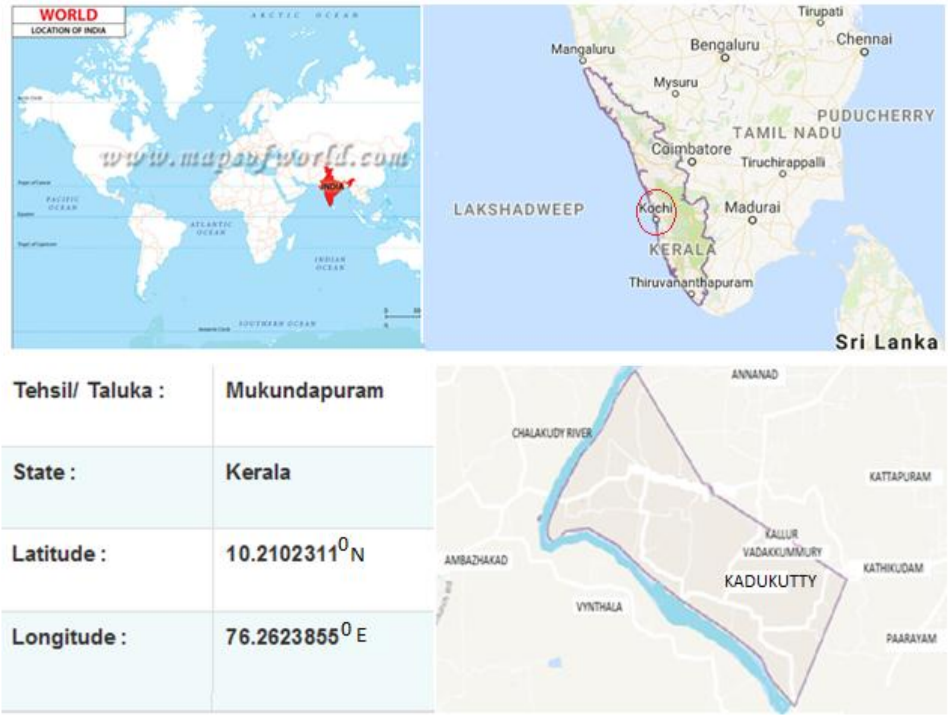
At the same time, safe economic disposal of the plastic accumulated and scattered around also is equally important. It is in this respect that AOPs are being examined as viable technologies for the irreversible destruction of plastics. The present research work is an attempt in this direction to test the application of the most widely investigated AOP, i.e. photocatalysis for plastic waste disposal. As a precursor to these investigations, a survey has been conducted on the quantity and pattern of plastic use in a typical residential village (semiurban region) in the southern state of Kerala, India. The results indicate unambiguously that the quantity of plastic waste generated from even an ordinary low income household is much more than what was generally believed and if corrective measures are not taken expeditiously, the consequences will be disastrous.

The sample size is kept small for precise collection and data management within the time frame available. The data and its analysis are expected to be useful in identifying appropriate disposal methods for domestic plastic wastes in regions with comparable households across the region.

3.2 Methodology

Any scientific method designed and developed for the safe disposal of plastic should be based on a clear understanding of the quality and type of plastic waste generated in the target location. It is often suggested that decentralized disposal facilities will be more suitable for plastic waste so that the transportation and collection cost can be minimized and any untoward transportation hazard can be controlled. It is with this possibility in mind that the location is identified, data on the actual quantity of plastic waste generated there is collected and identified.

The survey and data collection were conducted for a continuous period of four months from 1 October 2014 to 31 January 2015. All sample households were located in and around Kadukutty, Kallur Vadakkummuri village (population 25,259 as per census India, 2011) in Mukundapuram Taluk of Thrissur district, Kerala state. The precise location is shown in the map (figure 3.1).



Tehsil/ Taluka :	**Mukundapuram**
State :	**Kerala**
Latitude :	**10.2102311^{0}N**
Longitude :	**76.2623855^{0} E**

Figure 3.1: Geographical location of Kadukutty village

The sample households were so chosen as to bring diversity in terms of the number and age of family members, education level, economic affluence etc. Only exclusive residential homes were considered here. Commercial establishments, shops, offices, educational institutions etc. which also generate substantial quantity of plastic waste were excluded. However they have to be included in an expanded future study for more comprehensive analysis. The sample size was eleven (11) households.. The income and age distribution of family members are summarized in table 3.1.

Table 3.1: Income category and age of members of individual family who participated in the survey

Family No.	**Income Category**	**Members**							
		Age Group							**Total**
		0-5	**5-10**	**10-15**	**15-30**	**30-50**	**50-70**	**Above 70**	
1	>100,000	Nil	1	Nil	Nil	2	Nil	Nil	3
2	>100,000	1	Nil	Nil	2	Nil	2	1	6
3	70,000-100,000	Nil	Nil	1	Nil	1	1	Nil	3
4	70,000-100,000	Nil	Nil	2	Nil	2	1	Nil	5
5	70,000-100,000	Nil	Nil	1	2	2	Nil	Nil	5
6	50,000-70,000	1	1	Nil	Nil	2	1	1	6
7	50,000-70,000	Nil	1	Nil	2	2	Nil	1	6
8	20,000-50,000	Nil	Nil	Nil	3	2	Nil	Nil	5
9	20,000-50,000	Nil	Nil	1	2	2	Nil	Nil	5
10	< 20,000	1	Nil	Nil	Nil	2	Nil	2	5
11	< 20,000	Nil	Nil	Nil	Nil	Nil	2	Nil	2

The actual quantity of plastic waste generated in each of the households is computed individually by physical verification. The collection of plastics was personally monitored and the quantities were precisely calculated. Before the actual study began, the family members were made aware of the objectives and were encouraged to ask any questions/clarifications on it. They had the option to remain anonymous if they so desired and to opt out of the survey at any time. Before actually starting the collection of data, minimum of three visits were made to each household to build confidence and rapport among the members and reassure them. Every household was provided with large plastic containers with lids and large thick black plastic bags (figure-3.2 (A) and (B) respectively) for collection of the waste. The plastic bags are fully opened and conveniently inserted in the containers with lids. The households were asked to deposit each and every item of their plastic waste irrespective of the size, thickness, weight, shape or any other parameters in the bags. It was always a responsible female member of the family who was assigned the task. On the first day of every month, the accumulated plastic wastes from the previous month were picked up personally by this investigator for detailed characterization. Initially the total weight was noted. The contents of each container were then sorted into different categories as casual carry bags, grocery bags, milk covers, diaper shield, chocolate wrapper, hard plastic, bottles, pipe strips etc. The weight of each category was also noted separately.

(A) (B)

Figure 3.2: (A) ‘Plastic waste’ collection containers with lids given to the sample households (B) Plastics wrapped in thick plastic bags

3.3 Results and Discussion

3.3.1 Quantity of plastic wastes generated

The total quantity of plastic wastes generated from the eleven households together in four months during the study period (October 2014-January 2015) is given in figure 3.3.

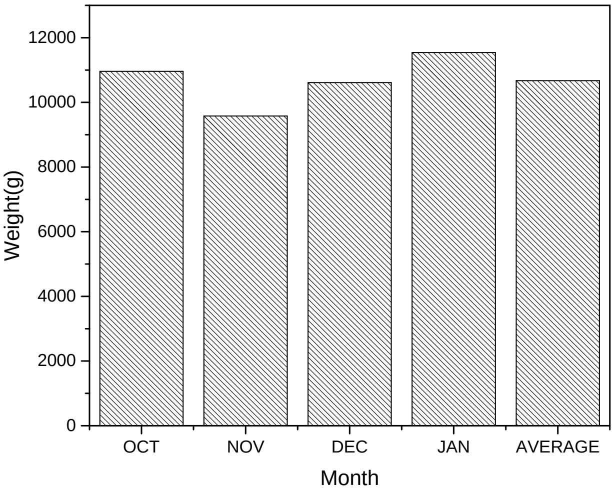


Figure 3.3: Total quantity of plastic waste generated from all sample households during the study period (2014-15)

As the figure shows, the total monthly generation of all types of plastic waste for the eleven households together is ~ 10kg. The average quantity is ~ 900-1000g/household/month. This implies that unless properly treated, an average of 11 kg/year of plastic waste will be dumped into the environment from every household. One can imagine the gravity of the problem in a densely populated state like Kerala (population ~37million). Even simple extrapolation of the data to the national level will give an indication of the potential for environmental disaster in a country with ~ 1.3 billion people.

3.3.2 Types of common plastic wastes

Among the various types of plastic wastes accumulated in households, maximum contribution comes from the 'carry-bags' used for carrying grocery, vegetables, stationery etc. purchased for daily consumption from different shops. Typical collection of such waste is shown in figure 3.4 A. The quantity of monthly accumulation of this type of plastic waste from the sample households combined is shown in figure 3.4 B.

Figure 3.4 A: Typical assorted 'carry bags' in the plastic waste

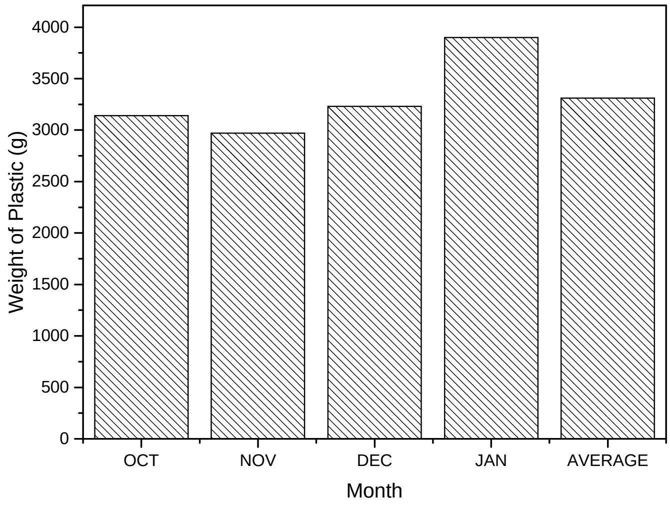


Figure 3.4 B: Combined monthly accumulation of 'carry bags' from all sample households

An average of 3.3kg/month of plastic 'carry-bag' waste is generated from the eleven households. Average individual household contribution is~ 300g/month. These bags are generally made from high density polyethylene (HDPE). The main advantages of these bags are: cost effectiveness, light-weight and convenience. Even though this plastic variety is recyclable/reusable, no serious or concerted effort is taking place in that direction. Careless and casual littering of used carry-bags leads to major environmental pollution. The new 'imported' supermarket culture in the country has made a major contribution to this menace. Of late, there has been a slight decline in the number of 'carry-bags' accumulated in households in Kerala as a result of campaigns and education on the plastic-related hazards. A small percentage of consumers are reusing old plastic bags. Charging a moderate price by shops for this kind of carry-bags is also making a positive impact on the reduction of this type of wastes. It is worth undertaking a detailed study on the impact of charging a price for plastic bags in reducing the accumulation of this waste. This will also help in arriving at an optimum price that will not be an undue burden to the customer and at the same time will be beneficial to the environment. During the survey many respondents informally suggested that the maximum reasonable price may be ₹ 1/bag

Another type of plastic bags, which has become a major menace of disastrous consequences to the environment, is light weight thinner plastic bags and wraps used for packing and selling light weight products. The monthly accumulation of this type of plastic waste in the combined households is shown in figure 3.5 A. As seen from the data, in this case the average rate of accumulation is ~1.4kg/month from all the sample households, i.e.~130g/month/household. They constitute~15 % of the domestic plastic waste by weight. However in terms of volume the quantity is much more due to the physical light-weight nature of the material. Low density polyethylene (LDPE) is used for making this type of bags and wraps. Most of these are carelessly thrown around and eventually end up in landfills, dumpsites and water bodies. The problem is further aggravated because these materials can fly around, reach and contaminate anywhere and everywhere. Some such typical lightweight plastic waste accumulated in an average household is shown in figure 3.5 B.

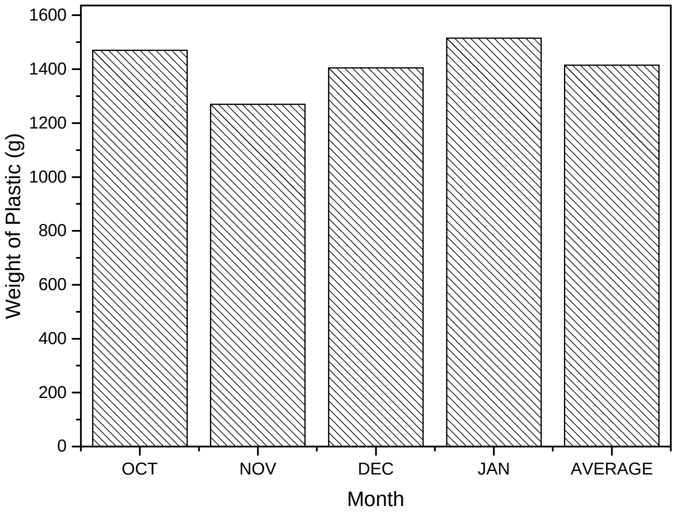


Figure 3.5 A: Month-wise accumulation of used lighter, thinner plastic bags/paper

Figure 3.5 B: Typical light weight waste plastic carry bags from an average household

Another major contribution to plastic waste comes from modern packed ‘ready to eat’ food sectors such as bakeries and ‘take away’ kiosks. The total quantity of plastic waste generation associated with such products in the households combined is shown in figure 3.6 A. The average quantity of bakery/food related plastic accumulated in the sample households combined is ~1.5kg/month. The average contribution is ~140g/month/household. Some of the typical plastic wastes of this type from an average household is shown in figure 3.6 B. The ever-increasing accumulation of this type of waste, even from low-income households is a reflection of the consequence of globalization and ‘closing the kitchen’ culture imported from the western world.

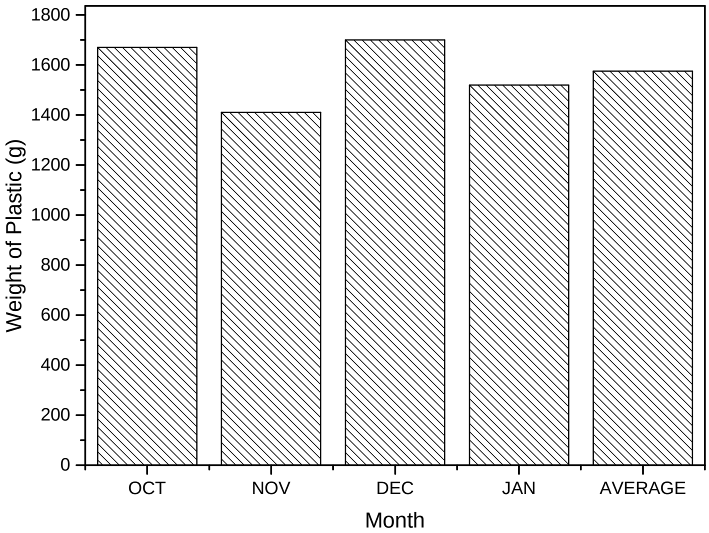


Figure 3.6 A: Month-wise accumulation of ‘ready to eat’ food- related plastic waste from all the sample households combined

Figure 3.6 B: Typical bakery/food related plastic waste

Yet another kind of plastic waste , though small in terms of number or volume, but significant in terms of weight is hard plastics such as containers for mineral water, soft drinks, 'ready to eat' food, cosmetics (shampoo, talcum powder, body creams etc.), disposable cups & plates, baby milk bottles, toys etc. These are made of different types of heavy and stronger plastics like polyethyleneterephthalate (PET), high density polyethylene (HDPE), polyvinylchloride (PVC), polypropylene (PP), polystyrene (PS) etc. They are not uniformly distributed month-wise or household-wise. Figure 3.7A shows the month-wise cumulative contribution of such hard items to the total plastic waste from the households during the study period. The average accumulation of this type of plastic wastes for all sample households together is 1.8kg/month, i.e. average contribution of 170g/month/household. Some of the typical hard plastics that accumulate in an average household are shown in figure 3.7 B.

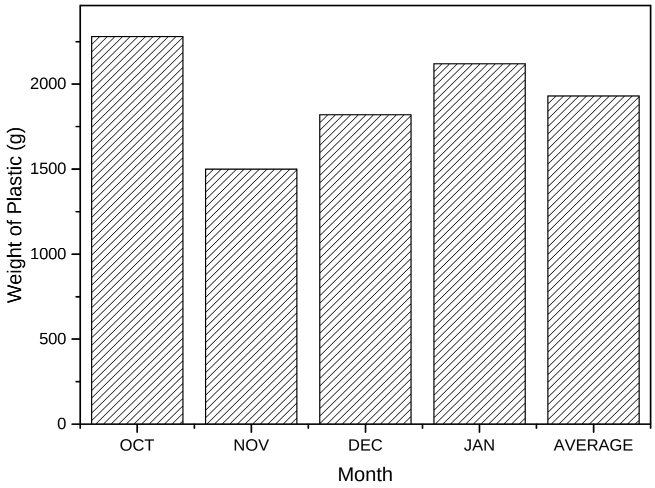


Figure 3.7 A: Monthly accumulation of hard plastics in all sample households combined

Figure 3.7 B: Typical hard plastic wastes from sample households

Another important observation is the presence of significant quantity of diaper shields in the plastic wastes from even middle class and lower middle class households with small babies and bed-ridden patients. Such diapers are replacing the traditional reusable clothes used earlier. This is not a common day-to-day plastic waste from all households. In the present context, of the eleven households subjected to the study, four have members of either below 3 years of age or bed-ridden patients (due to age-related illness) requiring bed pads/diapers. This was the cause for the unusually large proportion of this type of waste from those households.

3.3.3 Category-wise quantification of different types of waste

The quantity of different types of plastic waste from the sample households for the entire study period (4 months) is shown in figure 3.8. Various types of waste plastics in terms of weight is in the order; heavy carry-bags > diaper shields > hard plastic > fast food-related plastic > lighter carry-bags > milk cover > chocolate wrapper. Surprisingly even chocolate and candy wrappers constituted small but significant quantity. This clearly shows that change in lifestyle and economic affluence of the society contributes, among other things, to the plastic menace as well as deterioration of ecology and environment.

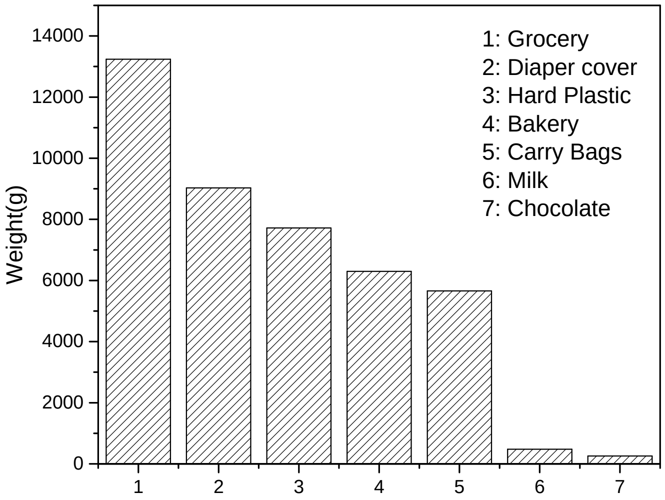


Figure 3.8: Cumulative category-wise distribution of different types of plastic wastes from all households during study period (4 months)

3.3.4 Quantity of plastic waste vs family size

Another finding of the study is that the quantity of plastic waste generated per household is more or less directly proportional to the number of family members among all income groups. With increase in the family income the quantity of waste generated per person also goes up. When the family income is > ₹ 100,000/pm, the average waste per person is ~ 400g/person/month. When the income is in the range of ₹ 50,000-100,000, the average waste generated is less by 40%, i.e. ~ 250g/person/month. The waste generation falls drastically when the income is in the range ₹ 20,000 – 50,000 and < 20,000 pm with the quantity being ~ 70g and ~ 60g/person/ month respectively. The findings are summarized in figure 3.9. [The income range as given by the households is taken as such with no verification of any kind]. The number of members in the families was different in different income segments and hence the average waste generated/person/month is chosen for comparison.

The study thus clearly indicates that affluence and life style of the family contributes significantly towards the generation of plastic waste. Almost anything and everything comes wrapped in plastic accompanied by high voltage advertisement in the name of hygiene and aesthetics. This is the root cause of plastic menace, especially the low quality thin plastics. It is frightening to note that even the traditional banana leaf which was believed to be essential for auspicious occasions in India is being replaced by plastics and related products.

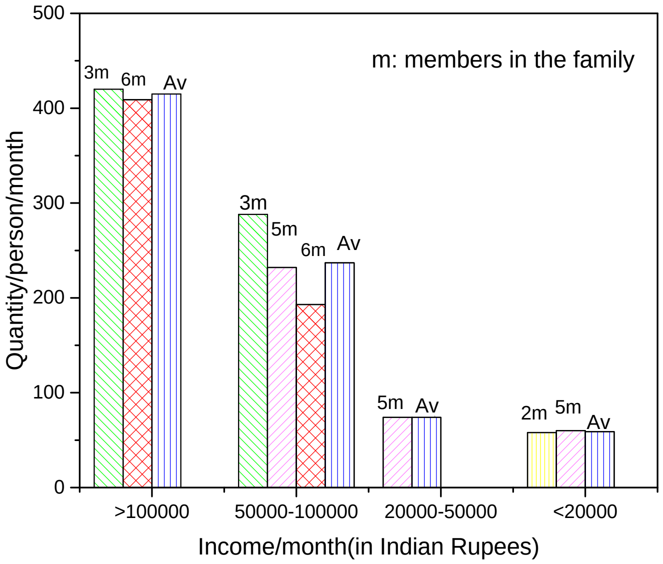


Figure 3.9: Family size vs income vs plastic waste generation
m: number of members in the family, Av: Average

3.4 Questionnaire survey of plastic pollution-related facts

As part of the study, an opinion survey on the use and disposal profile of plastic products in the community in a middle class village in central Kerala (including the households that participated in the study reported above) was conducted by direct interaction with respective families. A questionnaire for the purpose was designed in consultation with a cross-section of the society and social activists and was given to the participants. The questionnaire is given in Annexure -II. It was used to collect data from 75 randomly selected respondents. The objectives of the survey and the specific meaning of each question were explained to the participants and necessary clarifications were provided. Follow-up calls were made to see whether any assistance was needed with the questions or probable answers.

3.4.1 Findings from the questionnaire survey

The educational qualification of the respondents ranged from high school graduation to post graduation and professional degrees. The general awareness on various plastic-related matters is more or less the same, even though the in-depth knowledge on science and technology related aspects varied widely. All the respondents use plastic products extensively, in particular carry bags and bottles. More than 75% of the respondents were aware of different types of plastics, most common being polyvinylchloride (PVC) followed by polyethylene (PE). Almost all of them have heard about the ecological, environmental and health problems associated with plastics. Many are of them are of the view that plastics also cause cancer. The responses to some of the selected related questions are summarized in table 3.2.

Table 3.2: Selected questions in the questionnaire related to the general awareness of plastics and the answers provided by the respondents

No	Question	Response (Yes)	Response (No)	% Yes	% No
1	Are you aware of plastic/plastic products?	75	0	100	0
2	Do you use plastic products?	75	0	100	0
3	Have you heard of polyethylene plastic?	65	10	87	13
4	Have you heard of PVC plastic?	74	1	99	1
5	Are you aware of ecological problems associated with plastic/plastic products?	73	2	97	3
6	Do you think the use of plastic is more convenient for you?	54	21	72	28
7	Do you think that the use of plastic can affect your health?	73	2	97	3
8	Have you heard that plastic can cause deadly diseases like cancer?	66	9	88	12
9	Does plastic pollute the land?	73	2	97	3
10	Does plastic pollute the water?	72	3	96	4
11	Does plastic pollute the air?	72	3	96	4

In spite of the known adverse effects, they still find plastic products convenient and hence are not willing to abandon fully. Nearly 40% of the respondents burn the plastic periodically in their backyard or common open areas. More than 80% of the respondents experienced the foul odour and discomfort from burning plastic fumes. Nearly 50% believe that the fumes from open burning of plastic are toxic, generate suffocating odor and can cause dermatological problems and irritation to eyes. Many experienced cough, chest congestion and breathing difficulty from such fumes. The respondents (> 80%) are well aware that disposal of plastic waste by burying will be a threat to the environment and the people. Nearly ~30% hand over the plastic waste to 'waste collectors' from the local self-government. But this waste collection system is not functioning efficiently or regularly. The remaining respondents either accumulate waste plastics at home for possible future use or better sale price later. Only very few responded that they throw the waste plastic away and do not worry about them later. It is possible that there are more households that litter plastic and plastic products, but do not want to admit the same. Nearly 40% believe that there is nothing wrong or unsafe in open pit burning of plastics. Only a small % (~ 15%) of the respondents believe that burying is acceptable for the disposal of plastics.

More than half of the respondents reuse plastic containers, especially the thicker and stronger durable type. The responses to the questions related to the disposal of plastics are summarized in table 3.3.

Table 3.3: Responses to the questions related to the disposal of plastic waste

No	Question	Response (Yes)	Response (No)	% Yes	% No
1	Do you burn the plastic bags and bottles along with other wastes in your house?	30	45	40	60
2	Have you experienced any foul odour while burning plastic?	64	11	85	15
3	Did you experience any discomfort from the fumes of burning plastic?	63	12	84	16
4	Do you have a plastic collection system in your place?	24	51	32	68
5	Is it OK to dispose of plastic waste by burying?	12	63	16	84
6	Have you ever felt that plastic has been a threat to people?	66	9	88	12

Nearly 70% of the respondents collect plastic wastes separately from organic/food wastes for disposal. Nearly 25% responded that the plastic content of the product packaging influenced their decision to buy or not to buy the product, the more the plastic content, the less the probability of buying that product. [This need not necessarily be an honest comment as seen from the quantum of plastic waste even from educated/ high income households.] More than 50% said that they care about the safety of the materials used for making toys which they buy for the children. Majority of the respondents said that they have been packing their purchases optimally in recent times to ensure the use of minimum number of plastic bags. Nearly 25% of the respondents use the carry bags for repeated purchases. According to 35% of the respondents, the most common plastic item that get accumulated in their households is carry bags followed by thin light bags and bakery covers.

Many respondents confirmed that occasionally family members do engage in discussions on the long term hazards of plastics. Nearly 39% have seen domestic animals eating plastic at least once but did not do anything to dissuade them. More than 84% have seen plastics dumped in water bodies such as ponds, rivers and lakes. Many of them believe that the plastics may eventually decay and turn the water toxic. They are also aware that the plastic products are harmful to aquatic organisms including fish wealth. More than 65% of respondents are aware of the fact that plastic products can cause eye-sore, skin problems and allergies. Nearly 30% do not mind a complete ban on plastic products and can manage without. But only less than ~ 40% believe that a world without plastic of any kind is possible in today's context. The responses to the related questions are summarized in table 3.4.

Table 3.4: Responses to the questions related to the awareness of the hazards of plastic products

No	Question	Response (Yes)	Response (No)	% Yes	% No
1	When collecting garbage, do you collect the plastic items separately?	53	22	71	29
2	Does the plastic content of a product influence your selection to buy any item?	35	40	47	53
3	When buying toys for kids do you consider the material from which they are made?	44	31	59	41
4	Do you deliberately avoid getting new plastic bags each time you shop?	47	28	63	37
5	Have you seen animals eating plastic?	29	46	39	61
6	If so did you try to dissuade them?	25	50	33	67
7	Have you seen plastic dumped in water bodies?	63	12	84	16
8	Are you aware of any skin problems or allergies caused by plastic?	50	25	67	33
9	Do you think it is possible to have a world without plastic products?	31	44	41	59

More than 75% of the respondents feel that government sponsored initiatives on reducing plastic waste are not adequate and there must be more efforts to create awareness among the public. Only less than a quarter of the respondents have attended at least one awareness programme conducted by government/local bodies/Non-Governmental Organizations on plastic related hazards. Many have not heard about such programmes. This reveals the need for more concerted efforts on educating the people on the hazards of plastic waste and safer methods of disposal.

Nearly 53% favor stricter rules. However, only 18% recommend stringent punishment for plastic littering and prefer voluntary reduction through education and awareness programmes. About 30% will accept a government ban on plastic use without resentment or protest. Nearly all respondents are willing to reduce the use of plastic products progressively and are already doing it. There is near unanimity that the new lifestyle and supermarket culture are mainly responsible for the exponential growth in plastic waste generation. But only less than 60% think that it may be possible to go back to traditional customs including wrapping purchases in paper/cloth bags. The responses to the related questions are summarized in table 3.5.

Table 3.5: Responses to the questions related to what individuals can do to reduce related plastic related hazards

No	Question	Response (Yes)	Response (No)	% Yes	% No
1	Do you recommend banning of plastic altogether?	23	52	31	69
2	Have you attended any awareness program about the ill effects of plastic?	19	56	25	75
3	Has any such awareness program been conducted in your locality?	13	62	17	83
4	Are you willing to be a volunteer in your locality to create awareness on plastic?	64	11	85	15
5	Can you take a decision to reduce your plastic use progressively?	71	4	95	5
6	Do you think the new supermarket culture leads to increased use of plastic?	69	6	92	8
7	Do you think adoption of modern life style leads to increase in plastic use?	66	9	88	12
8	If so do you recommend going back to the old customs?	44	31	59	41

3.5 Conclusions

The study shows that an average of ~1 kg of plastic waste/month/household is generated even in a typical middle class/lower middle class community. Biggest contribution to plastic pollution in terms of volume and spread comes from thinner, lighter, so called ‘carry bags’ and disposable containers. This can be attributed to the new ‘supermarket’ culture and the packing used for ‘ready to eat’ bakery items and fast-food. The quantity of plastic waste in any household, irrespective of the income, is directly proportional to the number of family members. The generation of plastic waste is also dependent on the income of the household, the higher the income, the bigger the quantity of waste. Extremely light plastic wraps/bags cause severe environmental hazards. Although such items may look less in terms of weight they are more in volume and number and are also dispersed over larger area causing major long term pollution hazards. An encouraging observation is that the culture of reuse of plastic bags is slowly picking up and people are fully aware of the plastic menace. The survey shows that concerted efforts are needed by government agencies, NGOs and other citizens concerned to create more awareness among the public on the need for reduction in plastic waste and its safe disposal.

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Chapter 4

SEMICONDUCTOR OXIDE MEDIATED PHOTOCATALYTIC DEGRADATION OF LOW DENSITY POLYETHYLENE PLASTIC WASTES

Contents

4.1 Introduction

Polyethylene (PE) plastics commonly known as polythenes find a wide range of applications in daily human life because of their convenience, strength, light weight and many other desirable characteristics. They have a wide variety of applications including protective packaging, mobile phones, domestic appliances, furniture items, medical devices, automotive components etc [143]. The ever increasing volume of plastic bag usage is a growing environmental pollution problem. Each year around 1trillon plastic bags are used worldwide with most of them ending up in landfills, dumpsites and water bodies. Also it creates an uncomfortable visual pollution problem. Polythene is strong and highly durable and takes up to 1000 years for natural degradation in the environment. Further, plastic degrades slowly under sunlight into toxic components, thus contaminating soil and water from where they can be accidentally ingested by animals. Eventually they enter the food chain especially in the marine biota [144].

Among the different types of plastic wastes produced, polythene share is about 64% [145]. Around 40% of plastic bags are made of polyethylene. Traditionally, polyolefins are considered to be nonbiodegradable for three reasons. Firstly, the hydrophobic character of polyolefins makes them resistant to hydrolysis. Secondly, the use of anti-oxidants and stabilizers during manufacture protects polyolefins from oxidation and biodegradation [146]. Thirdly, polyolefins have high molecular weights of 4000 to 28,000. Different techniques such as use of biodegradable and photodegradable plastics, plasma technology, thermal and catalytical treatment etc have been proposed for the degradation of waste polyethylene or transformation to fuel oils. However, the problem of ''white pollution'' still eludes a satisfactory and safe solution [147-149].

Polyethylene is a thermoplastic made up of long chains of monomer ethylene. The repeating unit of polyethylene is [$-CH_2-CH_2-$]. The general formula of polyethylene is C_nH_{2n}, where 'n' is the number of carbon atoms [145]. Based on the degree of polymerization, PE plastics are mainly of two types: Low density polyethylene (LDPE) and High density polyethylene (HDPE). Crystallinity of LDPE is low at ~ 55% and has a density in the range of 0.910- 0.925g/cm^3. LDPE form is used to make carry bags, bottles, toys, mugs and a variety of other less expensive daily use products. It is tough, flexible, good insulator of heat and electricity and shows considerable resistance towards acid, alkali and salt solutions. Extensive use of LDPE plastics with no safer or convenient disposal avenues has been creating serious environmental hazards. New inexpensive and safer technologies have to be developed for the degradation of these plastic wastes.

Heterogeneous photocatalysis is a widely investigated Advanced Oxidation Process (AOP), for the degradation of organic pollutants in water and air [110,114,150-153]. The basic mechanism of photocatalysis involves the formation and interaction of highly reactive hydroxyl radicals [154-155]. Semiconductor oxides such as TiO_2 and ZnO and their modifications by doping, immobilizing, metal deposition, dye sensitization etc. are the most widely used photocatalysts [156-158].

Among the semiconductors, TiO_2 is the most widely used photocatalyst mainly due to its wide availability, stability, nontoxicity and reactivity. Another semiconductor oxide ZnO has received relatively less attention due to its corrosive nature under extreme pH conditions. At the same time ZnO is reported to be more efficient than TiO_2 for the visible light induced photocatalytic degradation of organic pollutants because the former can absorb a larger fraction of solar spectrum compared to the latter [159-164]. Basic mechanism of semiconductor photocatalysis involves photo excitation of the valence band electrons to the conduction band thereby creating electron deficiency or holes in the valence band. Dioxygen in the system, on the surface as well as in the bulk, serves as a sink for conduction band electron forming superoxide $O_2^{-\cdot}$ which leads to the formation of a number of Reactive Oxygen Species (ROS) [151-152, 154-156]. Holes in the valence band can react with water molecules or hydroxide anion to form $^{\cdot}OH$ radicals. The holes can also interact with adsorbed organic donors leading to their degradation and possible mineralization.

In spite of the severe hazards caused by LDPE to the environment and ecology, the number of research studies, especially AOP aimed at developing safer technologies for their disposal are relatively few. In the present study, the possibility of using photocatalysis mediated by TiO_2 and ZnO for the degradation of LDPE is investigated. The effect of various reaction parameters such as pH, catalyst dosage, presence of oxidizing agents, presence of anions, cations etc on semiconductor oxide mediated photocatalytic degradation of LDPE is examined, evaluated and optimized.

4.2 Materials and Methods

ZnO (>99.9%) and TiO_2 (>99.9%) used in the study were supplied by Merck India Limited. TiO_2 and ZnO were characterised by analysis of particle size and distribution, measurement of Brunauer–Emmett–Teller (BET) surface area, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), X-ray Diffraction (XRD), adsorption measurements etc.

4.2.1 ZnO

Pore size distribution of ZnO is shown in figure 4.1.

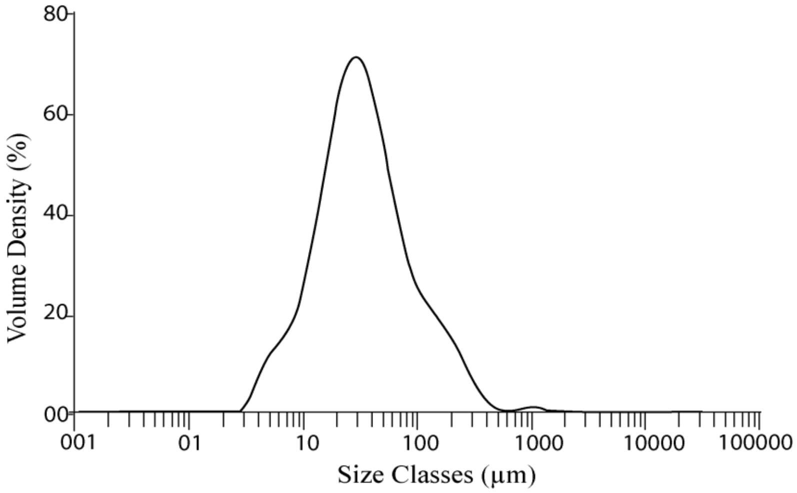


Figure 4.1: Pore size distribution of ZnO

The BET surface area (A) of ZnO is 12 m^2/g. Barrett-Joyner-Halenda **(**BJH) adsorption and desorption cumulative volume (V) of pores between 17.000 Å and 3000.000 Å diameter are 0.012142 cm^3/g and 0.012018 cm^3/g respectively. Adsorption average pore width (4V/A by BET) is 125.5911 Å.

The morphology, size distribution and surface characterization of ZnO were further verified by TEM. Figure 4.2 gives the TEM image of ZnO.

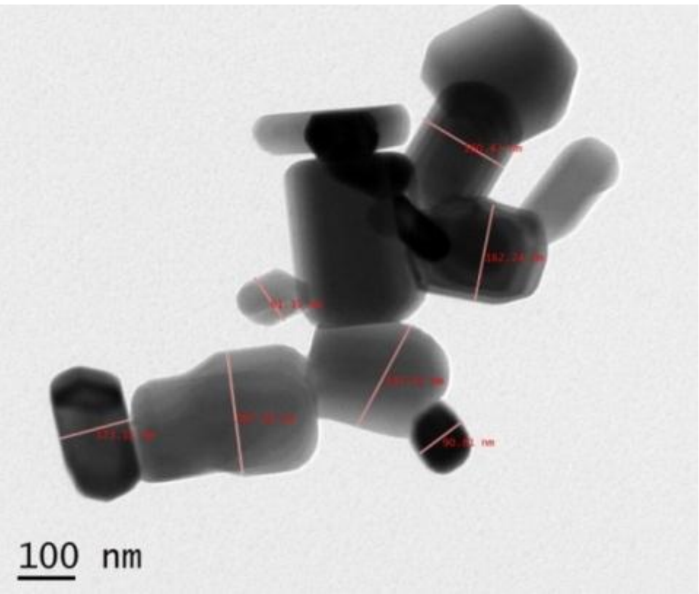


Figure 4.2: TEM image of ZnO

The particles are mostly rod-shaped with an average particle size of 0.14 µm.

XRD (figure 4.3) shows three sharp peaks between 30 and 40° with very high intensity which is typical of ZnO. Comparison with literature shows that ZnO has hexagonal phase with typical planes such as (100), (002), (101), (102), (110) etc.

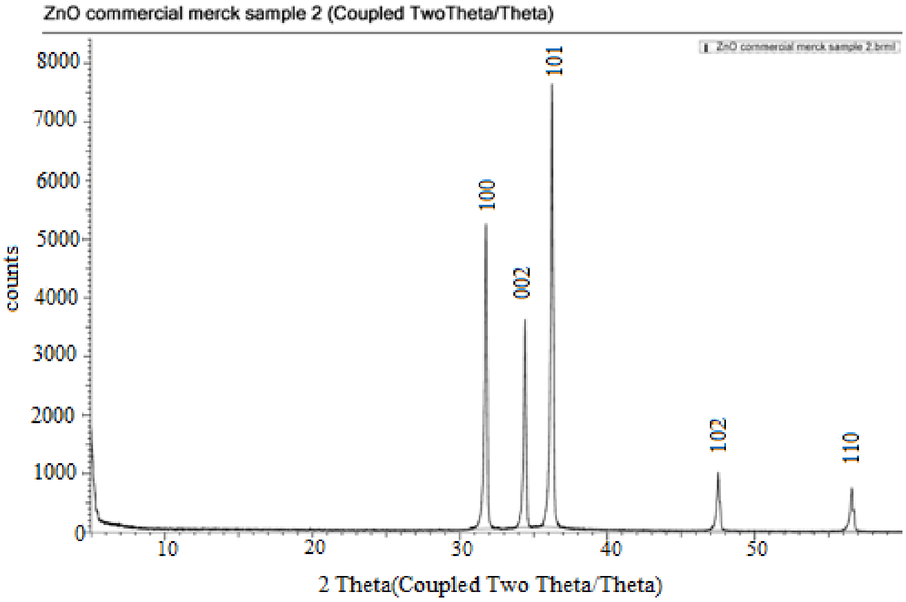


Figure 4.3: XRD pattern of ZnO

The SEM image of ZnO is given in figure 4.4. Most of the particles were rod-shaped with an average particle size of ~ 0.1 µm.

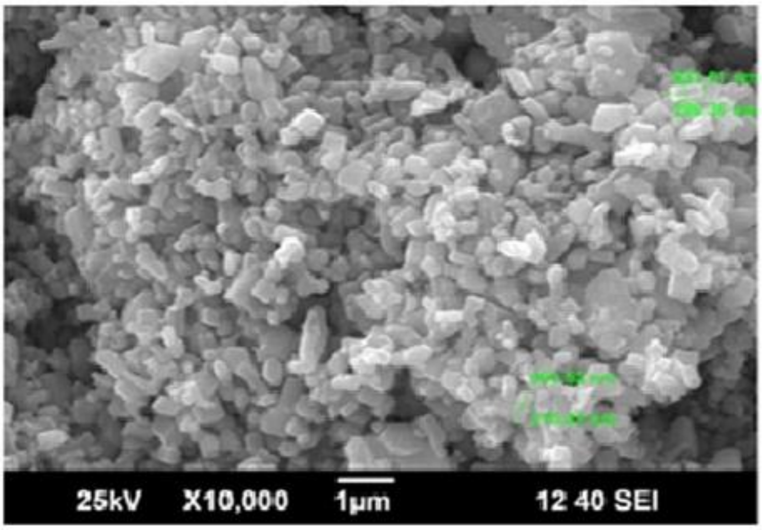


Figure 4.4: SEM image of ZnO

4.2.2 TiO$_2$

Pore size distribution of TiO$_2$ is shown in figure 4.5.

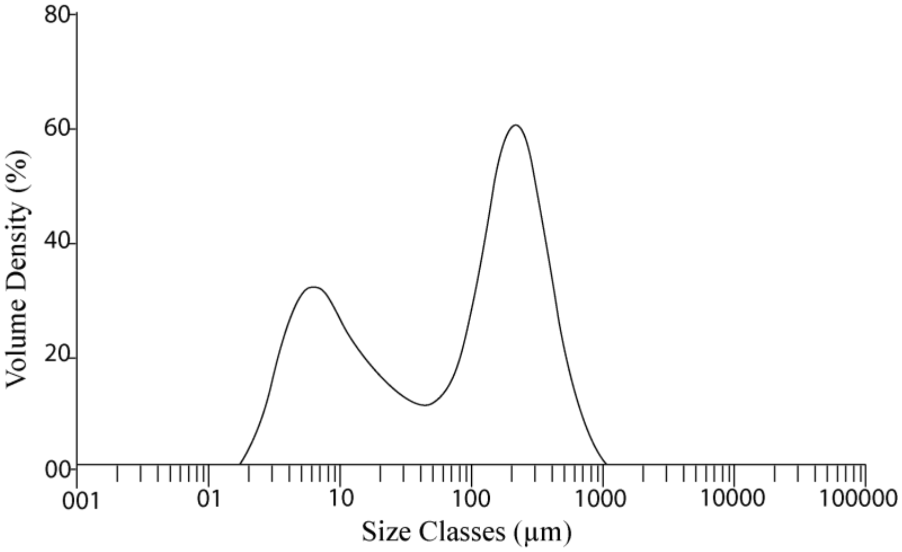


Figure 4.5: Pore size distribution of TiO$_2$

The BET surface area (A) of TiO$_2$ is 10.0236 m²/g. Barrett-Joyner-Halenda (BJH) adsorption and desorption cumulative volume (V) of pores between 17.000 Å and 3000.000 Å width are 0.039211 cm³/g and 0.039376 cm³/g respectively. Adsorption average pore width (4V/A by BET) is 163.3022 Å.

TEM image of TiO$_2$ is shown figure 4.6. The size and shape of the particles can be seen clearly.

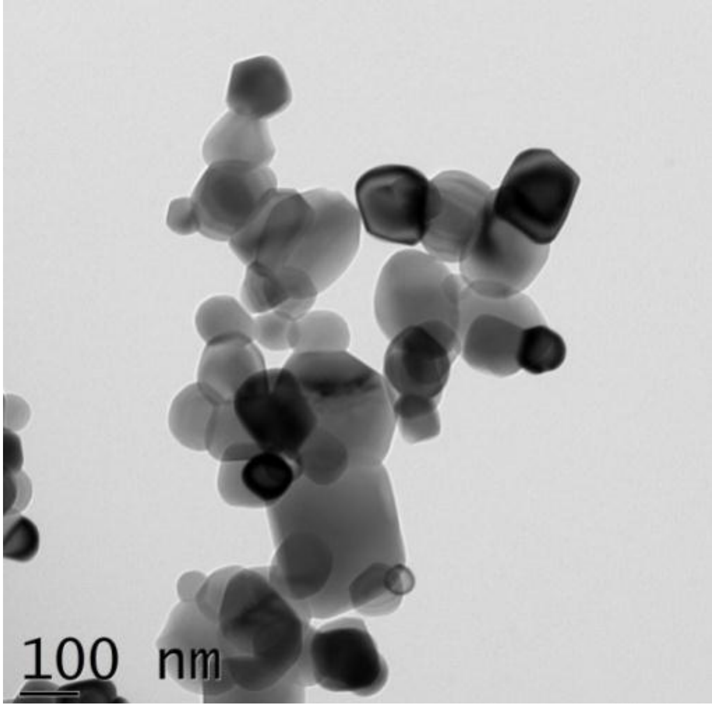


Figure 4.6: TEM image of TiO_2

The particles are not of uniform shape with moderate agglomeration. The particle diameter is nanosized at ~100 nm and the length is micro sized.

The XRD images of TiO_2 (anatase), TiO_2 (rutile) and TiO_2 (anatase and rutile) are given in figures 4.7, 4.8 and 4.9 respectively.

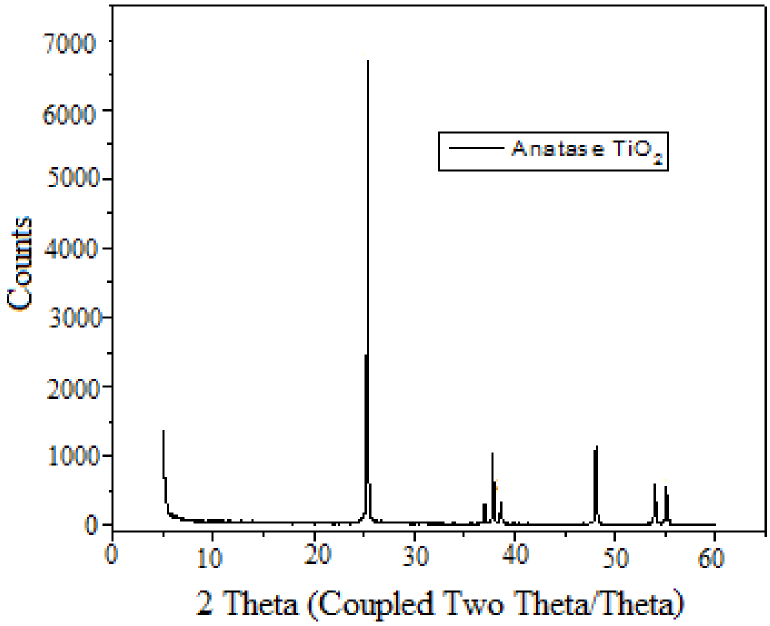


Figure 4.7: XRD pattern of TiO_2 (Anatase)

Examination of the XRDs of the commercial TiO_2, TiO_2 (anatase) and TiO_2 (rutile) shows that the commercial sample is a pure mixture of the two types. The XRD peak of anatase at $2\Theta = 25.4$ (crystal plane 101) and rutile at $2\Theta = 27.5$ (crystal plane 110) are typical of the two phases and are often used to quantify them. Other typical peaks of anatase and rutile are also seen in the commercial sample (figure 4.9) thereby confirming that commercial TiO_2 is a combination of these two. In the current sample, the approximate ratio of anatase and rutile is 70:30.

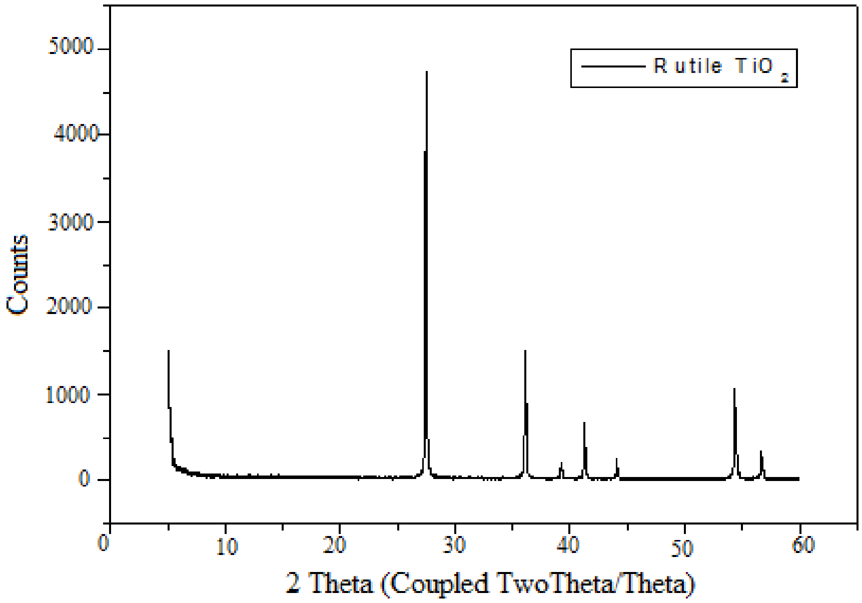


Figure 4.8: XRD pattern of TiO_2 (Rutile)

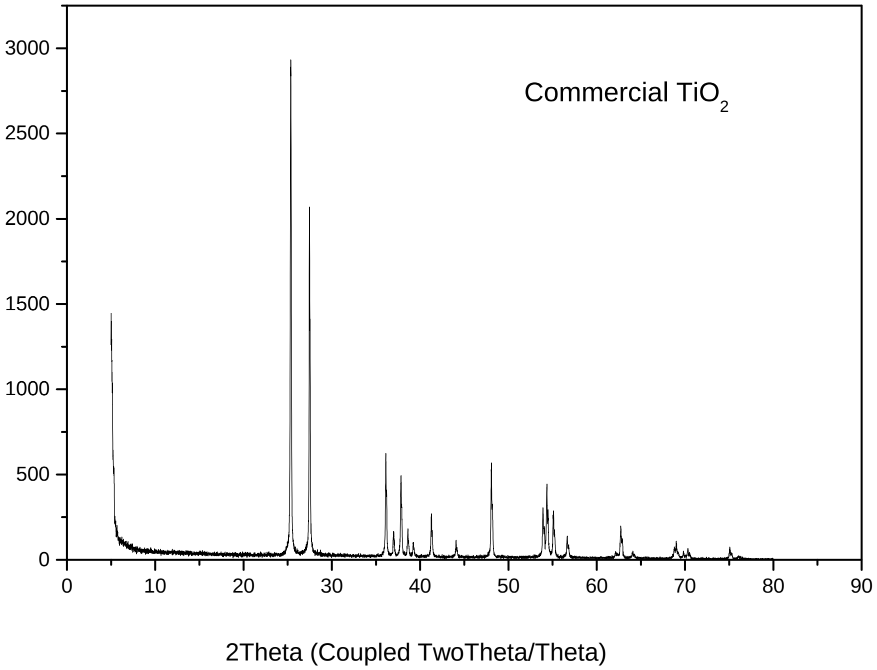


Figure 4.9: XRD pattern of commercial TiO_2 (Anatase and Rutile)

The surface morphology of TiO_2 was examined by SEM analysis. Typical SEM image of TiO_2 is shown in figure 4.10.

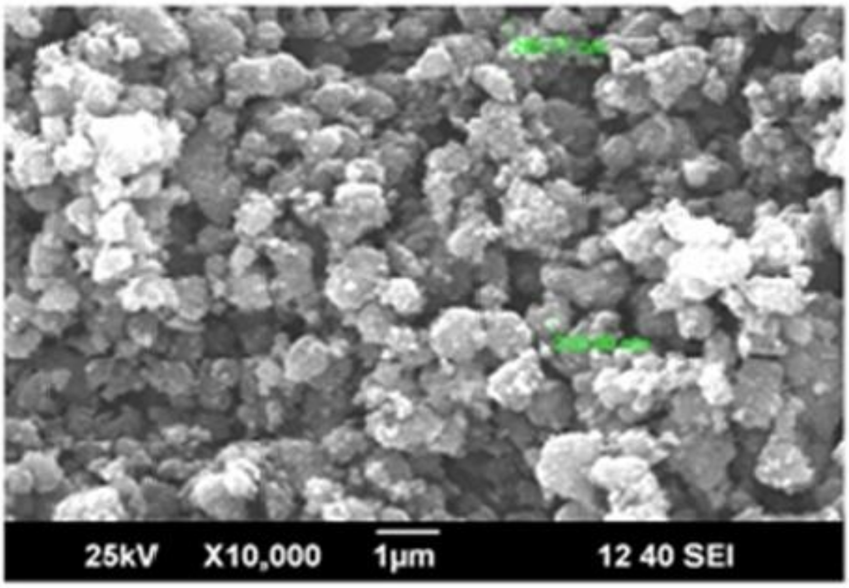


Figure 4.10: SEM image of TiO_2

Particles of TiO_2 are more agglomerated than ZnO and flower like with non uniform size distribution. Majority of the particles are of size in the range ~0.1 - 0.2µm.

4.2.3 Miscellaneous chemicals

All other chemicals/reagents used were of AnalaR grade or equivalent unless indicated otherwise.

4.3 Photocatalytic experiments

Typical LDPE strips made from disposable type ‘used’ carry-bags collected from streets/households were used in the study. Dimensions of the strips were as follows: Length 25cm, breadth 1cm and thickness 41 microns. The strips were washed thoroughly, dried in air until constant weight is reached and then fully immersed in aqueous suspension of the catalyst TiO_2 or ZnO (as the case may be) in a tubular reactor made of pyrex glass. The suspension containing catalyst and the plastic strip is then irradiated by UV light with frequent mixing. A multi lamp photo-reactor (Heber Scientific India) which consisted of a lamp-housing with eight UV lamps of 8W each is used for the irradiation. The primary wavelength of the lamps was 365nm. The photoreactor and its different views are presented in figures 4.11, 4.12, 4.13 and 4.14.

Figure 4.11: Multilamp photoreactor-external view

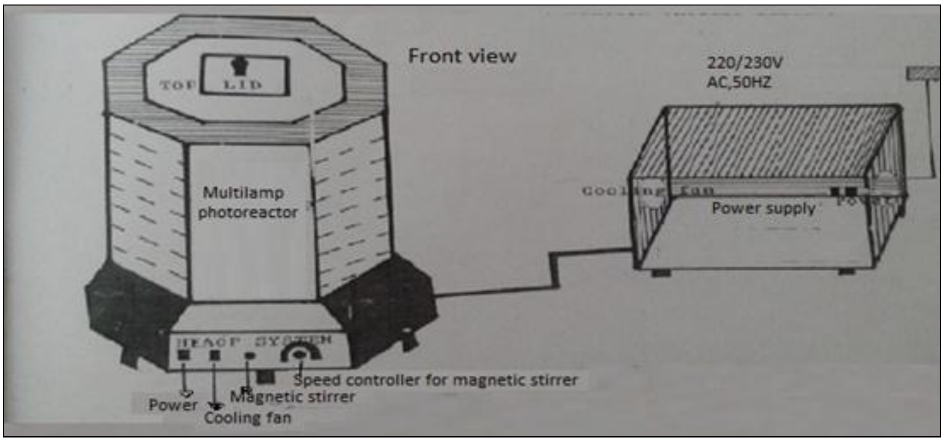


Figure 4.12: Schematic diagram of the multilamp photoreactor

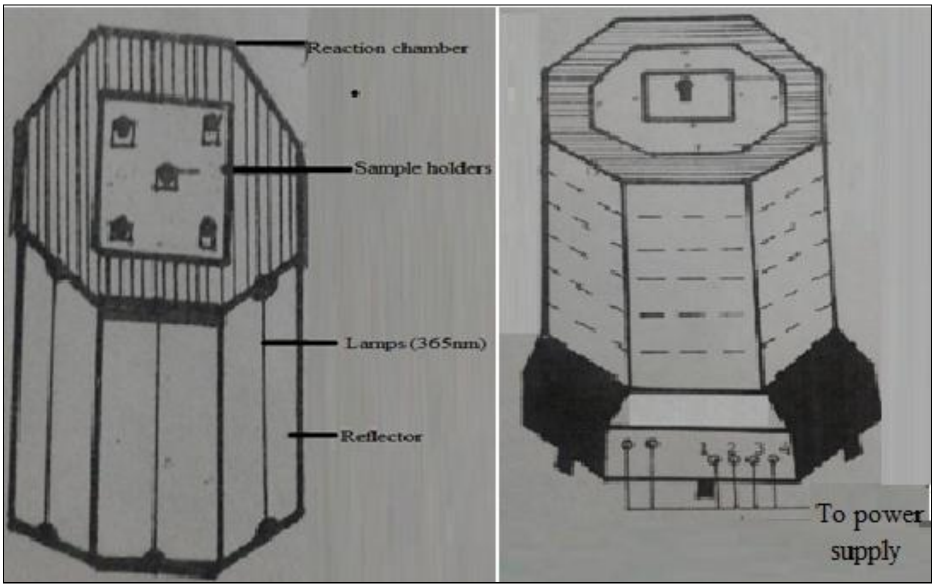


Figure 4.13: Schematic diagram of the multilamp photoreactor
-reaction chamber and rear view

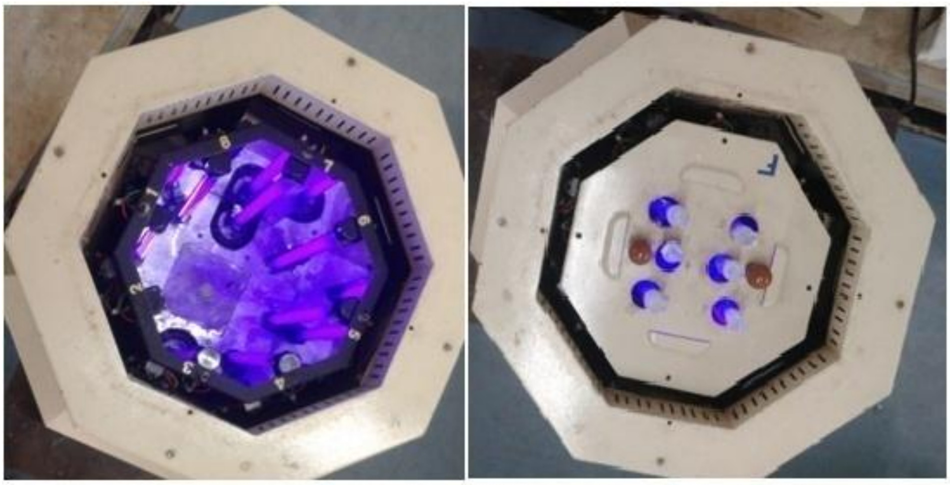


Figure 4.14: Multilamp photoreactor-inside and top view

After specific time intervals (often long duration of 10-20 hr irradiation is required to get measurable changes due to the very poor degradation of plastic) the plastic strips are taken out, washed well with distilled water to remove sticking particles of catalyst, if any, and dried at room temperature in air flow until constant weight is reached. The weight loss, change in physical appearance including smoothness/coarseness, visible decrease in thickness, increased crumbling, periodic SEM imaging, IR spectroscopy, tensile strength measurements etc were used to identify and quantify the destruction of LDPE under photocatalysis under different conditions.

4.4 Results and Discussion

Preliminary investigations on the photocatalytic degradation of LDPE using ZnO and TiO_2 catalysts under identical conditions showed that no significant degradation took place in the absence of UV light or the catalyst suggesting that both catalyst and light are essential to effect degradation. The ultimate reaction products were expected to be CO_2 and H_2O formed by the degradation of polyethylene. Since the amount of CO_2 formed is very small, that too over a long period, its quantitative estimation is difficult. The Total Organic Carbon (TOC) content and Chemical Oxygen Demand (COD) of water in which LDPE is suspended is ‘nil’ even after continued irradiation and moderate loss in the weight of the LDPE sheet. This indicates the mineralisation of the LDPE as well as the intermediates, if any, formed from it. The effect of various reaction parameters relevant in photocatalysis on the degradation of LDPE is investigated and the results are reported below.

4.4.1 Effect of catalyst dosage

Comparative efficiency of TiO_2 and ZnO at various loadings for the photodegradation of LDPE under identical conditions is shown in figure 4.15. The efficiency is measured by the weight loss of the LDPE strip. As seen from the figure, TiO_2 is more efficient than ZnO and the optimum loading for both is 1400 mg/L. Beyond the optimum loading, the light photon absorption coefficient decreases radially and the degradation slows down. However such light attenuation over the radial distance does not obey the Beer-Lambert law due to the strong absorption and scattering of light photons by the catalyst particles [165]. Excess catalyst particles result in screening and scattering of light which reduce the quantum of photons available for activation. Beyond the optimum, the catalyst particles also get agglomerated, form clusters and this results in decrease in the effective surface area of the semiconductor being exposed to illumination. This naturally reduces the photocatalytic efficiency.

Since TiO_2 is more efficient for the degradation compared to ZnO under identical conditions, all further investigations were carried out using the former at the optimized loading as above, unless mentioned otherwise.

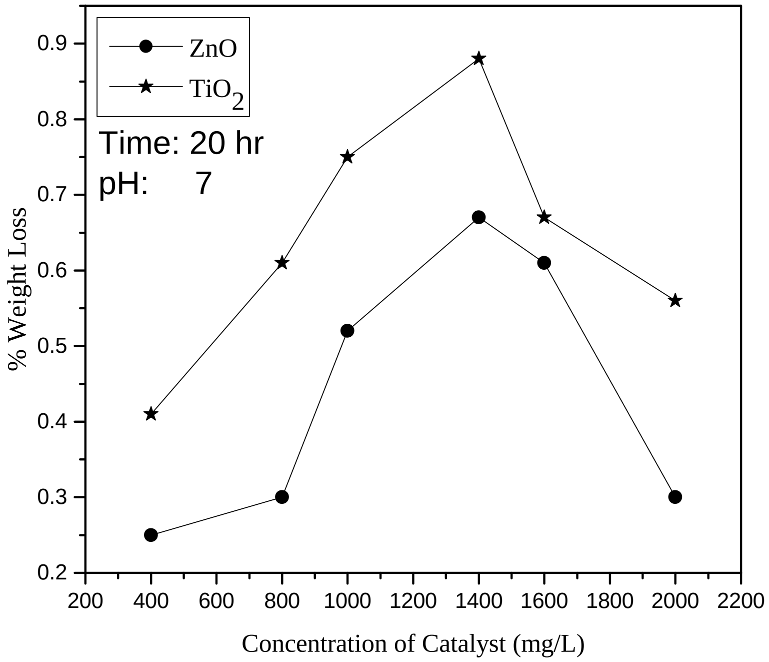


Figure 4.15: Comparative efficiency of TiO_2 and ZnO at different dosages for the photocatalytic degradation of LDPE plastic

4.4.2 Effect of irradiation time

Effect of optimised dosage of TiO_2 on the photocatalytic degradation of LDPE plastic at different irradiation times is shown in figure 4.16. The degradation (weight loss) increases with increase in irradiation time at a more or less steady rate during the entire duration of 400 hrs of the study. This implies that the catalyst TiO_2 remains active throughout and unlike in the case of photocatalytic degradation of many organic pollutants, the substrate or the reaction intermediates do not get adsorbed on the surface or deactivate the catalyst. This is an important parameter in the commercial application of the process.

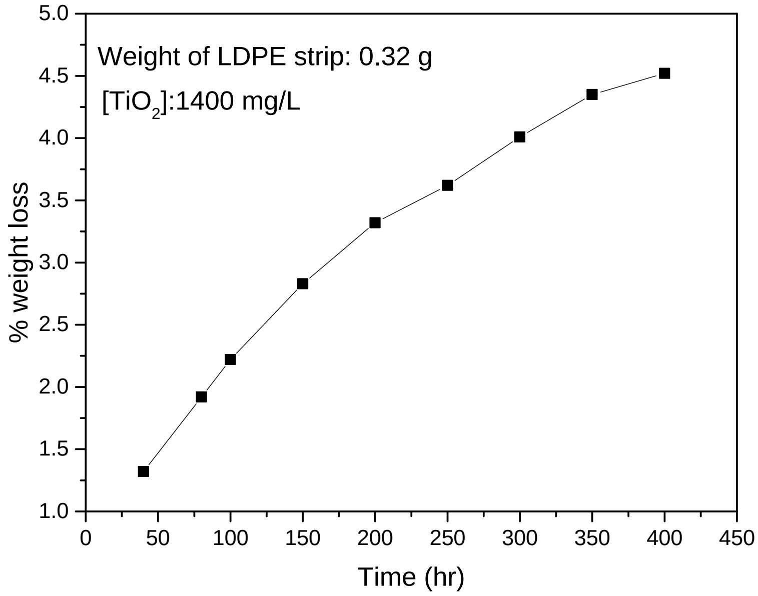


Figure 4.16: Effect of irradiation time on the TiO_2 mediated photocatalytic degradation of LDPE plastic

4.4.3 Effect of pH

The photocatalytic degradation of organics is reported to be generally dependent on the pH value of the solution/suspension. Earlier studies in our laboratory using a variety of substrates on ZnO, TiO_2 and their combination as catalysts also confirmed this [166-167]. Hence the effect of pH on the photocatalytic degradation of LDPE was investigated in the range 2.5-10. The pH of the suspension was adjusted before irradiation and was not controlled thereafter. The results are presented in figure 4.17.

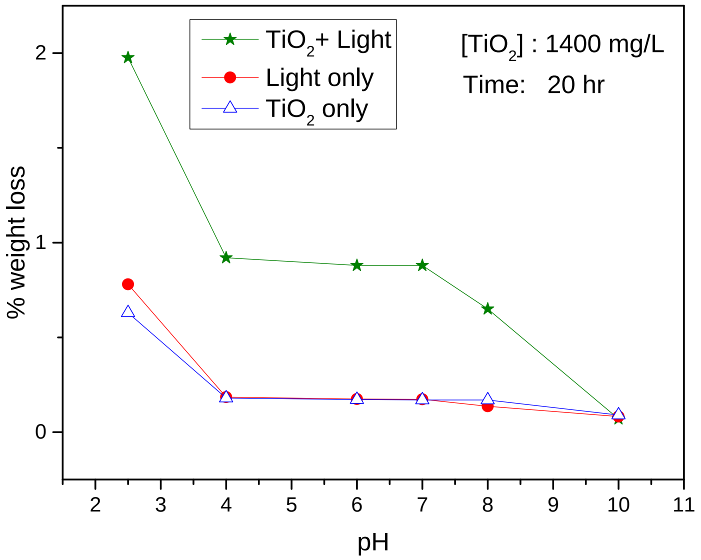


Figure 4.17: Effect of pH on the photocatalytic degradation of LDPE plastic

Slight degradation takes place in the acidic region even in the absence of the catalyst or light. However at the natural pH of the catalyst/LDPE suspension (~ 6-7), noticeable degradation takes place only in the presence of both catalyst and light. Degradation at extreme acidic conditions, even if feasible, is not a viable solution economically or ecologically since it requires expensive and hazardous neutralization and disposal processes. High acidity also requires expensive equipments and special material of construction. Hence it is more prudent to optimize the parameters at the natural pH of the system ie, ~6.5 at which reasonable degradation of the plastic is noted in presence of TiO_2 and light.

4.4.4 Effect of oxidizers on the degradation

Hydrogen peroxide is detected as a by-product/intermediate in the photocatalytic degradation of organic pollutants [166]. It has also been reported that the H_2O_2 thus formed undergoes simultaneous decomposition resulting in periodic increase and decrease (oscillation) in its concentration [166-167]. In the present instance of photocatalytic degradation of plastics also, H_2O_2 is detected in the reaction medium. However, its concentration is very small (< 2 mg/L) and is hence not followed up. The reactive free radicals such as $^{\cdot}OH$ (oxidation potential: 2.80) and $HO_2^{\cdot}$ (oxidation potential: 1.70) formed from H_2O_2 (oxidation potential: 1.77) are more powerful oxidants and often have a positive effect on the degradation of organics. The oxidation potential of some of the important oxidants are given in table 1.4 in Chapter 1. Thus added H_2O_2 is expected to enhance the degradation of many pollutants. However, instances of inhibition of the AOP degradation of organics by H_2O_2 also have been reported [168]. Another powerful oxidant is peroxydisulphate (PDS) which also serves as an accelerator for the degradation of pollutants including petrochemicals, pesticides and dyes [162]. In view of these, the effect of the oxidants H_2O_2 and PDS on the degradation of LDPE is investigated. The results are plotted in figure 4.18.

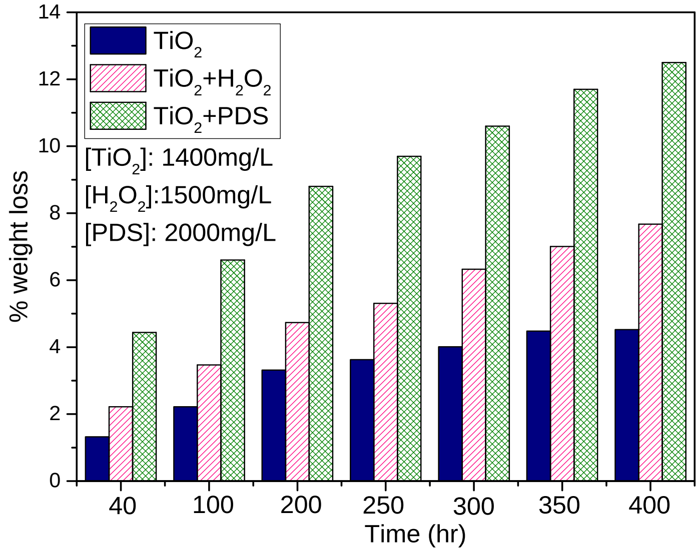


Figure 4.18: Comparative efficiency of H_2O_2 and $S_2O_8^{2-}$ for the photocatalytic degradation of LDPE plastic in presence of TiO_2

In both cases, the degradation of LDPE is enhanced and the enhancement continues even for longer periods of irradiation. PDS is a much better oxidant compared to H_2O_2. However, the degree of enhancement slows down with time.

It is possible that this decrease in the rate of degradation may be due to the consumption of the reagent and consequently inadequate availability of the oxidising species. Hence studies were conducted by replenishing the (TiO_2+PDS) system with fresh PDS (2000mg/L) after 40 hr and 80 hr of reaction. The results show that the addition of fresh PDS after regular intervals of time enhances the degradation of LDPE plastic. This is shown in figure 4.19. This result also indicates that higher the concentration of PDS, greater will be the degradation of LDPE.

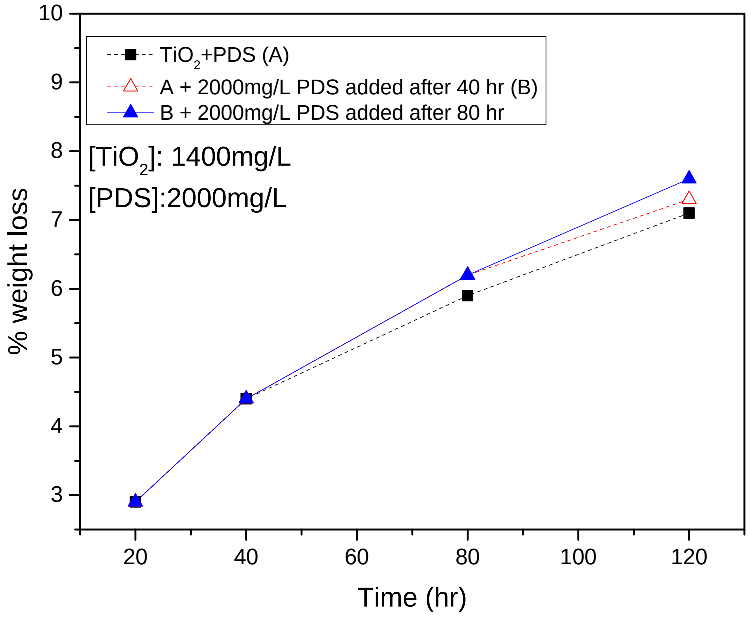


Figure 4.19: Effect of in-between addition of PDS on the photocatalytic degradation of LDPE plastic in presence of TiO_2 + PDS

Hence, experiments were made with different concentration of PDS and H_2O_2. The effect of concentration of the oxidant is shown in figure 4.20. In the case of PDS, increase in concentration of the oxidant increases the degradation of plastic fairly steeply upto ~2000mg/L and stabilises thereafter. In the case of H_2O_2 the increase in degradation is relatively slower and 1500mg/L may be considered as the optimum concentration.

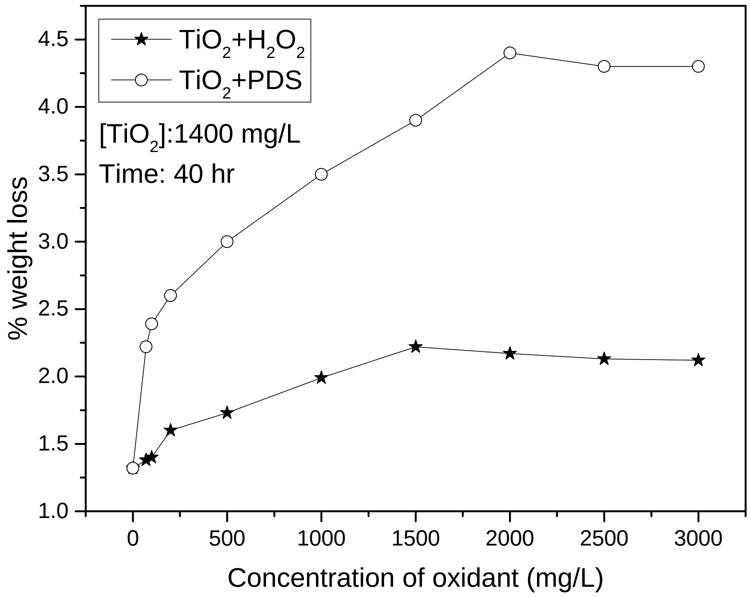


Figure 4.20: Effect of concentration of H_2O_2 and PDS on the photocatalytic degradation of LDPE plastic in presence of TiO_2

Above this optimum concentration the degradation of LDPE is stabilised in the case of both oxidants. This also explains the relatively milder increase in degradation when extra PDS is added to the system (figure 4.19). However these optimized parameters are applicable only under the reaction conditions employed. For another set of parameters, reactor size and shape as well as LDPE strip size and shape the optimum may be different. The photocatalytic degradation efficiency in presence of PDS and H_2O_2 with and without of catalyst shows that presence of catalyst enhances the degradation rate. The results are shown in figure 4.21.

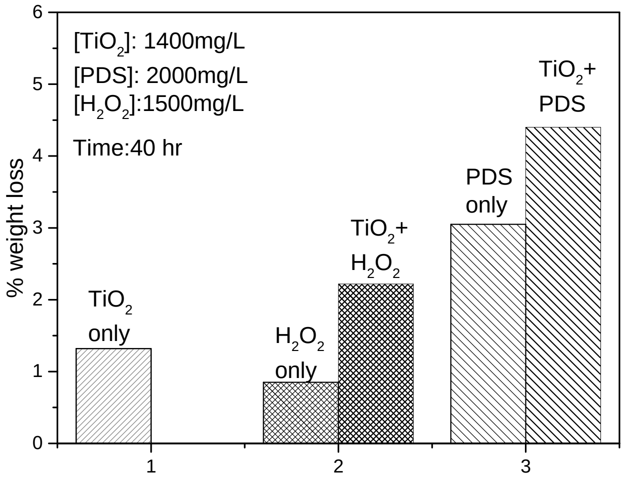


Figure 4.21: Effect of TiO_2 on the photocatalytic degradation of LDPE plastic in presence of PDS and H_2O_2

The effect of the catalyst and the oxidant is cumulative with no significant synergy or inhibition.

The effect of combination of oxidisers PDS and H_2O_2 on the phocatalytic degradation of LDPE in presence of TiO_2 was investigated. The result is shown in figure 4.22.

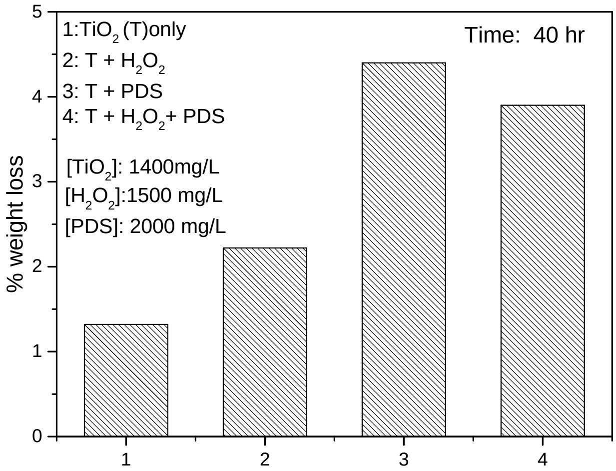


Figure 4.22: Effect of combination of H_2O_2 and PDS on the photocatalytic degradation of LDPE plastic in the presence of TiO_2

The combination is less effective than PDS but more effective than H_2O_2. Possible reasons for this effect are discussed under the section 4.4.17.

Another oxidant widely used in many water decontamination processes is Fenton reagent [FR] which is a combination of Fe^{2+} and H_2O_2 in appropriate ratio. The advantage of FR is its simplicity in terms of reagents, process conditions and operational procedures. The possibility of using FR for the degradation of LDPE is investigated and the findings are as described below.

4.4.5 Use of Fenton reagent for the degradation of LDPE

Fenton reagent (FR) is a mixture of ferrous iron (catalyst) and hydrogen peroxide. Since H_2O_2 was already observed to enhance the photocatalytic degradation of LDPE, the effect of FR on the degradation was also studied in detail.

Fenton reagent has been reported to be active for the degradation of many water pollutants, even in the dark. Investigation on the effect of Fenton reagent on the degradation of LDPE in the dark shows that the degradation of plastic is promoted slowly. Hence experiments were conducted to optimise the ferrous sulphate (FS)/H_2O_2 ratio and the results are plotted in figure 4.23. In the absence of any irradiation (dark) the optimum FS/H_2O_2 ratio was found to be 40:200 (1:5).

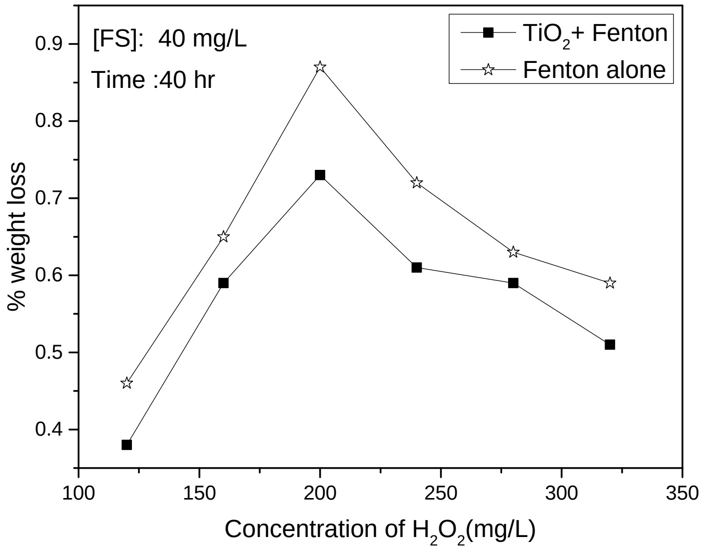


Figure 4.23: Effect of FS/H_2O_2 ratio on the efficiency of Fenton degradation of LDPE plastic under ambient conditions

It has been reported that the presence of semiconductor oxides such as TiO_2 inhibits the FR initiated degradation of many organics [169]. In this context, the effect of added TiO_2 on the FR induced degradation of LDPE is tested under ambient conditions. As expected, TiO_2 inhibits the degradation (figure 4.23). This is in contrast to the results under UV irradiation (as reported in a later section) in which TiO_2 enhances the photofenton degradation of LDPE plastic by the extra photocatalytic activity provided by the semiconductor. In the case of FR/TiO_2 also, for the reaction without light irradiation the optimum ratio of FS/H_2O_2 is same (1:5) as in the case without TiO_2.

The optimum concentration of FR at the optimised ratio (1:5) of FS/H_2O_2 is determined by measuring the degradation at various dosages. The dosage FS/H_2O_2 = 80:400 mg/L was identified as the optimum under the standard experimental conditions as shown in figure 4.24. Beyond the optimum dosage, any further increase in FR (at the optimised ratio of FS/H_2O_2) decreases the degradation of LDPE plastic.

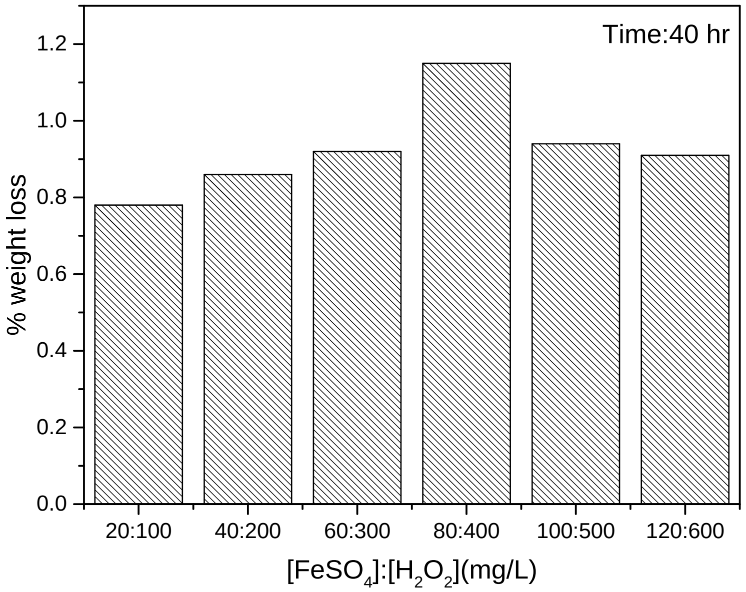


Figure 4.24: Effect of concentration of Fenton reagent on the rate of degradation of LDPE plastic under ambient conditions

In the case of FR induced reactions, the rate decreases with time which is attributed to the consumption of the FR (H_2O_2, FS or both). The inference is verified by adding these reagents individually to a reaction in progress. When the system was replenished at 40 hr and 80 hr with Fenton reagent as such, H_2O_2 and $FeSO_4$ individually the rate of degradation is enhanced in the order Fenton reagent > H_2O_2 > $FeSO_4$. The results are shown in figure 4.25.

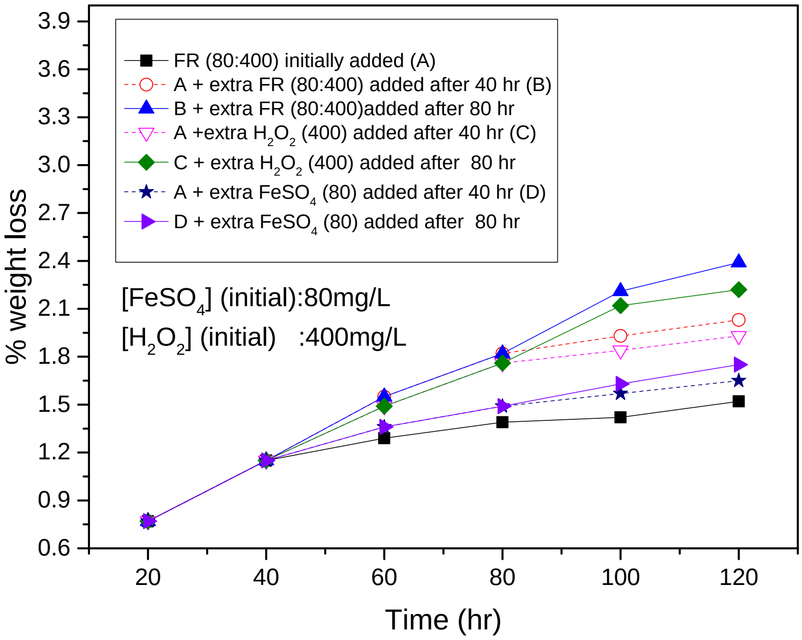


Figure 4.25: Effect of in-between addition of FR/H_2O_2/$FeSO_4$ on the Fenton degradation of LDPE plastic under ambient conditions

4.4.5.1 Photofenton process

The above data clearly shows that the efficiency of the Fenton process depends on the relative concentration of $FeSO_4$ (FS) and H_2O_2 as well as the total quantity of FR used. Preliminary studies have shown that UV irradiation of the Fenton system (photofenton) is more effective than Fenton oxidation or (Fenton +TiO_2) oxidation in the ambient condition for the degradation of LDPE plastic. Hence detailed investigations were made on optimizing the ratio of critical components for LDPE degradation under photofenton conditions in the presence and absence of TiO_2. The efficiency at varying ratios of FS and H_2O_2 on the photoefficiency is evaluated by keeping the former constant and varying the latter. The optimum ratio of FS/H_2O_2 (mg/L) is identified as 40:320 (1:8) in both cases as shown in figure 4.26.

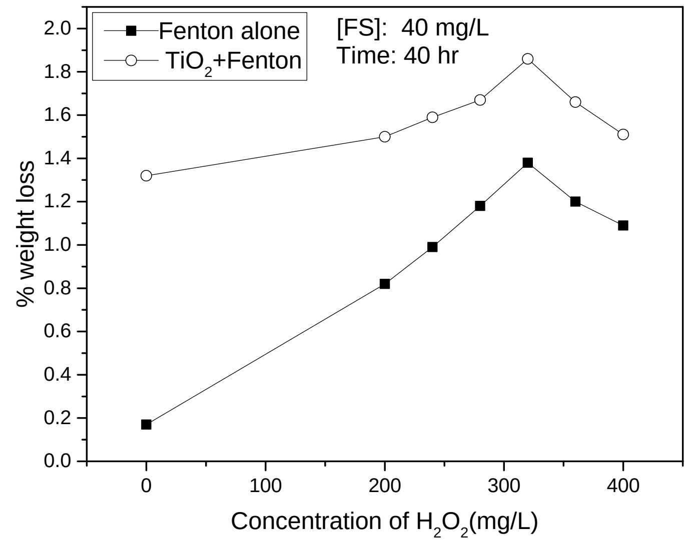


Figure 4.26: Optimisation of FS/H_2O_2 ratio for the photofenton degradation of LDPE plastic with and without TiO_2

In the presence of TiO_2 as catalyst the FR induced degradation of LDPE under UV irradiation is enhanced significantly. Obviously, this is due to the additive effect of TiO_2 photocatalysis and photofenton process. Once the optimum ratio of the constituents is fixed (Fe^{2+}: H_2O_2=1:8), the effect of concentration of the Fenton reagent in this ratio on the photodegradation of LDPE is examined. The results presented in figure 4.27 show that the degradation increases with increase in quantity of FR and reached an optimum when the quantity is 80:640 (Fe^{2+}: H_2O_2).

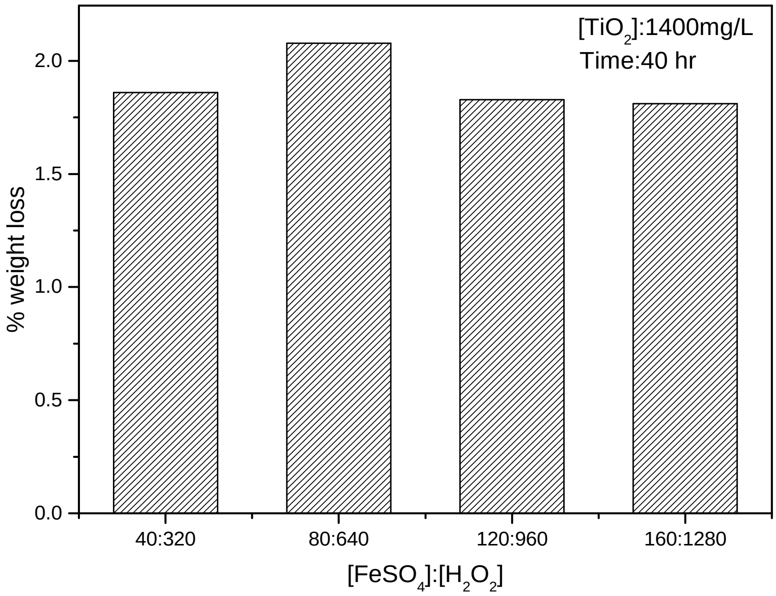


Figure 4.27: Effect of concentration of Fenton reagent on the rate of photodegradation of LDPE plastic in presence of TiO_2

Comparative evaluation of the degradation of LDPE plastic under TiO_2 photocatalysis, Fenton process under ambient conditions, photofenton and photocatalytic fenton in the presence of respective optimised ratio of components is presented in figure 4.28. The results clearly show that photofenton process is more efficient for the degradation of LDPE compared to Fenton under ambient conditions. Similarly TiO_2/Fenton/UV is much more efficient (> 2% weight loss of LDPE in 40 hr) than TiO_2/Fenton under ambient conditions (~1.2% weight loss in 40 hr). Enhancement under FR/TiO_2/UV relative to TiO_2/UV is less than the additive effect of FR/UV and TiO_2/UV especially towards later stages of reaction, probably because, the efficiency of FR/UV has decreased due to the consumption of H_2O_2.

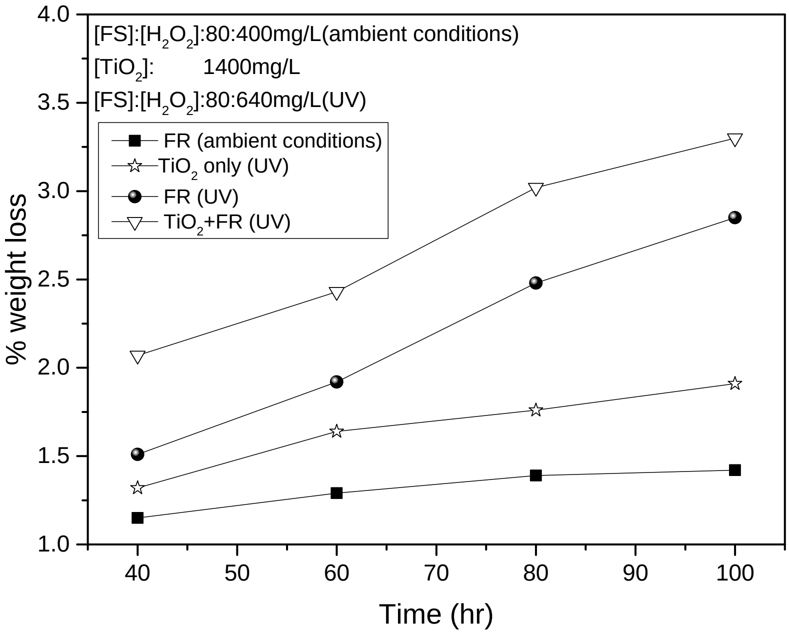


Figure 4.28: Efficiency of Fenton Reagent for the Photocatalytic degradation of LDPE Plastic with and without TiO_2

It has been demonstrated earlier that decrease in the rate of degradation of LDPE with time in the case of FR experiments is due to the consumptions of the reagent and consequently their inadequate availability. Hence studies were conducted in photofenton process also by replenishing the (TiO_2+Fenton) system after 40 hr and 80 hr of reaction with fresh Fenton reagent, H_2O_2 and $FeSO_4$ individually. The results are plotted in figure 4.29. It is seen that addition of the above reagents at regular intervals enhances the degradation in the order FR > H_2O_2 >$FeSO_4$.

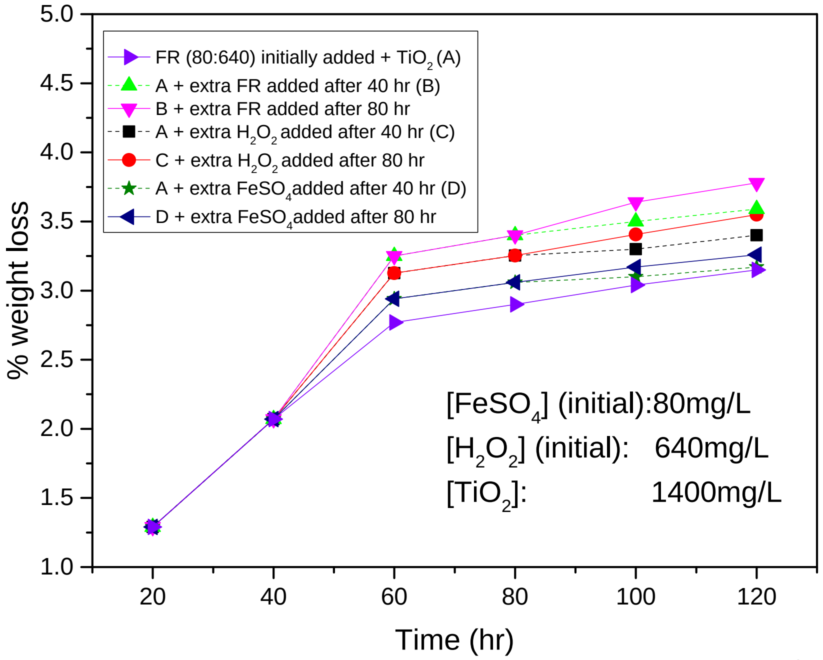


Figure 4.29: Effect of in-between addition of FR/H_2O_2/Fe^{2+} on the TiO_2/Fenton/UV degradation of LDPE plastic

Investigations were carried out in order to find out the effect of combination of the best oxidants with TiO_2/UV. For this purpose, the presence of TiO_2/PDS/UV, TiO_2/H_2O_2/UV and TiO_2/FR/UV is compared for the degradation of LDPE plastic. The results show that the combinations do not lead to any significant enhancement in the degradation of LDPE over that has been already achieved in the case of TiO_2/PDS/UV.

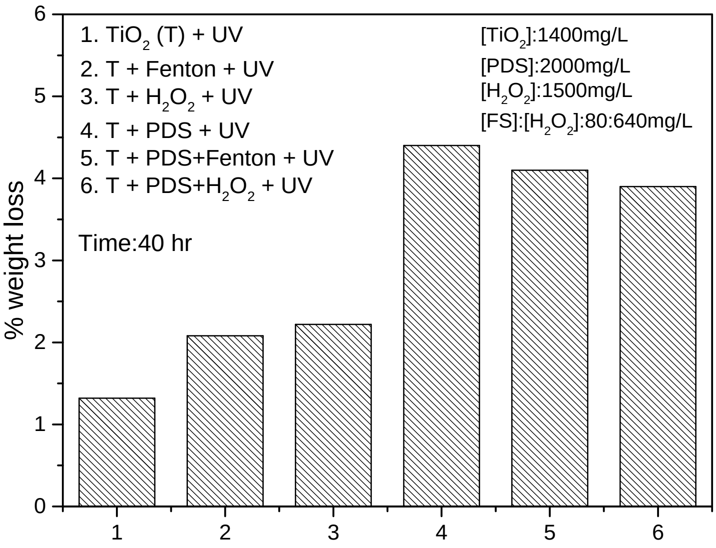


Figure 4.30: Comparative efficiency of various oxidant containing systems for the photocatalytic degradation of LDPE plastic

Comparison of the degradation of LDPE in presence of TiO_2, TiO_2+Fenton reagent, $TiO_2+H_2O_2$ and TiO_2+PDS shows that the efficiency of the oxidant is in the order PDS > H_2O_2 > Fenton reagent (figure 4.30). The efficiency of photocatalytic degradation of LDPE plastic in various combination systems in the descending order is:

(TiO_2+PDS) > (TiO_2+PDS+FR) > (TiO_2+PDS+ H_2O_2) >
($TiO_2+H_2O_2$) ≈ (TiO_2+FR) > TiO_2.

The detailed mechanism of Fenton process may be explained as follows:

The first step in the Fenton reaction is the oxidation of ferrous to ferric ions and decomposition of H_2O_2 into $^{\cdot}OH$ radicals.

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\cdot}OH$ ....(24)

In dark condition the reaction stops when the Fe^{2+} is completely converted to Fe^{3+}. In presence of UV irradiation, the ferric ions (Fe^{3+}) formed are photocatalytically converted back to ferrous ions (Fe^{2+}), with the formation of an additional equivalent of hydroxyl radicals. The hydroxyl radicals formed react with organic species, promoting their oxidation.

The Fe^{3+} is reduced by excess H_2O_2 to regenerate $Fe^{2+}$and more free radicals as in reaction (25)

$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^+$ ....(25)

Other possible reactions are:

$Fe^{2+} + {}^{\cdot}OH \rightarrow Fe^{3+} + OH^-$ ....(26)

$Fe^{2+} + HO_2^{\cdot} \rightarrow Fe^{3+} + HO_2^-$ ....(27)

$Fe^{3+} + HO_2^{\cdot} \rightarrow Fe^{2+} + O_2 + H^+$ ....(28)

The highly reactive free radicals may get deactivated by self-scavenging, interaction with other radicals and/or H_2O_2

${}^{\cdot}OH + {}^{\cdot}OH \rightarrow H_2O_2$ ....(29)

${}^{\cdot}OH + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O$ ....(30)

$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2$ ....(31)

${}^{\cdot}OH + HO_2^{\cdot} \rightarrow H_2O + O_2$ ....(32)

In the absence of any organic substrate to be oxidized, H_2O_2 self-decomposes as in reaction (33).

$2\ H_2O_2 \rightarrow 2H_2O + O_2$ ....(33)

In presence of organic molecules (R), such as LDPE in the current instance, the degradation can take place as in reactions (34) – (36) or dimerization occurs as in (37). Eventually mineralization takes place as in (38).

$^{\cdot}OH + R \rightarrow H_2O + R^{\cdot} \rightarrow$ (Partial mineralization + intermediates) ..(34)

$R^{\cdot} + Fe^{2+} \rightarrow R^{-} + Fe^{3+}$ ....(35)

$R^{\cdot} + Fe^{3+} \rightarrow R^{+} + Fe^{2+}$ ....(36)

$R^{\cdot} + R^{\cdot} \rightarrow RR$ ....(37)

$R^{\cdot}$ or R^{-} or R^{+} or RR + $^{\cdot}OH$, $HO_2^{\cdot}$, H_2O_2 etc. →
intermediates → $CO_2 + H_2O$ + salts (mineralization) ....(38)

Thus a series of reactive free radicals are generated under photofenton conditions and these can interact with the LDPE plastic in a variety of ways to produce intermediates and eventually mineralize the plastics.

Of the many AOPs tested here ie, photocatalysis, Fenton, Photofenton, combination of the processes with oxidants etc, the most efficient for LDPE degradation is PDS/TiO_2/UV.

4.4.6 Effect of anions and cations on TiO_2/UV system

Anions and cations are often present as respective salts in natural water systems and hence the study of the effects of anions and cations on the photocatalytic degradation of pollutants is important, particularly in the context of commercial application of the method. In the present study we have investigated the effect of added anions and cations on the degradation of LDPE plastic under the optimized conditions of other parameters. The anions and cations are found to influence photocatalytic degradation of LDPE plastic. The effect of some anions on the photocatalytic degradation in the presence of TiO_2 is shown in figure 4.31. The cation in all cases is Na^+.

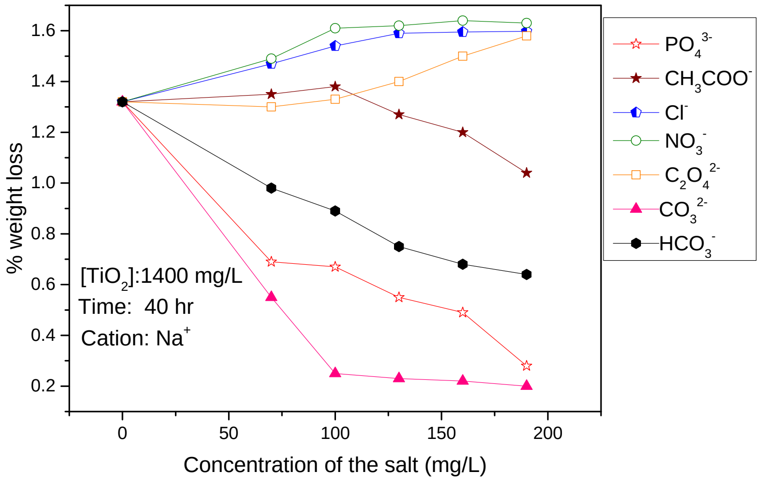


Figure 4.31: Effect of various anions on the photocatalytic degradation of LDPE plastic in presence TiO_2

In the case of NO_3^- and Cl^- the degradation of LDPE increases moderately with increase in concentration of the anions upto 100 mg/L and levels off thereafter. In the case of $C_2O_4^{2-}$ and CH_3COO^- ions the degradation is not affected at lower concentration of the anions. However, as the concentration increases above 100mg/L, oxalate enhances the degradation while acetate inhibits the degradation. The degradation of LDPE is severely inhibited in the presence of HCO_3^-, PO_4^{3-} and CO_3^{2-} ions.

Since 100mg/L is found to be the approximate optimum concentration for many anions tested above, the effect of a series of other anions on TiO_2/UV mediated degradation of LDPE is also evaluated at this concentration.

Comparative effect of various anions at this concentration of 100mg/L on the photocatalytic degradation is presented in Figure 4.32.

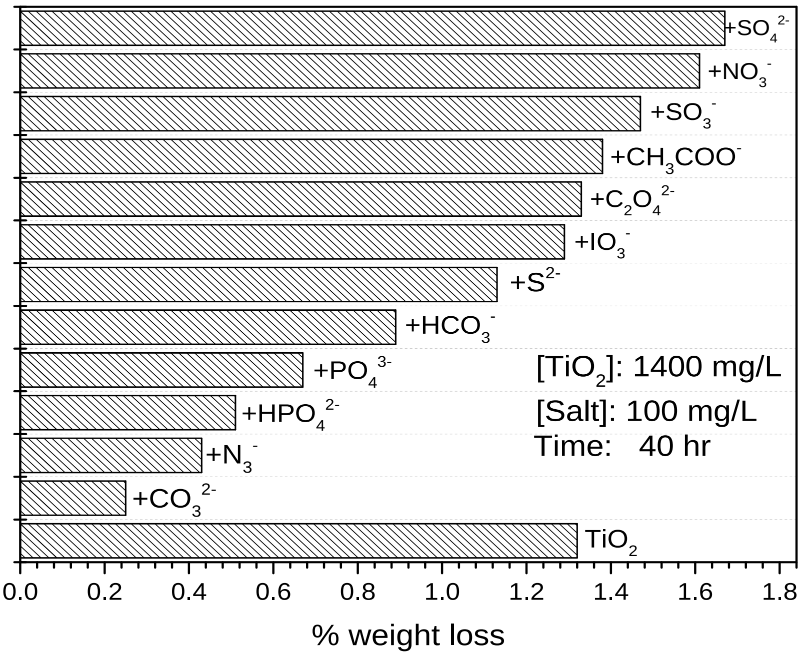


Figure 4.32: Effect of various anions on the photocatalytic degradation of LDPE in presence of TiO_2

The study shows that anions such as CO_3^{2-}, N_3^-, HPO_4^{2-}, PO_4^{3-}, HCO_3^- and S^{2-} inhibit the degradation of LDPE plastic while anions such as IO_3^-, $C_2O_4^{2-}$ and CH_3COO^- have more or less no impact at least at the concentration used in the current study. Anions such as SO_3^{2-}, NO_3^- and

SO_4^{2-} enhance the degradation moderately in the order $SO_4^{2-} > NO_3^- > SO_3^{2-}$.

Figure 4.31 shows that chloride anion enhances the degradation of plastic mildly under photocatalytic condition. Hence the effect of other halides also is examined. Figure 4.33 shows the comparative effect of various halides on the photocatlytic degradation of LDPE on TiO_2. The anions F^-, Cl^- and Br^- ions are found to enhance the degradation slightly in the order $Cl^- > F^- > Br^-$ whereas I^- ions strongly inhibit the degradation.

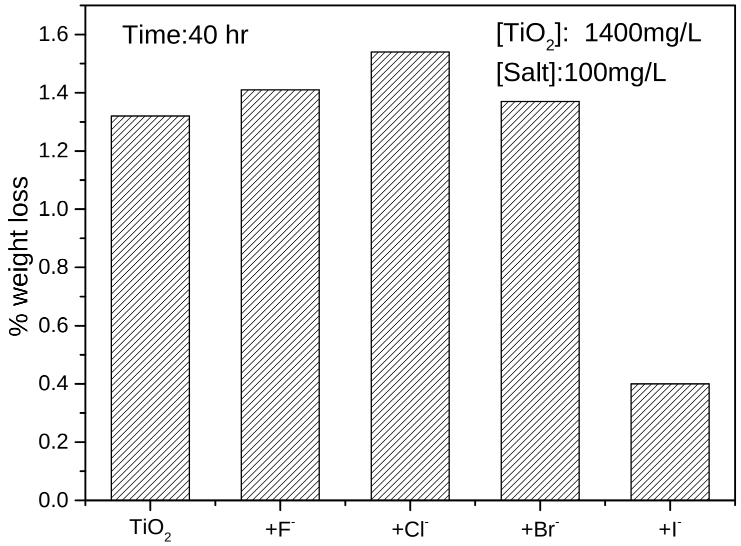


Figure 4.33: Effect of various halides on the photocatalytic degradation of LDPE in presence of TiO_2

The results show that the effect of anions/salts on the AOP degradation of LDPE plastics does not follow any consistent pattern. This is similar to many earlier reports on the effect of anions in AOPs [170].

Same anion can function as ‘inhibitor’ or enhancer depending on the relative concentration, nature of the substrate, reaction time, catalyst and other components, presence of cross-contaminants and the source activation (light, sound, MW etc) etc [170]. Some of the parameters which can influence the anion effect are briefly discussed below.

4.4.6.1 Adsorption of anions on the catalyst

In the case of most AOPs, anions are reported to inhibit the degradation of the pollutants, which is often attributed to the competitive adsorption and consequent reduction in the number of active sites on the catalyst available for the substrate. This can also affect the activation of the catalyst and inhibit the formation of reactive oxygen species (ROS).

The inhibition by anions can be broadly explained by the general mechanism of photocatalysis. In the current instance, experiments were conducted at ~ pH 6.0, which is below the PZC of TiO_2 (6.3). Hence, the semiconductor particles will be carrying positive charge. Consequently, the anions can be strongly adsorbed onto these particles through ionic forces. This will affect the efficiency of the catalyst to absorb the light, get activated and generate electron-whole pairs. Detailed mechanism of photocatalysis is explained in section 4.4.17. The interaction of surface holes (which are responsible for the oxidation of the substrate) with these undesirable ions leads to a decrease in the formation of hydroxyl radicals, resulting in low photocatalytic efficiency. PO_4^{3-} ions are well known to get strongly adsorbed on the surface of semiconductor oxide [170]. Adsorption of PO_4^{3-} on TiO_2 is confirmed from the FTIR spectrum of pure TiO_2, pure Na_3PO_4, and ‘TiO_2 brought in contact with Na_3PO_4’

(figure 4.34). Characteristic bands of PO_4^{3-} are seen in the case of 'TiO$_2$ brought in contact with Na_3PO_4' showing the strong adsorption.

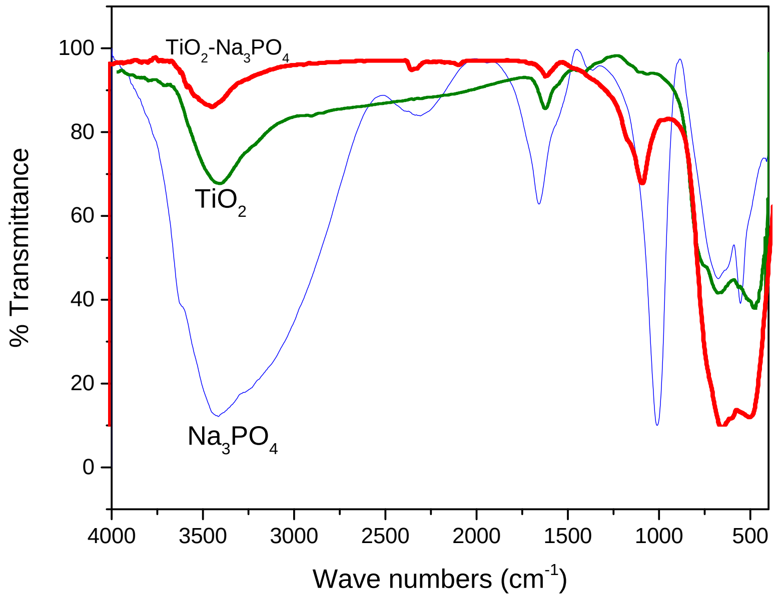


Figure 4.34: FTIR spectrum showing adsorption of phosphate on TiO_2

Similar adsorption is proven in the case of many other anions also. However, more than, simple competitive adsorption and blocking of surface sites there may be other reasons also for the strong influence of anions on photocatalytic processes.

4.4.6.2 Scavenging effect of anions

Anions are also known to scavenge the highly reactive $^{\cdot}OH$ radicals which results in their decreased availability for the degradation of plastic. The scavenging rate constants of $^{\cdot}OH$ by some of the anions tested here are summarized in table 4.1 [171-173].

Table 4.1: The scavenging rate constants of $^{\cdot}OH$ by some of the anions

Anions	**Scavenging Rate constants ($mol^{-1}s^{-1}$)**
Cl^-	4.3×10^9
CO_3^{2-}	3.9×10^8
SO_4^{2-}	1×10^{10}
$H_2PO_4^-$	2×10^4
Ac^-	7.0×10^7
HCO_3^-	8.5×10^6
NO_3^-	1.4×10^8
Br^-	1.06×10^8
I^-	1.1×10^{10}

The scavenging rate constant values of SO_4^{2-} and I^- are high and similar. However, I^- inhibits the degradation while SO_4^{2} enhances it. Comparison of the effect of various other anions, with the scavenging rate constant values also shows that there is no direct correlation between them in the case of many of the anions.

4.4.6.3 Surface layer formation

Another possible reason for the inhibitory effect of anions towards the photocatalytic degradation of pollutants is the formation of an inorganic layer on the surface of the catalyst. The efficiency of the inorganic layer formation is reported to depend on the solubility of the salts [174]. Salts with higher solubility show lower layer formation. The solubility of some of the salts (in mg/g of water at 20^0C) used in the study is in the order;

NaI (191) > NaBr (98.4) > $NaNO_3$ (94.9) > CH_3COONa (54.6) > Na_2SO_4 (40.8) ≥ Na_2CO_3 (39.7) > NaCl (36.1) > Na_3PO_4 (16.3) > NaHCO3 (11.1) > NaF (4.22) > $Na_2C_2O_4$ (3.81)

The layer formation will be in the reverse order, i.e.

$C_2O_4{}^{2-} > F^- > HCO_3{}^- > PO_4{}^{3-} > Cl^- > CO_3{}^{2-} > SO_4{}^{2-} >$ CH3COO$^-$ $>$
$NO_3{}^- > Br^- > I^-$

If the layer formation by the anions is a cause of inhibition, $C_2O_4{}^{2-}$ and F^- ions with highest tendency for layer formation are expected to show maximum inhibition towards LDPE degradation. Similarly I^- ions with the least layer formation is expected to show the least inhibition. This is not followed in the degradation of LDPE. Even though there is no strict correlation between the layer formation and inhibition, it may be inferred that generally the inhibition by $PO_4{}^{3-}$, $CO_3{}^{2-}$, HCO_3- etc can be correlated at least partially with the layer formation. It is also possible that more soluble anions can influence the processes in the liquid bulk thereby generating more (or less) reactive species which may enhance or inhibit the degradation as the case may be.

$PO_4{}^{3-}$ is a stronger inhibitor but posses very low scavenging rate constant while $NO_3{}^-$ and $SO_4{}^{2-}$ are enhancers and have a higher scavenging rate constant. The scavenging rate constants of other anions also indicate the lack of correlation of this parameter with the anion effect.

The formation of radical anions by interaction of the anion and $^{\cdot}OH$ is presented in the following reactions.

$^{\cdot}OH + NO_3^- \rightarrow OH^- + NO_3^{\cdot}$ ....(39)

$^{\cdot}OH + SO_4^{2-} \rightarrow OH^- + SO_4^{-\cdot}$ ....(40)

$^{\cdot}OH + HCO_3^- \rightarrow H_2O + CO_3^{-\cdot}$ ....(41)

$^{\cdot}OH + CO_3^{2-} \rightarrow OH^- + CO_3^{-\cdot}$ ....(42)

$CH_3COO^- + {}^{\cdot}OH \rightarrow OH^- + CH_3COO^{\cdot}$ ....(43)

$CH_3COO^{\cdot} \rightarrow CH_3^{\cdot} + CO_2$ ....(44)

$^{\cdot}OH + Cl^- / Br^- / I^- \rightarrow OH^- + Cl^{\cdot} / Br^{\cdot} / I^{\cdot}$ ....(45)

$Cl^{\cdot} + Cl^- \rightarrow Cl_2^{-\cdot}$ ....(46)

$Br^{\cdot} + Br^- \rightarrow Br_2^{-\cdot}$ ....(47)

$I^{\cdot} + I^- \rightarrow I_2^{-\cdot}$ ....(48)

These radical anion species such as $CO_3^{-\cdot}$, $NO_3^{-\cdot}$, $Cl_2^{-\cdot}$, $CH_3^{\cdot}$ etc can also react with and oxidize the organic compound even though less efficiently than $^{\cdot}OH$ [171]. The radical anions undergo slower radical-radical recombination or deactivation compared to $^{\cdot}OH$. They are therefore more readily available in the system for longer time to react with the substrate and effect the degradation for longer time compared to the $^{\cdot}OH$ radicals. Hence the relatively low reactivity of the radical anion species is compensated by their better and sustained availability for the substrate. In the absence of any reaction with the anions, some of the $^{\cdot}OH$ would get deactivated by recombination forming H_2O_2 or even (H_2O+O_2). Hence it can be assumed that the anions are indirectly protecting the $^{\cdot}OH$ radicals from deactivation by unproductive recombination and/or other reactions. The enhancement of the degradation of LDPE in presence of anions is possible only when the reaction rate between anions and $^{\cdot}OH$, which results in the formation of radical anions is higher compared to that between substrate and $^{\cdot}OH$. The more frequent interaction of the readily available radical anion with the substrate, compared to the $^{\cdot}OH$ radical which takes part in a number of interactions including self-destroying recombination, can be a reason for the enhancement by the anions. However when the anions do not form reactive radical anions and interfere with the surface processes as explained earlier, enhancement is not possible and instead inhibition can result.

In view of the complexity of the anion effect, it may not be appropriate to draw general conclusions or commonly applicable explanations. For example in the case of NO_3^- ion the enhancement can also be linked to direct and indirect formation of $^{\cdot}OH$ radical as follows [175]

$NO_3^- + h\nu \rightarrow NO_2^- + O$ ....(49)

$NO_3^- + H_2O + h\nu \rightarrow NO_2^- + {}^{\cdot}OH + {}^{\cdot}OH$ .... (50)

$O + H_2O \rightarrow 2{}^{\cdot}OH$ .... (51)

Similarly in the case of SO_4^{2-} and SO_3^{2-} also, the $SO_4^{-\cdot}$ and $SO_3^{-\cdot}$ formed by interaction with the anions are efficient oxidisers which lead to the enhancement in the degradation of LDPE.

4.4.6.4 Steric effect

The size of the anion may be an important factor that influences its effect on the photocatalytic activity of TiO_2 and degradation of organic pollutants, especially when surface initiated process is important.

Bigger ions may block more surface sites on the catalyst even at lower concentration, which prevents the access of the substrate molecule to the catalyst surface and may inhibit the degradation. In order to verify this, the case of halide ions is considered. The size of the anions decreases in the order $I^- > Br^- > Cl^- > F^-$ as shown in table 4.2.

Table 4.2: Ionic radius of halide ions

Halide ion	Ionic radius (nm)
F^-	0.136
Cl^-	0.181
Br^-	0.195
I^-	0.216

Accordingly the inhibition/slowdown of enhancement must be in the order $I^- > Br^- > Cl^- > F^-$. In the current study this order is followed in the case of I^-, which is a strong inhibitor. Cl^- acts as a better enhancer than F^-. It is also possible that the smaller ions can occupy surface sites more effectively especially at higher concentration and influence the surface processes. However, as in the case of many earlier studies, in this case also no consistent conclusions on the correlation of anion effect with any single parameter is possible. For example, the CO_3^{2-}anions which are of smaller size (thermochemical radius: 178pm) inhibit the degradation. SO_4^{2-} (thermochemical radius: 230pm) enhances the degradation over a wider concentration range while PO_4^{3-} (thermochemical radius: 238pm) inhibits the degradation. This shows that there cannot be any consistent correlation between steric factors of the anions and their effect on the photocatalytic degradation.

Presence of salts is known to diminish the colloidal stability. This is followed by surface charge neutralization which increases the mass transfer limitation and reduces the contact of the pollutants with the catalyst. Screening of the UV light, competitive adsorption at the surface sites, competition for photons, surface layer formation and deposition of elemental metals, radical and hole scavenging etc. can influence the photocatalytic degradation. Depending on the domination of one or more of these factors in the reaction system, the anion effect can be ‘inhibition’,’no effect’ or ‘enhancement’.

In general it may be concluded that the ‘anion effect’ depends on a number of parameters and complex interactions in the reaction system. Hence it is not possible to draw any general conclusions on the effect of anions on the photocatalytic degradation of organic pollutants in water. For every pollutant/catalyst system, the effect of each anion has to be evaluated individually.

4.4.7 Effect of cations

The effect of anions cannot be fully delineated from the effect of respective cations. Hence the effect of various cations on the photocatalytic degradation of LDPE was also studied keeping the anion same (Cl^-). Among the cations which were subjected to study, K^+, Ba^{2+} and Na^+ were found to enhance the degradation while Ca^{2+} have almost no effect on the degradation. Al^{3+} inhibits the degradation moderately. The results are shown in figure 4.35.

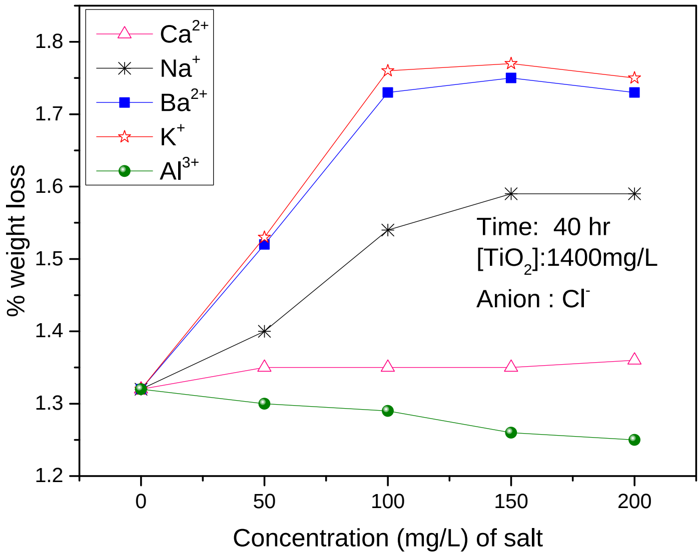


Figure 4.35: Effect of various cations on the photocatalytic degradation of LDPE plastic on TiO_2

Hence the mild positive effect of Cl^- (NaCl salt) can also be due to the positive effect of Na^+ as well. The stronger enhancement by KCl and $BaCl_2$ compared to that by NaCl shows that K^+ ions and Ba^{2+} ions do play a significant role in the enhancement. This can be further verified by keeping the cation same and varying the anion.

The effect of various potassium salts on the photocatalytic degradation of LDPE plastic in presence of TiO_2 is studied and the results are shown in figure 4.36. The study shows that all the potassium salts which were subjected to the study enhance the degradation mildly except KI which is a strong inhibitor just as in the case of NaI. This shows that the enhancing effect of K^+ is more than neutralised and overtaken by the inhibiting effect of I^-. I^- is known to be a strong scavenger of $^{\cdot}OH$ radicals and inhibit the degradation of most organics under AOP involving the participation by $^{\cdot}$OH radicals. Hence it may be inferred that, in the case of salts, it is the anion that has more influence as its characteristic than the cations, especially with respect to their effect on photocatalysis.

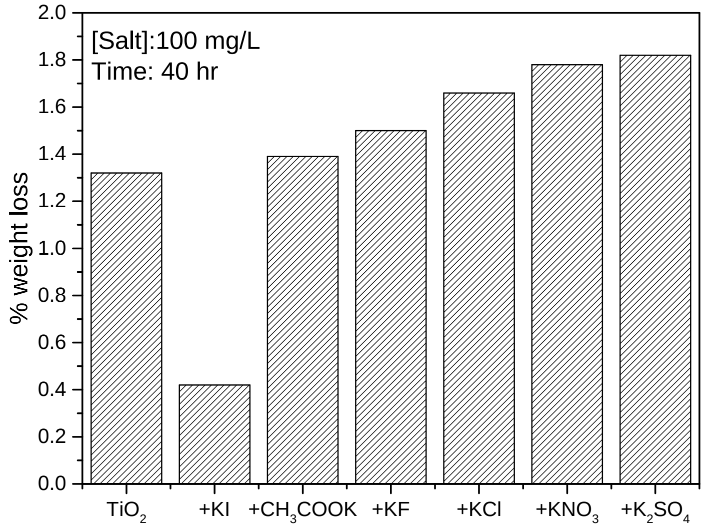


Figure 4.36: Effect of various potassium salts on the photocatalytic degradation of LDPE in presence of TiO_2

The comparatively superior enhancing efficiency of K^+ in relation to Na^+ on the degradation of LDPE is further verified in the case of the oxidant PDS by using both Na^+ and K^+ salts (persulphate). Higher enhancement in the degradation is observed with potassium persulphate (figure 4.37) which reconfirmed the enhancing effect of K^+ cation on the photocatalytic process, at least in the case of LDPE degradation.

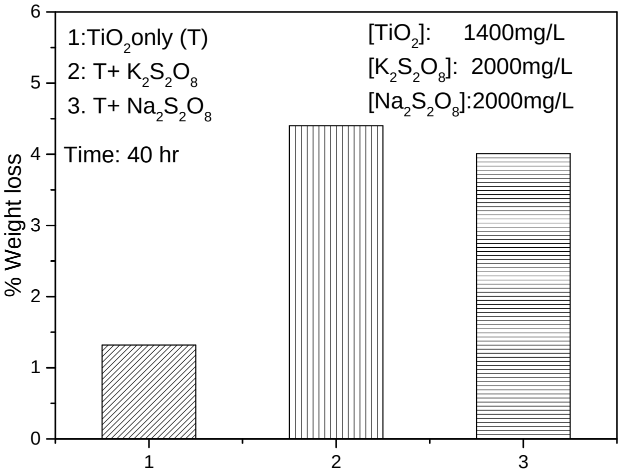


Figure 4.37: Comparative efficiency of $K_2S_2O_8$ and $Na_2S_2O_8$ on the Photocatalytic degradation of LDPE in presence of TiO_2

4.4.8 Effect of anions on TiO_2/PDS/UV system

TiO_2/PDS/UV has been observed to be very efficient for the degradation of LDPE. Hence the effect of various anions on the photocatalytic degradation of LDPE under TiO2/PDS/UV was investigated keeping the cation as Na^+ and the results are shown in figure 4.38. The effect is comparable to the effect of respective anions on the TiO_2 photocatalytic degradation of LDPE. NO_3^-, SO_4^{2-} and Cl^- enhance the degradation while CO_3^{2-}, HCO_3^- PO_4^{3-} etc inhibit, though mildly.

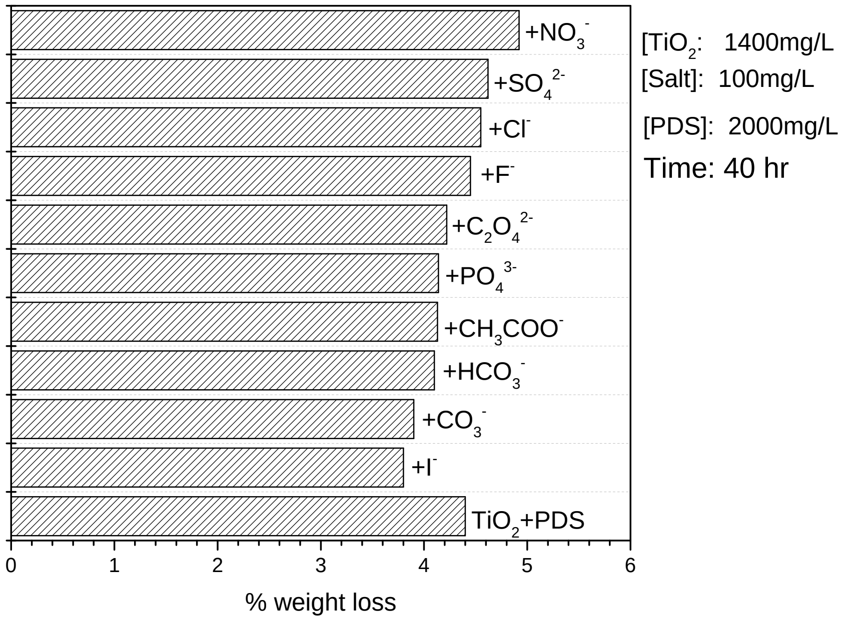


Figure 4.38: Effect of various anions on the photocatalytic degradation of LDPE plastic in presence of TiO_2+PDS

However the effect is not significant enough to be of any major consequence on the TiO_2/PDS system. It may be concluded that in the presence of powerful oxidant like $K_2S_2O_8$, the effect of anions at the concentrations tested here is not significant. Even moderately strong inhibitors like CO_3^{2-} and HCO_3^- have only mild effect in presence of PDS. Similarly enhancers such as SO_4^{2-} and NO_3^- do not have much effect in this case. Hence TiO_2/PDS is an efficient system which can be used for the photodegradation of LDPE even in natural water containing a variety of salt contaminants.

4.4.9 Degradation of LDPE plastic in sea water

It has been widely reported that a good percentage of used plastic materials end up in the oceans and other water bodies. Because of the presence of salts and various physicochemical characteristics of sea water, the degradation of these plastics is extremely slow. Debris composed of plastic, is one of the most persistent pollution problems affecting our oceans and inland waterways [176]. Plastic pollutants are causing major hazards to marine environment and ecology. Properties of plastics such as buoyancy and durability aggravate the problem [177-178]. Since the chemical as well as physical and biological characteristics of sea water are different from those of fresh water, the rate of degradation of pollutants also will be different. In this context, the degradation of LDPE in actual sea water is investigated. The moderate enhancement of the degradation of LDPE plastic by Cl^- and other anions suggested the possibility of enhanced degradation in salt rich sea water. The relative rate of degradation of plastic in sea water vs regular water is investigated here under the optimized conditions. Characteristics of water collected from the Arabian sea are given in table 4.3. The results of the degradation are shown in the figure 4.39.

Table 4.3: Characteristics of sea water relevant in photocatalysis

Water sample	**pH**	**Total Dissolved Salts(TDS) (mg/L)**	**Total Hardness (mg/L)**	**Chloride (mg/L)**	**Dissolved oxygen (mg/L)**	**Phosphate (mg/L)**	**Nitrate (mg/L)**	**Sulphate (mg/L)**	**Turbidity (NTU)**
Sea water	~8.2	~35000	~7700	~22500	~7	~4	~10	~5320	~2.0

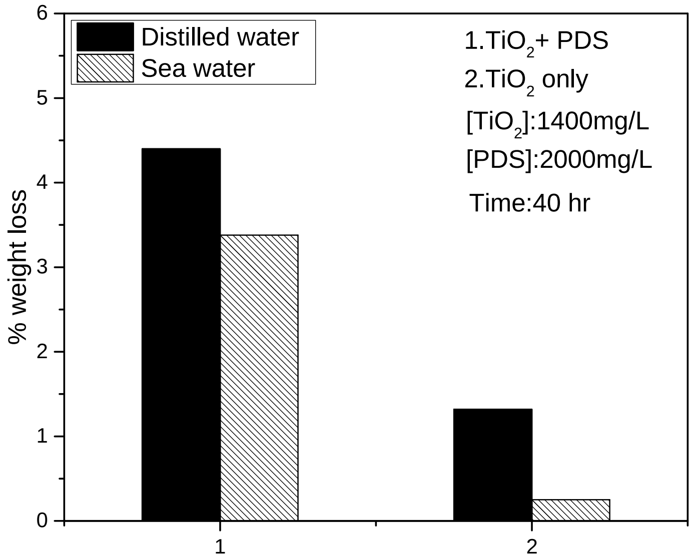


Figure 4.39: Comparative photocatalytic degradation of LDPE plastic in sea water and distilled water

Photocatalytic degradation of LDPE in sea water is much less compared to that in distilled water with only TiO_2 as the photocatalyst. Even in the presence of oxidant also, the degradation is less in sea water. However, in this case, the decrease in degradation is comparatively less. Sea water contains a large amount of dissolved salts. Concentration of dissolved salts in sea water is approximately 35000mg/L, the most important among them being the chloride. As reported earlier in this chapter (figure 4.31, 4.33) presence of NaCl enhances the degradation of LDPE plastic at lower concentrations. However in the case of sea water, with higher concentrations of the salt, the degradation is severely inhibited. Hence it is possible that the effect of salts/anions is concentration dependant. In order to verify this, the effect of NaCl on the degradation of LDPE plastic is investigated at higher concentrations varying from

20-20,000mg/L. The solution is prepared in distilled water. The results are plotted in figure 4.40.

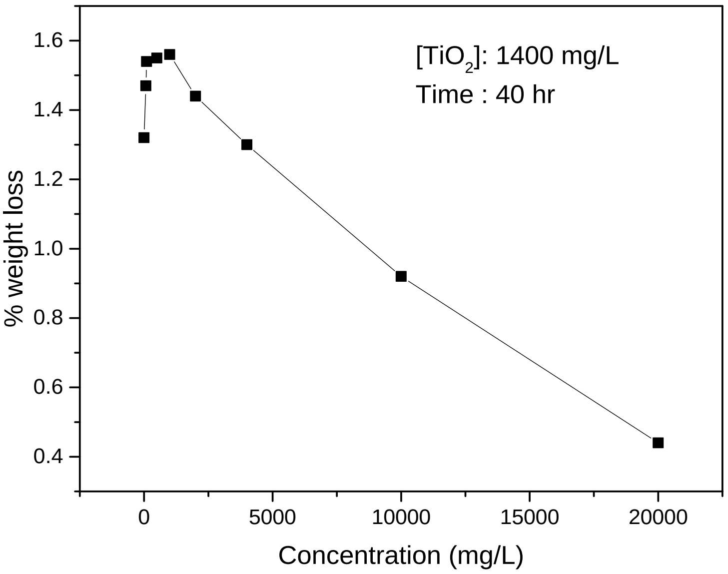


Figure 4.40: Effect of NaCl at various concentrations on the photocatalytic degradation of LDPE plastic in presence of TiO_2

The data clearly shows that chloride at higher concentration can inhibit the degradation. The degradation rate dropped from 1.54% to 0.4% as the concentration of NaCl increased from 100mg/L to 20,000mg/L. This result agrees with the very low degradation rate observed in real sea water. This is also in agreement with the earlier results reported from our laboratory on the concentration and reaction time dependence of anion effect [170]. Even those anions which were enhancers of the photocatalytic degradation of phenol at low concentrations eventually became inhibitors at higher concentration and after extended reaction time. This may lead to the conclusion that plastic waste present in sea water degrades very slowly compared to that present in fresh water bodies. Hence it is all the more important that our oceans have to be protected from any kind of plastic pollution. The comparative results in the presence of TiO_2 and TiO_2+PDS show that the inhibition of the degradation caused by higher concentration of the salts can be minimised to a great extent by the oxidiser. However, the feasibility of using persulphate as an oxidant or any other alternatives for the degradation of plastics in the ocean needs more in-depth investigations.

4.4.10 Effect of carbon

Presence of carbon in certain semiconductor oxides has been reported to enhance the photocatalytic activity [179]. Presence of active carbon at different concentrations serves as an effective template. Upon calcinations carbon is eliminated leaving features favourable for surface–substrate interaction and the generation of more ROS [180]. This possibility is tested in the current study. At the optimised concentration of TiO_2, carbon particles are intimately mixed with it at different concentrations, calcined at 350^0C and the activity of the combination is tested for LDPE degradation under optimum reaction conditions. TiO_2 calcined with carbon (TC) shows slightly enhanced degradation. However, the enhancement is much less compared to that in presence of PDS or H_2O_2. The effect of TC + oxidants is tested with TC+PDS and TC+H_2O_2. In this case there is not much enhancement over that in the case of TiO_2+oxidant. The results are shown in figure 4.41 and figure 4.42.

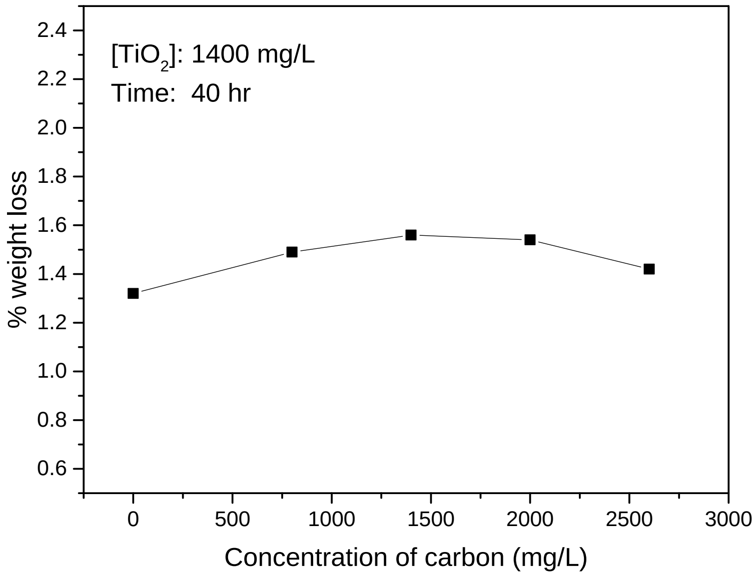


Figure 4.41: Effect of 'TiO$_2$ calcined with carbon (TC)' on the photocatalytic degradation of LDPE

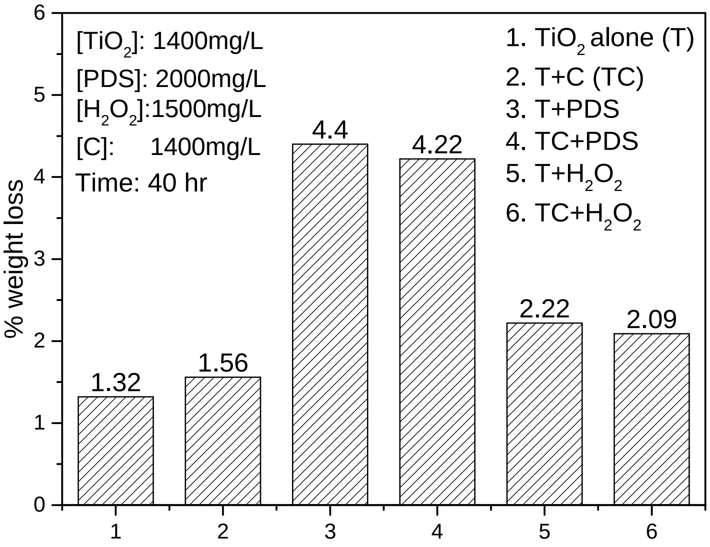


Figure 4.42: Effect of calcination of TiO$_2$ with carbon (TC) on of the photocatalytic degradation of LDPE plastic in presence of PDS and H$_2$O$_2$

Hence it is concluded that the addition of carbon or the carbon treatment has no extra enhancing effect on TiO_2 or PDS- TiO_2 or H_2O_2-TiO_2. Hence this approach was not pursued further.

4.4.11 Effect of colour of the plastic sheet on the degradation

Plastic carry bags are often available in different colours and shades. The colour may influence the rate of photodegradation of the LDPE plastic. Detailed investigation of the role of colour on the environmental/photo-degradation of plastic is beyond the scope of the present study. Hence a preliminary investigation is made to find the effect of colours of the plastic on the photocatalytic degradation. Waste plastic carry-bags of different colours are collected from the litter for the study. Figure 4.43 shows the coloured plastic strips used in the study.

Figure 4.43: Samples of coloured LDPE plastic

All plastic sheets are of 41 micron thickness. The strips are suspended in water containing the optimised concentration of TiO_2 and

PDS and are then irradiated for 40 hr under UV light. The degradation (represented as weight loss) is shown in figure 4.44. It is observed that the colour has no impact on the degradation rate. All the samples give more or less same degradation as that of colourless one.

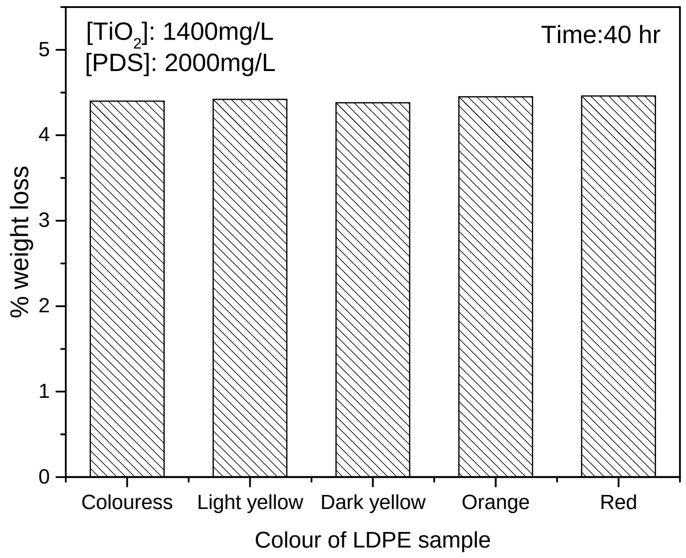


Figure 4.44: Effect of colour of the plastic on the photocatalytic degradation rate in presence of TiO_2/PDS/UV

4.4.12 Effect of thickness of plastic sheet

The thickness of plastic product available in the market varies depending on their intended use. Hence, the effect of thickness of plastic sheet on the photocatalytic degradation was studied by taking three plastic sheets of different thickness ie, 31microns, 41microns and 51microns. The length, breadth and hence the surface area exposed to UV is the same in all cases. The results presented in table 4.4 show that irrespective of the thickness, the weight loss is more or less same.

Table 4.4: Effect of thickness of LDPE plastic sheet on its photocatalytic degradation in presence of TiO_2 and PDS

Thickness of Plastic sheet (microns)	Weight of sample (g)	Weight loss in 40 hr (g)
31	0.22	0.0142
41	0.33	0.0145
51	0.39	0.0143

The results show that the rate of degradation is independent of the thickness of the sheet as long as the surface area (of the plastic sheet) exposed to UV irradiation is the same. This observation is significant in the field application because it demonstrates that the thickness of the plastic waste is immaterial for the efficiency of the photodegradtion.

4.4.13 Role of O_2/air in photocatalysis

Oxygen plays an important role in photocatalytic degradation reactions by scavenging the electrons generated on photo activated TiO_2 and thereby inhibiting the recombination of electrons and holes. The electron is picked up by O_2 to generate superoxide radical anion and other reactive species (Details are discussed in section 4.4.17). Thus both the electrons and holes will be available for the formation of free radicals and further interaction with the pollutant. Hirakawa et al. [181] demonstrated the role of dissolved O_2 and superoxide ion in TiO_2 photocatalysis and even developed a method to follow photocatalytic reactions by measuring the consumption of dissolved oxygen. In order to confirm the effect of O_2 on the photocatalytic degradation of LDPE, the reaction system is deaerated with N_2 and the experiments were carried out under otherwise identical conditions. The results are shown in figure 4.45 which shows that the photocatalytic degradation of LDPE proceeds slowly in systems deaerated with N_2. This confirms that O_2 plays an important role in the photocatalytic degradation of LDPE. The effect of deaeration is less in the system TiO_2/PDS indicating that the persulphate can make up for the O_2 removed by N_2 bubbling at least partially. The PDS also can act as an electron acceptor thereby preventing the recombination of electrons and holes, as done by the O_2 in the system. More details are discussed in section 4.4.17.

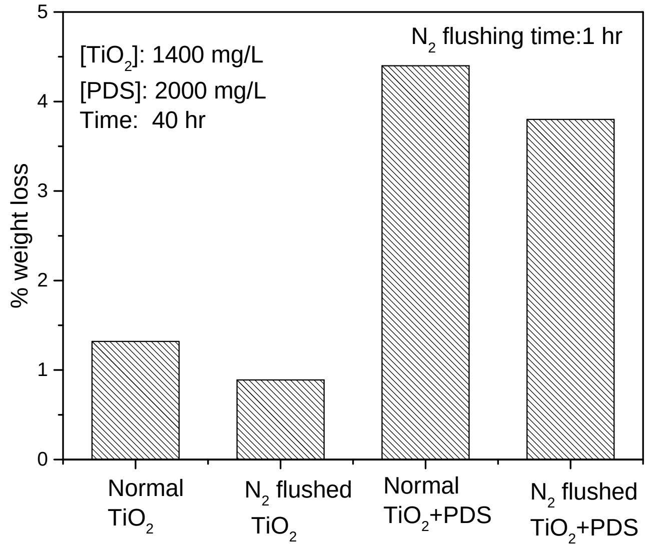


Figure 4.45: Effect of deaeration (by N_2 flushing) on the photocatalytic degradation of LDPE

4.4.14 Recycling of TiO_2

The efficiency of any photocatalytic process depends on the possibility of using the catalyst repeatedly with or without treatment. The commercial application of photocatalysis depends on the economy of the process. In this respect the recycling of the catalyst is very important. Hence the possibility of recycling of used TiO_2 for the photocatalytic degradation of LDPE is tested. The catalyst used (for 40hr) with and without PDS is filtered, washed with distilled water, dried at room temperature (~35^0C) until constant weight is reached and then used as catalyst again in fresh experiments. The activity was found to be same (as seen from the weight loss of plastic in successive experiments) showing that the catalyst can be reused many times without loss of efficiency. However in the current study the catalyst was used only for shorter duration (in terms of plastic degradation). It is possible that the catalyst will remain active for longer periods, for many recycles since the surface sites are not used for adsorption of any substrate. The role of the catalyst is to absorb light, get activated and generate reactive free radicals. Unlike in the case of organic pollutants soluble in water, there is no possibility of adsorption of the substrate or the intermediate on the surface. The catalyst is almost exclusively available for the generation of reactive oxygen species. The results of LDPE degradation using recycled TiO_2 with and without PDS are shown in figure 4.46 and figure 4.47. Each time, the catalyst was used for 40 hr degradation reaction under UV irradiation, separated thereafter, washed and dried as explained above before reuse again. In both cases, the catalytic activity remains more or less intact after repeated use with only marginal decrease.

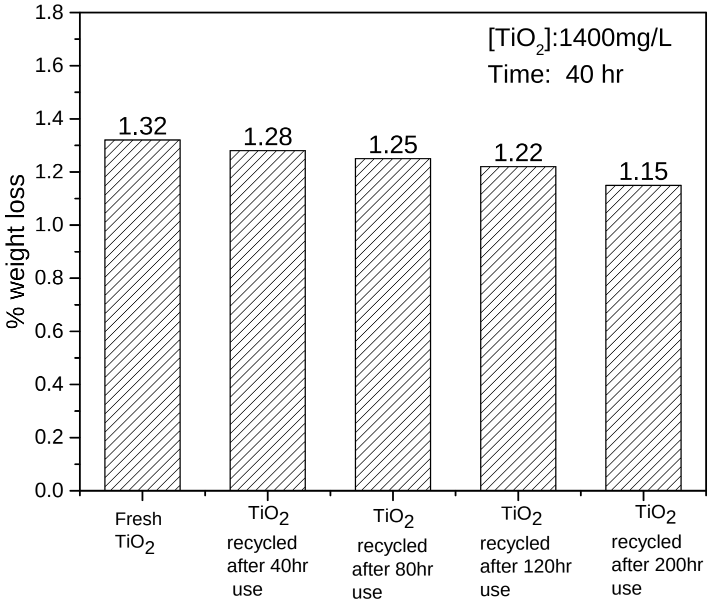


Figure 4.46: Effect of recycled TiO_2 for the photocatalytic degradation of LDPE plastic

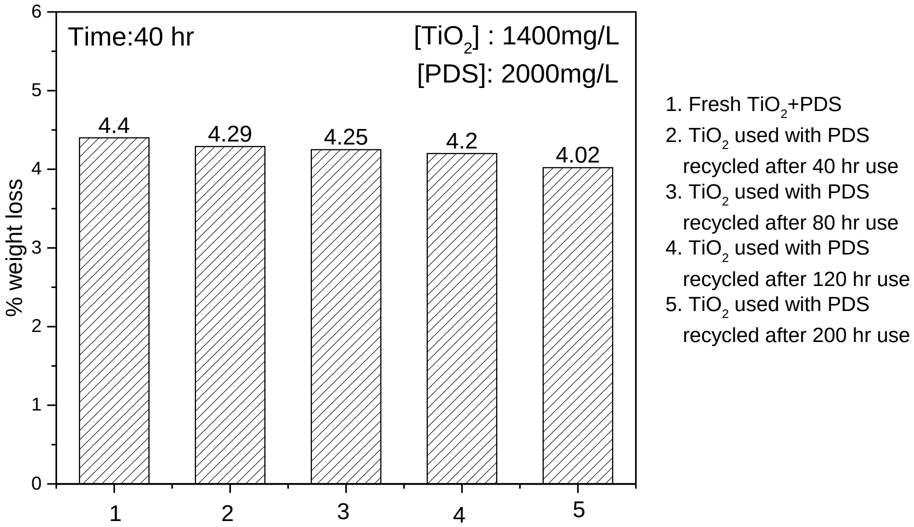


Figure 4.47: Effect of recycled TiO_2 for the photocatalytic degradation of LDPE plastic in presence of PDS

4.4.15 Characterisation of used TiO_2 catalyst

The SEM images of TiO_2 after the phocatalytic process with and without PDS presented respectively in figures 4.48 and 4.49, show that the particles are more agglomerated and non uniform. The average particle size is ~ 150nm.

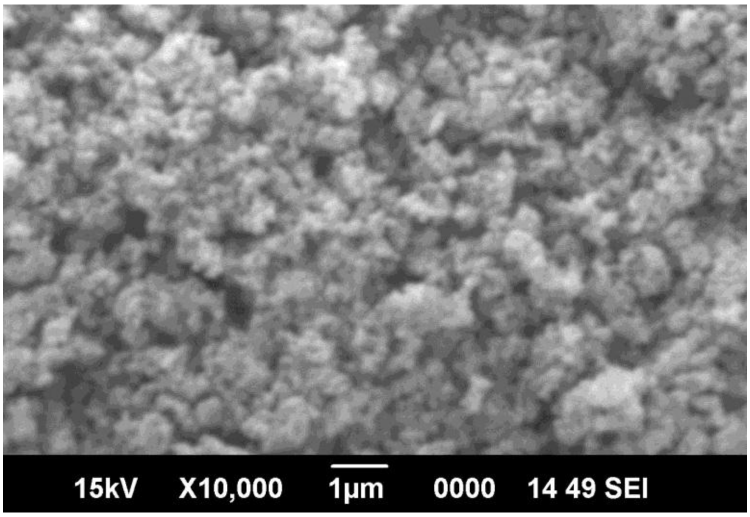


Figure 4.48: SEM image of TiO_2 used for 120 hr

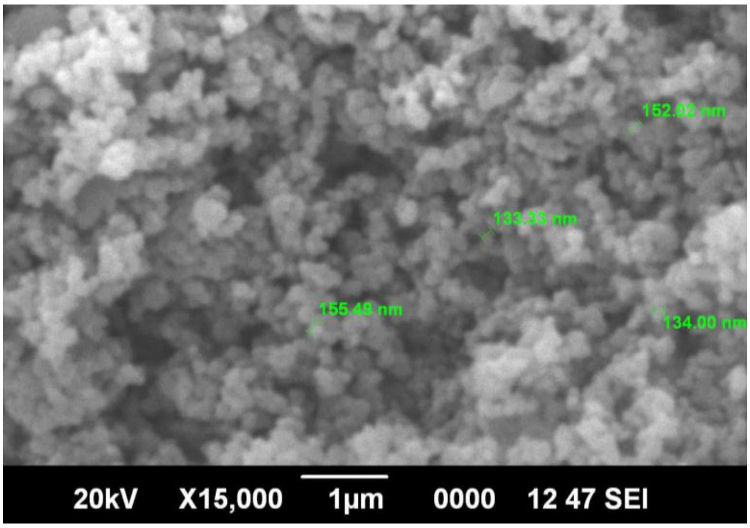
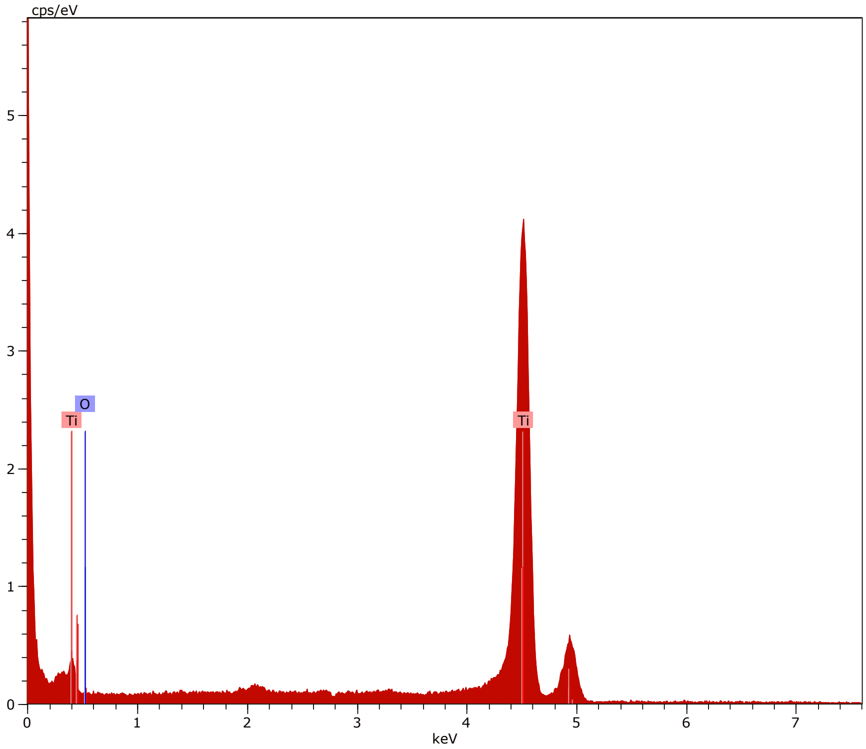


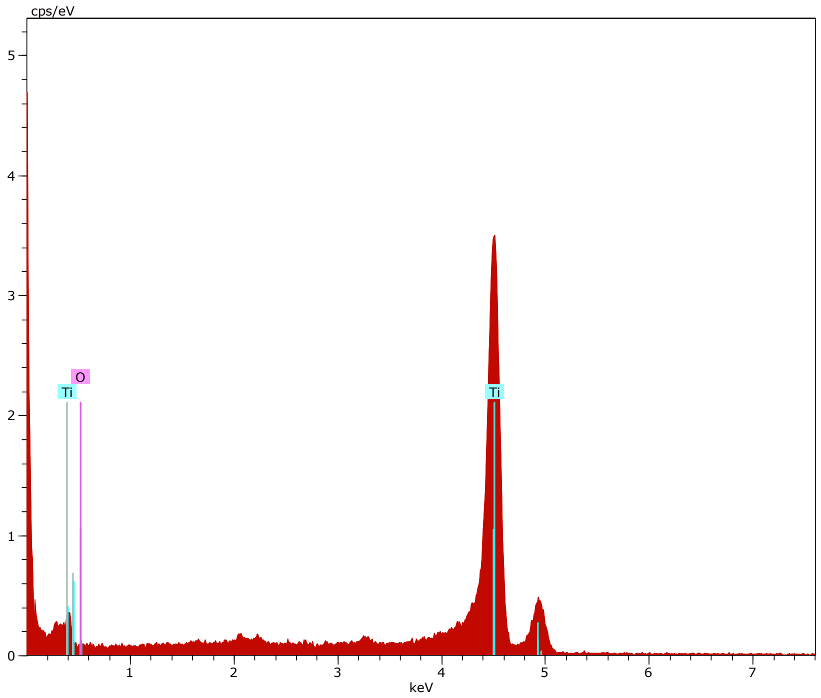
Figure 4.49: SEM image of TiO_2 used with PDS for 120 hr

SEM EDAX images of TiO_2 before and after use for LDPE degradation under irradiation show that the chemical composition remains same. In the presence of PDS, the catalyst gets enriched with O_2.

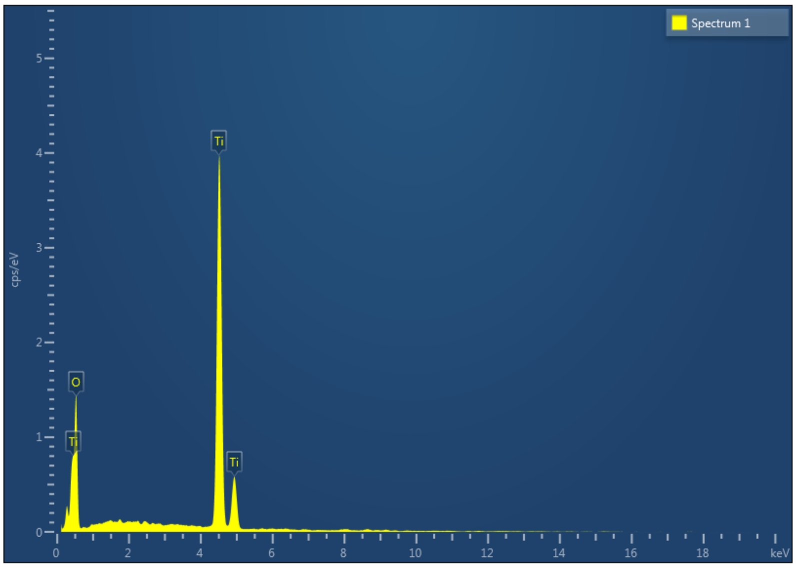
SEM EDAX of fresh and used TiO_2 (with and without PDS) are shown in figures 4.50 (a), (b) and (c).



(a)



(b)



(b)

Figure 4.50: SEM EDAX of (a) fresh TiO_2 (b) TiO_2 used (120 hr) and (c) TiO_2 used with PDS (120 hr)

Comparison EDAX data of TiO_2 before and after the irradiation are shown in table 4.5.

Table 4.5: Comparison of EDAX data of TiO_2 before and after use for the LDPE degradation

Catalyst	At. % of Ti	At. % of O
Fresh	63.67	36.33
Used	62.59	37.41
Used in presence of PDS	25.06	74.94

BET surface area (A) of used TiO_2 in the absence of PDS is 10.3491 m^2/g. Barrett-Joyner-Halenda (BJH) adsorption and desorption cumulative volumes (V) of pores between 17.000 Å and 3000.000 Å width are 0.053904 cm^3/g and 0.054156 cm^3/g respectively. Adsorption average pore width (4V/A) is 211.7812 Å.

BET surface area (A) of used TiO_2 in the presence of PDS is 10.3110 m^2/g. Barrett-Joyner-Halenda (BJH) adsorption and desorption cumulative volumes (V) of pores between 17.000 Å and 3000.000 Å width is 0.051943 cm^3/g and 0.051927 cm^3/g respectively. Adsorption average pore width (4V/A) are 204.2202 Å. These data show that the surface area remains practically unaffected by the use with or without PDS. However the BJH adsorption/desorption volumes of the pores and the average pore width undergo changes (table 4.6).

Table 4.6 : Physical characteristics of TiO_2 before and after UV treatment

Catalyst	BET surface area (m^2/g)	BJH adsorption volume of pores (cm^3/g)	Pore width (Å)
Fresh	10.0236	0.039211	163.3022
Used	10.3491	0.053904	211.7812
Used in presence of PDS	10.3110	0.051943	204.2202

Hence, it may be concluded that the physical characteristics of the catalyst undergo changes after use as a photocatalyst. However, in the current instance, where there is no adsorption of any substrate or intermediate on the surface, this variation is immaterial for the reuse of the catalyst.

The XRD images of used TiO_2 with and without PDS are shown in figure 4.51(a) and (b) respectively.

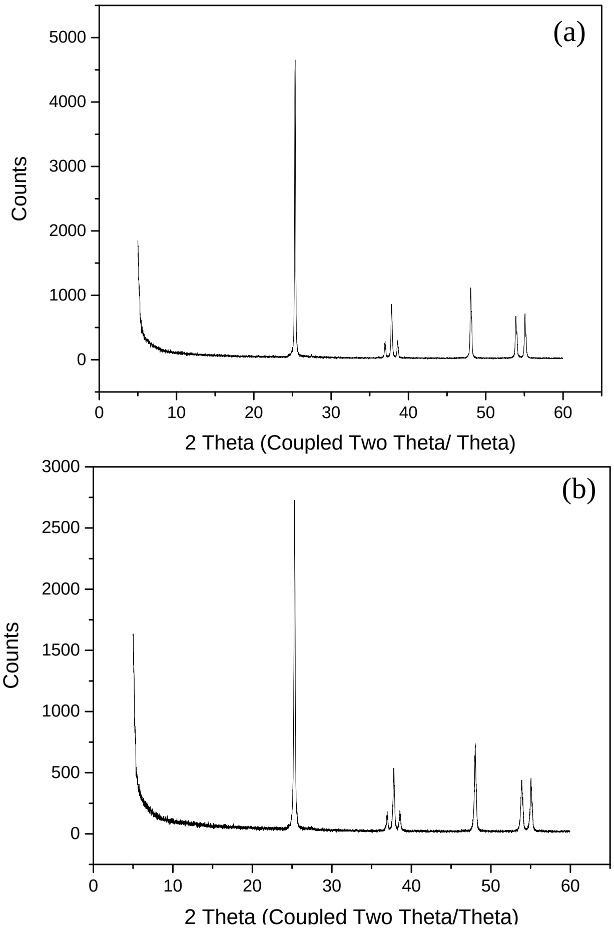


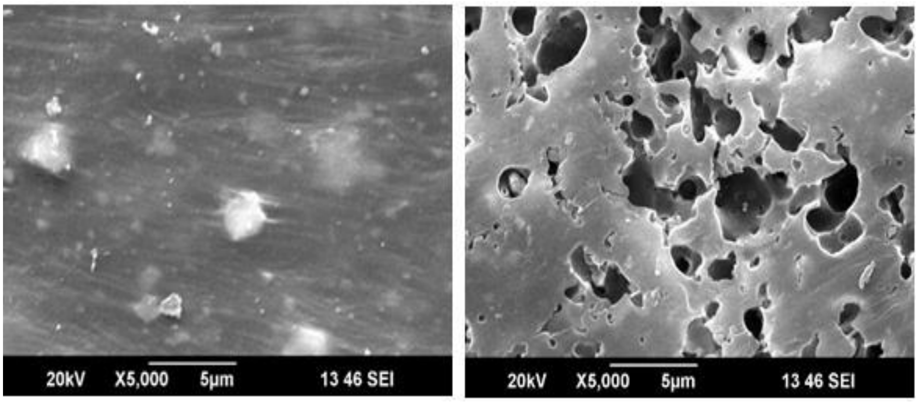
Figure 4.51: XRD of (a) TiO_2 used (120 hr) and (b) TiO_2 used with PDS (120 hr)

The XRD image of fresh TiO_2, when compared with the image of used TiO_2 (with and without PDS) shows that the characteristics remains the same.

4.4.16 Physical and chemical changes in LDPE after photocatalysis

In addition to the determination of weight loss and physical observation, the changes taking place on the plasic sheet under photocatalysis are observed by SEM and FTIR.

SEM images of typical LDPE strips before and after photocatalytic treatment are shown in figures 4.52 (a) and (b) respectively.

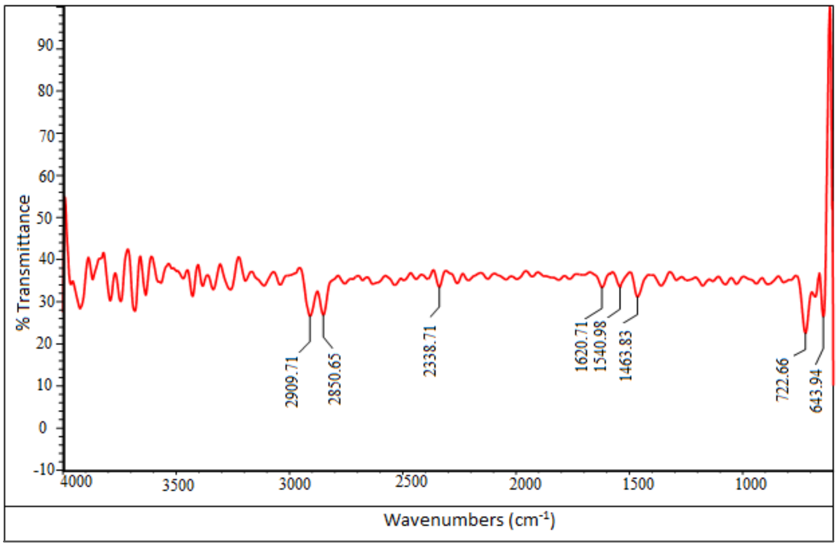


(a) (b)

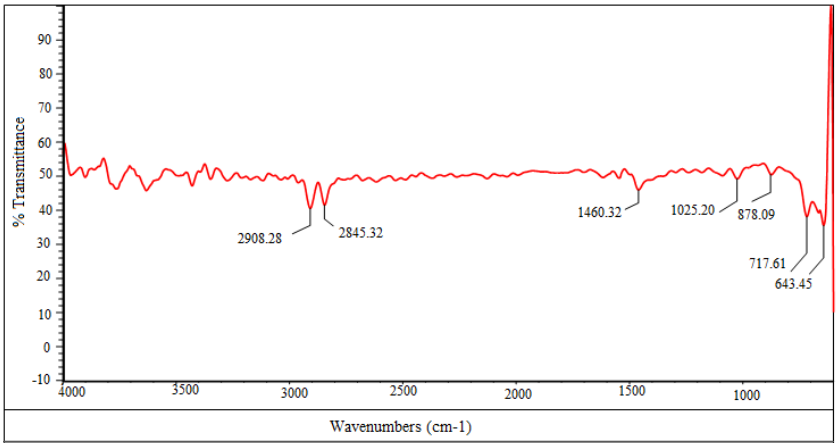
Figure 4.52: SEM images of LDPE (a) before and (b) after Photocatalytic treatment using TiO_2 (1400 mg/L) and PDS (2000 mg/L), Time: 300 hr

The figure clearly illustrates that the surface morphology of plastic is severely changed under photocatalysis. As irradiation progresses, the plastic sheet becomes thinner and thinner, crumbles and breaks. Over 12% of LDPE mineralisation could be achieved in 400 hr time in presence of PDS as oxidizer and TiO_2 as photocatalyst. It is logical to assume that the cavities inside the plastic film also expand under irradiation and the photocatalytic degradation happens both on the surface and inside the film simultaneously.

The FTIR spectra of untreated and treated LDPE plastic are shown in figure 4.53 (a) and (b) respectively.



(a) Untreated



(b) Treated

Figure 4.53: FTIR spectra of (a) untreated and (b) treated LDPE

The spectrum shows that except minor changes, the characteristic bands remain the same before and after photocatalytic treatment. Hence it may be inferred that the degradation does not lead to major structural changes or stable intermediates. Since the spectra were recorded under identical conditions using identical samples, it may be qualitatively inferred from the decrease in the intensity/disappearance of the transmittance that the LDPE is degrading. The characteristic bands of long alkyl chains in the regions 2909, 2850, 1460 and 720 cm^{-1} are seen in both cases with minor changes in the intensity and wave number range in the case of the treated plastic. This shows that the plastic is getting directly mineralised.

The technique is effective for the degradation of recalcitrant plastics and the simple extrapolation of the data shows that complete degradation of thinner LDPE plastic sheets can be achieved by this technique. However, the real success of the technique lies in developing suitable photocatalytic systems which are capable of getting activated under sunlight or which can more efficiently utilize the UV component of the solar spectrum.

4.4.17 Mechanism of semiconductor photocatalysis

Polyethylene (PE) macromolecules are known to absorb UV light leading to the creation of excited states followed by chain scission, branching, cross-linking and oxidation reactions. [182]. However in presence of semiconductor oxide catalyst, photocatalytic degradation is the main reaction which is quite different from the photolytic degradation of pure LDPE. The general mechanism of semiconductor photocatalysis is schematically illustrated in figure 4.54. In this case the mechanism involves the formation of reactive oxygen species (ROS) and their interaction with the plastic.

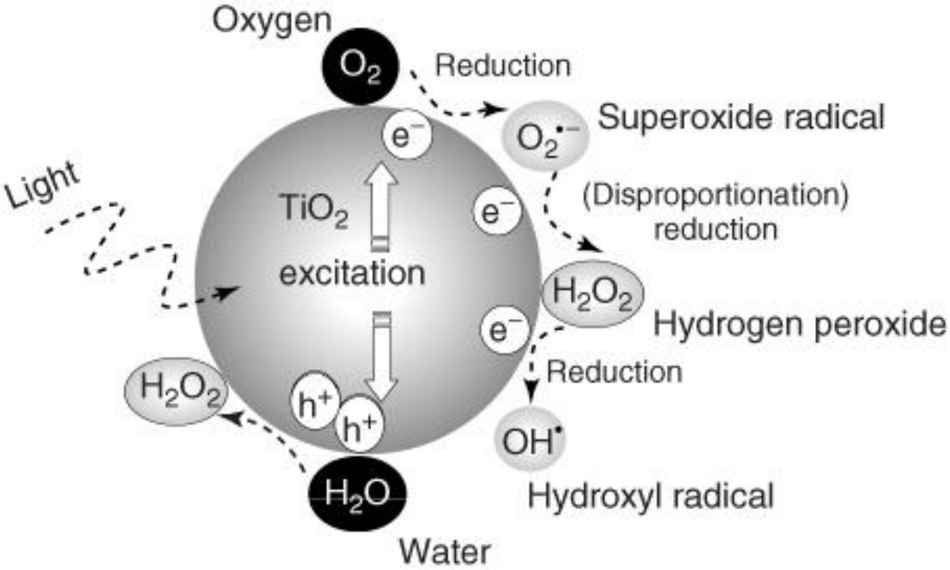


Figure 4.54: Mechanism of TiO_2 photocatalysisshowing formation of $^{\cdot}OH$ and H_2O_2 [151]

When a semiconductor is irradiated with photons of energy equal to or greater than its band gap energy (3.2 eV in the case of TiO_2 as well as ZnO) the photons are absorbed and electron hole pairs are created. These electrons and holes can either recombine or migrate towards the surface participating in several redox reactions eventually leading to the formation of Reactive Oxygen Species (ROS) such as $^{\cdot}OH$ radicals and H_2O_2. These transitory ROS can initiate and promote a number of reactions which end up in complete mineralisation of the pollutants into harmless products such as CO_2, water and salts as follows:

Semiconductor + hν → h^+ + e^- ....(52)

$h^+ + e^- \rightarrow$ Heat ....(53)

$O_2 + e^- \rightarrow O_2^{-\cdot}$ .... (54)

$h^+_{VB} + H_2O \rightarrow H^+ + {}^{\cdot}OH$ ....(55)

$O_2^{-\cdot} + 2H^+ + e- \rightarrow H_2O_2$ ....(56)

$^{\cdot}OH + {}^{\cdot}OH \rightarrow H_2O_2$ ....(57)

$h^+_{VB} + OH^- \rightarrow {}^{\cdot}OH$ ....(58)

Pollutant (LDPE) + ROS (H_2O_2, $O_2^{\cdot-}$, $HO_2^{\cdot}$, $^{\cdot}OH$ etc**)** →
Intermediates → H_2O + CO_2 + Salts [163] ....(59)

H_2O_2 is known to decompose under photocatalytic conditions forming more reactive $^{\cdot}OH$ and $HO_2^{\cdot}$ radicals as in reactions 60 and 61. Further H_2O_2 itself is a good electron and hole acceptor capable of preventing the recombination of photogenerated electrons and holes on the surface.

$H_2O_2 + H^+ + e^- \rightarrow {}^{\cdot}OH + H_2O$ ....(60)
$H_2O_2 + {}^{\cdot}OH \rightarrow HO_2^{\cdot} + H_2O$ ....(61)
$H_2O_2 + 2h^+_{VB} \rightarrow O_2 + 2H^+$ ....(62)
$H_2O_2 + {}^{\cdot}OH/h^+_{VB} \rightarrow HO_2^{\cdot} + H_2O/H^+$...(63)
$HO_2^{\cdot} + {}^{\cdot}OH/h^+_{VB} \rightarrow O_2 + H_2O/H^+$ ....(64)

Hence the degradation is enhanced moderately in presence of added H_2O_2 at lower concentrations. However at higher concentration of H_2O_2 the reactive free radicals as well as the electrons and holes interact more with it and less with the pollutant. This leads to stabilization or even decrease in the degradation of LDPE. The concentration effect of H_2O_2 on the photocatalytic degradation of organic pollutants and the transition from ‘enhancement’ to ‘no effect’ or even ‘inhibition’ was reported by other workers also [183-184].

The TiO_2 catalysed photodegradation of LDPE is almost doubled in the presence of even smaller concentration of PDS (5% with respect to TiO_2) as in figure 4.20. At the optimized concentrations of the oxidants, PDS is at least three times more efficient than H_2O_2. The mechanism of enhancement in LDPE degradation by PDS may be proposed as follows:

The first step in PDS accelerated degradation of organics is the formation of sulphate ions and sulphate radical anion under photocatalytic conditions.

$S_2O_8^{2-} + e^- \rightarrow SO_4^{2-} + SO_4^{\cdot-}$ ....(65)

SO_4^{2-} gets adsorbed on the surface and interacts with the photoproduced holes forming reactive sulphate radical anion as in reaction-66.

$h^+ + SO_4^{2-} \rightarrow SO_4^{\cdot-}$ ....(66)

Since S is a strong oxidizing agent, the sulphate radical (Reduction potential of $SO_4^{\cdot-}$ = 2.6 V) can accelerate the degradation process according to reactions 67 and 68.

$SO_4^{\cdot-} + H_2O \rightarrow SO_4^{2-} + {}^{\cdot}OH + H^+$ ....(67)

$SO_4^{\cdot-}$ + Pollutant $\rightarrow SO_4^{2-}$ + Intermediate $\rightarrow$
$SO_4^{2-} + H_2O + CO_2$ + Salts ....(68)

Thus more $^{\cdot}OH$ radicals are also provided in presence of PDS. The intermediate may go through many reactions before eventual mineralization. As seen in reaction 67, extra $^{\cdot}OH$ radicals which can enhance the degradation of the pollutants are also formed in presence of PDS. The two highly reactive free radical species ($^{\cdot}OH$ and $SO_4^{\cdot-}$) together can more than compensate for the inhibition, if any, caused by the depletion of surface sites taken up by the sulphate ions.

The holes generated and the $O_2^{\cdot-}$ participate in the degradation directly as well as through various radicals generated as follows:

$h^+ + -(CH_2CH_2)- \rightarrow -(CH_2CH_2)-^+$ ....(69)

$-(CH_2CH_2)-^+ + O_2^{\cdot-} \rightarrow -(^{\cdot}CHCH_2)- + HO_2^{\cdot}$ ....(70)

$HO_2^{\cdot}$ radicals combine to form H_2O_2 which in turn can photodecompose to yield $^{\cdot}OH$ radicals.

$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2$ ....(71)

$H_2O_2 + h\nu \rightarrow 2^{\cdot}OH$ ....(72)

The degradation is faster in the beginning and it slows down with time. This is similar to the observations by Shang etal [9] who demonstrated that photocatalytic degradation of polystyrene plastic and evolution of CO_2 and volatile organic compounds under fluorescent light deteriorate gradually. The initial faster rate can be attributed to the interaction of reactive oxygen species with adjacent polymer chains. These molecules have to be etched out so that the catalyst surface is available for interaction with more molecules and generation of reactive free radicals. It is also possible that the degradation is initiated by photons attacking the polymer to create excited state followed by chain scission, branching, cross linking and oxidation as indicated earlier. During the irradiation, the $^{\cdot}OH$ radicals can attack the polymer as follows:

$-(CH_2CH_2)- + {}^{\cdot}OH \rightarrow -(CH_2{}^{\cdot}CH)- + H_2O$ ....(73)

$-(CH_2{}^{\cdot}CH)- + {}^{\cdot}OH \rightarrow -({}^{\cdot}CH{}^{\cdot}CH)- + H_2O$ ....(74)

The carbon centred radicals thus formed react with more O_2 leading to chain cleavage and production of new reactive radicals as shown below [185-186].

$-(CH_2{}^{\cdot}CH)- + O_2 \rightarrow -(CH_2(OO^{\cdot})CH)-$ ....(75)

$-({}^{\cdot}CH{}^{\cdot}CH)- + O_2 \rightarrow -(CH(OO^{\cdot})CH)-$ ....(76)

$-(CH_2(OO^{\cdot})CH)- + -(CH_2CH_2)- \rightarrow$

$-(CH_2(OOH)CH)- + -(CH_2{}^{\cdot}CH)-$ ....(77)

$-(CH_2(OOH)CH)- \rightarrow -(CH_2OCH)- + {}^{\cdot}OH$ ....(78)

$-(CH_2OCH)- + O_2 \xrightarrow{\text{Catalyst + hv}}$ Intermediates such as HCHO,

HCOOH etc $\xrightarrow{\text{Catalyst + hv}} CO_2 + H_2O$ ....(79)

The intermediates are not detected in water indicating that they are getting degraded faster than the plastic. Absence of any TOC in water in which the plastic strip was suspended also confirms this.

4.5 Conclusions

Semiconductor photocatalysis mediated by TiO_2 is found to be a promising method for the safe removal of LDPE plastic pollutants from the environment. Acidic pH enhances the degradation. However, due to economic and environmental concerns, this possibility is not explored and reaction parameters for efficient degradation were optimized in the pH range of 5.5-6.0. H_2O_2 and PDS which are powerful oxidants enhance the degradation and the latter is at least three times more efficient than the former. Optimum concentration of PDS in presence of TiO_2 as photocatalyst could achieve over 12% of LDPE mineralisation in 400 hr time. Fenton reagent, in the presence of TiO_2 as catalyst enhances the degradation of LDPE significantly. Presence of anions and cations in water do influence the photocatalytic degradation of LDPE plastic moderately with the effect varying from ‘enhancement’ to ‘no effect’ or ‘inhibition’. The degradation of LDPE is extremely slow in sea water which is experimentally proven to be due to the presence of high concentration of Cl^- which can deactivate the catalyst. It was observed that the colour of the plastic has no impact on the degradation rate. Oxygen plays an important role in the photocatalytic degradation of LDPE and the degradation proceeds slowly in systems deaerated with N_2. The catalytic activity of TiO_2 remains more or less intact with only marginal decrease after repeated use. The study demonstrates that photocatalysis under appropriately optimised conditions offers good potential for the safer mineralisation of one of the worst environmental pollutants of the day, ie, polyethylene plastic.

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Chapter 5

PHOTOLYTIC/PHOTOCATALYTIC DEGRADATION OF POLYVINYL CHLORIDE PLASTIC WASTES FROM THE ENVIRONMENT

Contents

5.1 Introduction

Rigid polyvinyl chloride (PVC) is one of the most widely used thermoplastic materials in the world today with extensive applications due to a variety of beneficial properties such as high chemical resistance, barrier properties and low cost [187-188]. However the disposal of PVC waste in land and water is a major global environmental issue. Most waste plastic products are disposed off by unlawful land filling or burnt thereby leading to serious secondary pollution problems [189-192]. The waste plastics left in the open are exposed to sunlight and other natural conditions of rain, wind, dust etc. Chemical inertness and non-biodegradable nature of PVC make its natural degradation extremely slow. Hence it does not get easily decomposed in natural environment. When PVC products are disposed off by unscientific and improper means, they break down and release harmful chemicals like dioxins.

PVC is a thermoplastic consisting of long chains of monomer vinyl chloride.

$$n\ CH_2{=}CHCl \longrightarrow -[CH_2\text{-}CHCl]_n-$$

where n is the number of monomer units.

Plasticized PVC is obtained by adding plasticizers to rigid PVC.

Heterogeneous photocatalysis is an advanced oxidation process (AOP), widely investigated for the degradation of organic pollutants in water and air [112,154,159,193-194]. Solid-phase photocatalytic degradation of polymers under ambient conditions represents an attractive and efficient technique for the treatment of waste plastics with UV light or sunlight as the irradiation source [195-199]. The basic mechanism of photocatalysis involving hydroxyl radicals has been well established [159].

Semiconductor oxides such as TiO_2 and ZnO and their modifications obtained by doping, immobilizing, metal deposition etc are the most widely used photocatalysts [156-158]. Most of the studies on the photo degradation of plastics are made using TiO_2 as the catalyst, mainly due to its wide availability, stability, non-toxicity and reactivity. Another semiconductor oxide ZnO has received relatively less attention due to its corrosive nature under extreme pH conditions. At the same time ZnO is reported to be more efficient than TiO_2 for the visible light induced photocatalytic degradation of organic pollutants because the former can absorb relatively larger fraction of solar spectrum compared to the latter [158,200]. In photocatalysis photo excitation of the semiconductor oxide promotes valence band electrons to the conduction band thereby generating electron deficiency or hole in the valence band. Dioxygen provides a sink for conduction band electron forming superoxide anion radical $O_2^{\cdot -}$ which leads to the formation of reactive hydroperoxide radical $HO_2^{\cdot}$. Holes in the valence band can react with water molecules or hydroxide anion to form OH radicals. The holes can also interact with an adsorbed organic donor leading to its eventual oxidation and possible mineralization.

In this chapter, the possibility of using photocatalysis and photolysis for the safe disposal of PVC plastic is examined. It is an extension of the study reported in previous chapter which showed that photocatalysis can be effectively used for the slow but safe mineralisation of LDPE plastics. The possibility of using TiO_2 and ZnO mediated photocatalysis for the degradation of PVC plastic is evaluated and compared. The effects of various reaction parameters on the photocatalytic degradation of PVC is also investigated and optimized.

5.2 Materials and Methods

The sources of various materials used, their characteristics etc are the same as provided in Chapter 4. Ordinary PVC pipes used and discarded after domestic applications were used in the study. The PVC pipe is cut into thin sheets of approximately 25cm length, 1cm breadth and 1mm thickness. Typical samples used are shown in figure 5.1. Various chemicals used in the study were of AnalaR grade or equivalent.

Figure 5.1: Typical PVC samples used in the study

As described in Chapter 4, the photodegradation experiments were carried out by placing the strips in a suspension of catalyst/water in a pyrex test tube. The test tubes are placed in lamp-housing box of the photoreactor assembly under eight 8W ultraviolet lamps of wavelength 365 nm. Photodegradation of PVC samples after irradiation was determined based on weight reduction, SEM images, tensile strength and visual observation.

5.3 Results and Discussion

Investigations on the photocatalytic degradation of PVC plastic using ZnO and TiO_2 catalysts under identical conditions showed that no significant degradation took place in the absence of UV light or the catalyst suggesting that both catalyst and light are essential to effect its degradation. Preliminary studies presented in figure 5.2 show that TiO_2 is more efficient as a photocatalyst compared to ZnO.

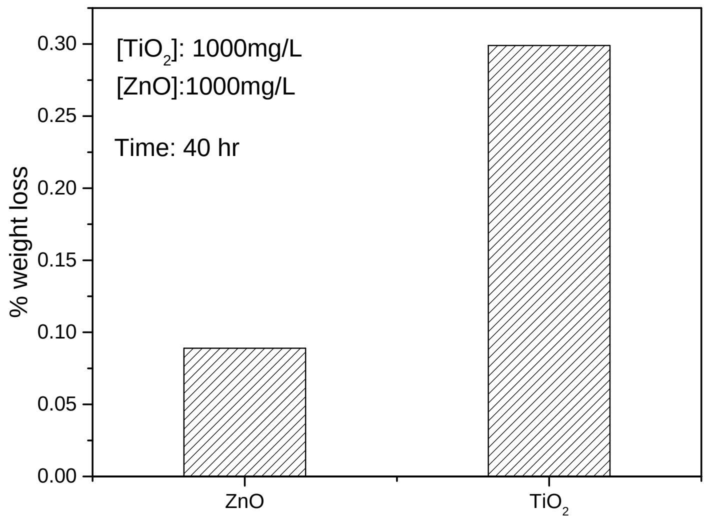


Figure 5.2: Effect of ZnO and TiO_2 on the photocatalytic degradation of PVC plastic

The weight loss of PVC plastic does not lead to the presence of organic carbon in water as determined by TOC and COD. This confirms the complete mineralization of PVC into CO_2, water and salts as explained later in this chapter (section-5.3.9).

5.3.1 Effect of dosages of TiO_2 and ZnO

Preliminary investigations of the effect of catalyst dosage on the photocatalytic degradation of PVC plastic were made using both ZnO and TiO_2 catalysts individually under identical conditions. The results are presented in figure 5.3.

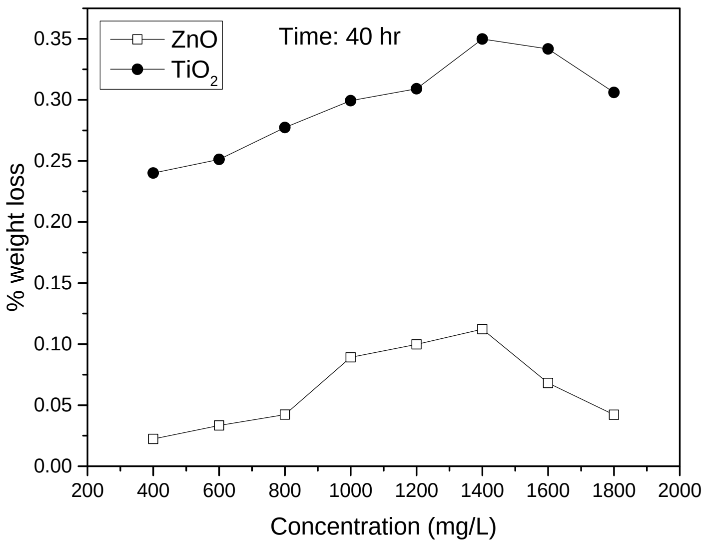


Figure 5.3: Effect of dosage of TiO_2 and ZnO on the photocatalytic degradation of PVC plastic

The optimum catalyst loading of both ZnO and TiO_2 is 1400 mg/L. Above this dosage, the degradation is stabilized or decreases. Possible reasons for the optimum in the catalyst dosage are discussed in Chapter 4, section 4.4.1. Beyond the optimum loading, the light photon absorption coefficient of the catalyst decreases radially. The decrease is steeper in the case of ZnO. However such attenuation over the radial distance does not obey the Beer-Lambert law due to the strong absorption and scattering of light photons by the catalyst particles [177]. Excess catalyst particles lead to aggregation and screening of light which reduce the effective surface area of the semiconductor oxide being exposed to illumination. This leads to decreased photocatalytic efficiency. The results further showed that TiO_2 is significantly more efficient for the photocatalytic degradation of PVC compared to ZnO under identical conditions. Hence all further investigations in this chapter were carried out using TiO_2 as catalyst at the optimized loading as above, unless mentioned otherwise.

5.3.2 Effect of pH

The UV-induced degradation of organics with or without catalyst is reported to be dependent on the pH value of the solution [177]. The effect of pH on photocatalytic degradation of PVC plastic was investigated in the range 2.5-10. The results are presented in figure 5.4.

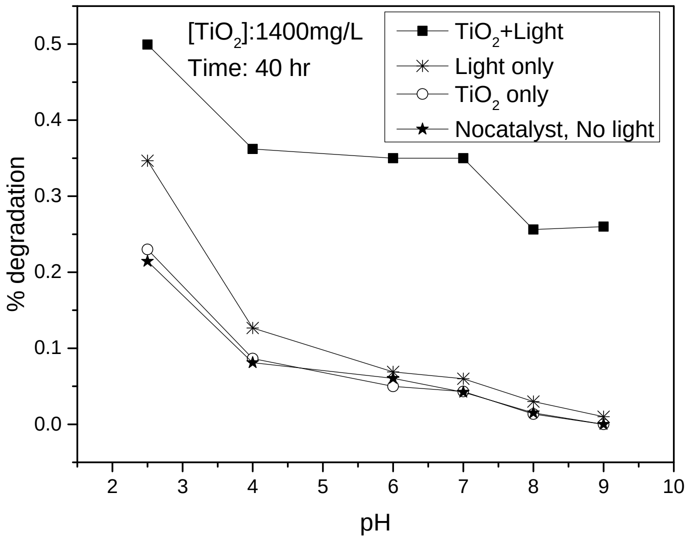


Figure 5.4: Effect of pH on the photocatalytic degradation of PVC plastic in presence of TiO_2

The pH of the suspension was adjusted before irradiation and was not controlled during irradiation. The degradation is more efficient in the acidic region than in the neutral or alkaline region. Mild degradation of PVC is seen in the acidic region of pH ~2.5 even in the absence of the catalyst or light. However at the natural pH of the catalyst suspension (~ 6.0-7.0), noticeable degradation takes place only in the presence of the catalyst and light. Degradation at extreme acidic conditions, even if feasible, is not a viable solution economically or ecologically since it requires expensive and hazardous neutralization and disposal processes. Hence it is more prudent to optimize the parameters at the natural pH of the system at which reasonable degradation of the plastic is observed in presence of TiO_2 and light. Hence all further studies are conducted at the natural pH of the reaction system.

5.3.3 Effect of H_2O_2 on the degradation

Hydrogen peroxide is detected as a by-product/intermediate/end product in the photocatalytic degradation of many organic pollutants. Simultaneous decomposition of the H_2O_2 thus formed results in oscillation, ie, periodic increase and decrease in its concentration [187, 199]. H_2O_2 is detected during the degradation of PVC plastic also in the reaction medium in the present instance. However, since the degradation is very slow, the concentration is very small (< 2 mg/L) and the possible oscillation could not be precisely followed with the analytical techniques available with us. In addition to being an oxidant by itself, the reactive free radicals such as $^{\cdot}OH$ and $HO_2^{\cdot}$ formed from H_2O_2 decomposition can enhance the degradation of organics. However, instances of inhibition of the degradation of organics by H_2O_2 also have been reported especially at higher concentrations (of H_2O_2).

The effect of added H_2O_2 at various concentrations on the photocatalytic degradation of PVC plastic is tested under standardized conditions and the results are plotted in figure 5.5. H_2O_2 alone or a combination of TiO_2 and H_2O_2 does not degrade PVC in the dark. The degradation and consequent weight loss occur only under irradiation. The decomposition of PVC, as measured by the weight loss, increases with increase in concentration of H_2O_2. Optimum H_2O_2 concentration is 300mg/L. After the optimum, the % degradation decreases sharply.

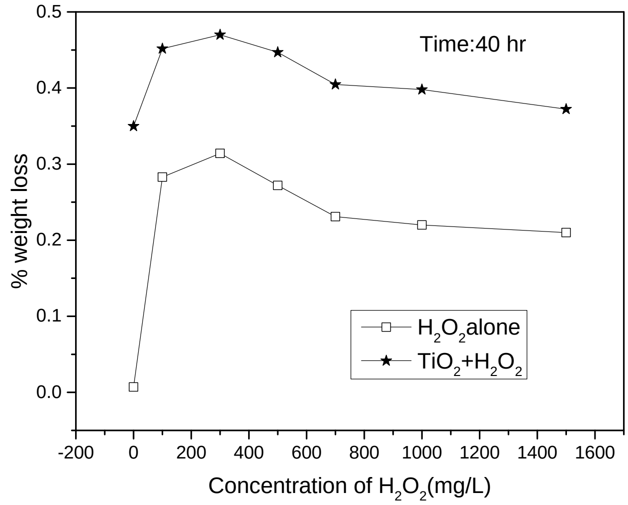


Figure 5.5: Effect of H_2O_2 on the photocatalytic degradation of PVC with and without TiO_2

The photoactivation of TiO_2 and subsequent formation of the reactive $^{\cdot}OH$ radicals are shown in reactions (80)-(83). H_2O_2 is formed primarily as in reaction (84). H_2O_2 is known to decompose under photocatalytic conditions forming more reactive $^{\cdot}OH$ and $HO_2^{\cdot}$ radicals as in reactions (85) and (86). Further H_2O_2 itself is a good electron and hole acceptor capable of preventing the recombination of photogenerated electrons and holes on the surface of TiO_2.

Semiconductor + hν $\rightarrow h^{+}_{VB} + e^{-}_{CB}$ ....(80)

$h^{+}_{VB} + e^{-}_{CB} \rightarrow$ Heat ....(81)

$O_2 + e^{-}_{CB} \rightarrow O_2^{-\cdot}$ ....(82)

$h^{+}_{VB} + H_2O \rightarrow H^{+} + {}^{\cdot}OH$ ....(83)

${}^{\cdot}OH + {}^{\cdot}OH \rightarrow H_2O_2$ ....(84)

$H_2O_2 + H^{+} + e^{-}_{CB} \rightarrow {}^{\cdot}OH + H_2O$ ....(85)

$H_2O_2 + {}^{\cdot}OH \rightarrow HO_2^{\cdot} + H_2O$ ....(86)

$H_2O_2 + 2h^{+}_{VB} \rightarrow O_2 + 2H^{+}$ ....(87)

PVC + ROS (${}^{\cdot}OH$, $HO_2^{\cdot}$, H_2O_2) → $H_2O + CO_2 + HCl$ (salt) ... (88)

Thus the reactive free radicals ${}^{\cdot}OH$ and $HO_2^{\cdot}$ formed from H_2O_2 can enhance the degradation of PVC. However at higher concentration of H_2O_2 the reactive free radicals as well as the electrons and holes interact more frequently with H_2O_2 and less with the pollutant.

$H_2O_2 + {}^{\cdot}OH/h^{+}_{VB} \rightarrow HO_2^{\cdot} + H_2O/H^{+}$ .... (89)

$HO_2^{\cdot} + {}^{\cdot}OH/h^{+}_{VB} \rightarrow O_2 + H_2O/H^{+}$ .... (90)

Thus the concentrations of H_2O_2 and the more reactive free radical ${}^{\cdot}OH$ become less and this leads to stabilization or even decrease in the degradation of PVC. The concentration effect of H_2O_2 on the photocatalytic degradation of organic pollutants resulting in transition from enhancement to inhibition was reported by other workers also [185, 188, 201].

5.3.4 Effect of Fenton reagent on the degradation

Since H_2O_2 at the appropriate concentration, enhances the degradation of PVC, the possibility of combining H_2O_2 with ferrous salt and the effect of the resultant Fenton reagent on the degradation of PVC is also examined. Efficiency of the Fenton process is very sensitive to reaction conditions. In particular it depends on the relative concentration of $FeSO_4$ (FS) and H_2O_2. Hence detailed investigations were made on optimizing the ratio of these critical components for PVC plastic degradation under UV light by varying ratios of FS and H_2O_2. The results are presented in figure 5.6. The optimization is done both in the presence as well as absence of TiO_2. The optimum ratio of FS/H_2O_2 (mg/L) is identified as 40:200, ie, 1:5 in both cases. Surprisingly TiO_2 does not have any additive effect in presence of Fenton reagent. In fact it has slight inhibition effect at lower H_2O_2 concentration. The effect of Fenton reagent on the degradation of PVC in the dark was investigated in the presence as well as absence of TiO_2 and the degradation was found to be almost nil.

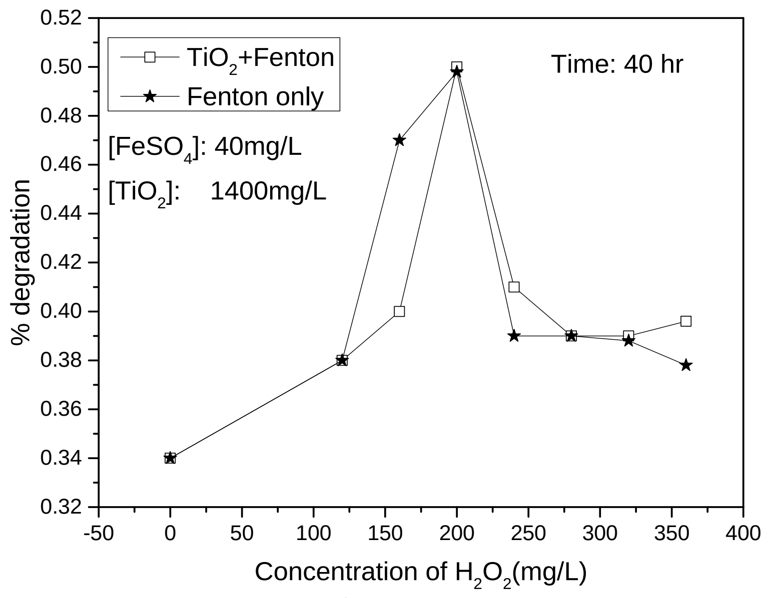


Figure 5.6: Effect of Fe^{2+}/H_2O_2 ratio on the efficiency of Fenton degradation of PVC plastic in UV light

Since the Fenton reagent (FR) mediated degradation is almost same with and without TiO_2, all further studies with FR were conducted without TiO_2. The effect of dosage of Fenton reagent at the optimized ratio (1:5) is tested and the results are shown in figure 5.7. The degradation increases with increase in quantity of FR and reached an optimum at $FS:H_2O_2$= 80:400.

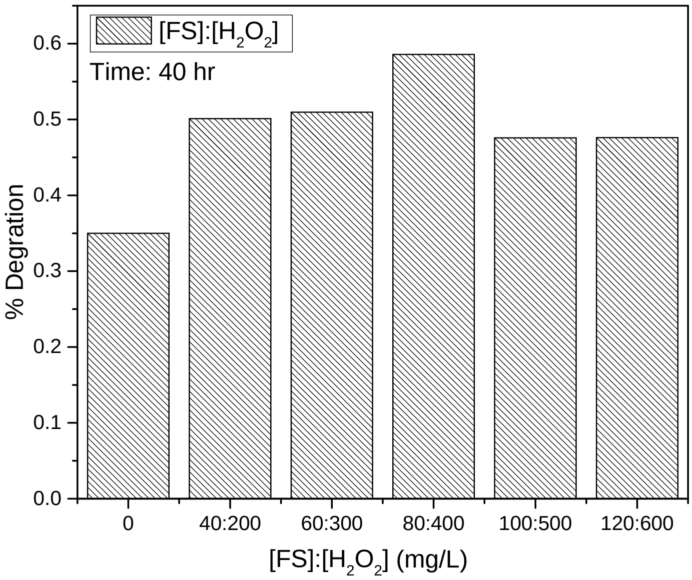


Figure 5.7: Effect of concentration of Fenton reagent on the rate of photodegradation of PVC plastic

The study of the effect of pH on Fenton reagent shows that the degradation is maximum in the acidic pH and is almost nil in the extreme alkaline conditions. The results are shown in figure 5.8. This is consistent with literature reports according to which Fenton reaction is sensitive to pH [202].

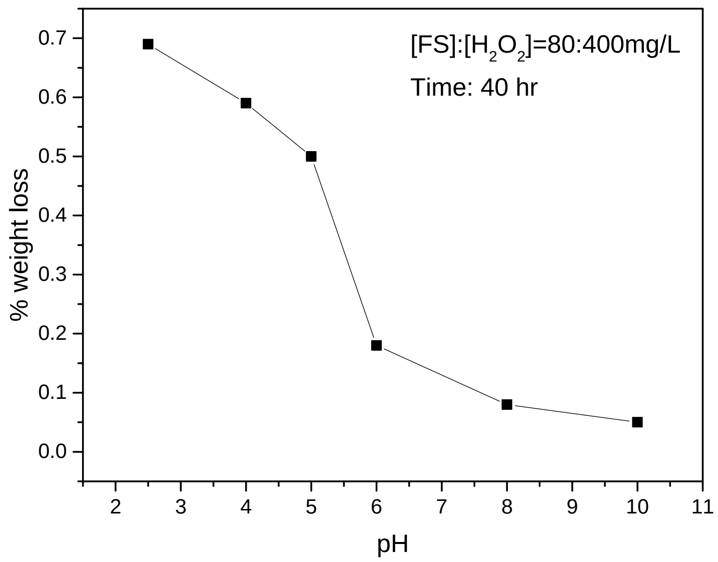


Figure 5.8: Effect of pH of Fenton reagent on the degradation of PVC plastic

The Fenton degradation of PVC under UV irradiation slows down with time. This slowdown after the initial faster rate may be due to the consumption of H_2O_2 and corresponding variation in the ratio of components in the Fenton. This is verified by replenishing H_2O_2, FS and FR itself in the system at two different time intervals, 40 and 80 hr. Addition of H_2O_2 and addition of FR itself in-between enhances the degradation while the addition of extra FS does not increase the degradation significantly. Hence it may be inferred that FS is not consumed in the system and the initial quantity is sufficient to carry the reaction forward as seen in figure 5.9. The effect is more or less same in the case of in-between added FR and H_2O_2 indicating that it is the decreasing concentration of H_2O_2 that is responsible for decrease in degradation with time. Thus under photolysis, the efficiency of the Fenton reagent mediated degradation can be enhanced and sustained by periodic addition of H_2O_2.

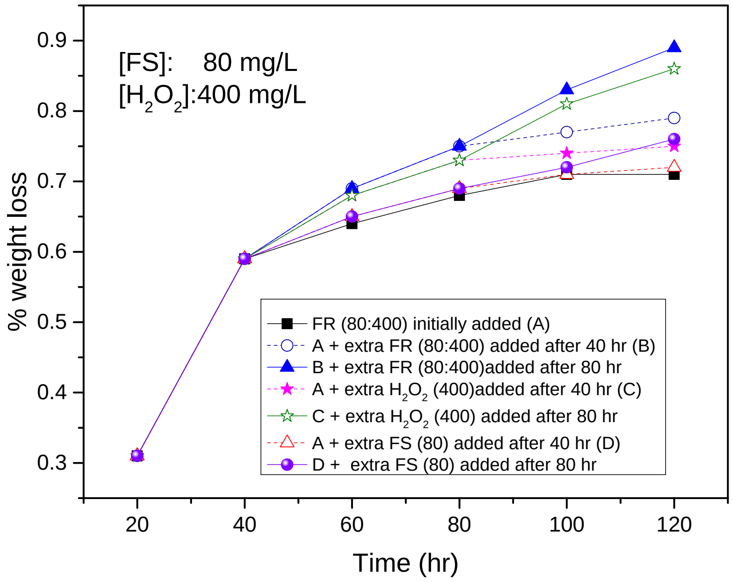


Figure 5.9: Effect of in-between addition of FR/H_2O_2/FS on the Fenton degradation of PVC plastic under UV irradiation

The basic mechanism of the process may be presented as follows.

The first step in the Fenton reaction is the oxidation of ferrous to ferric ions and decomposition of H_2O_2 into $^{\cdot}OH$ radicals:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{-} + {}^{\cdot}OH \quad \text{...(91)}$$

The Fe^{3+} is reduced by excess H_2O_2 to regenerate $Fe^{2+}$and more free radicals as in reaction (92)

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^{+} \quad \text{.. (92)}$$

Other possible reactions are:

$Fe^{2+} + {}^{\cdot}OH \rightarrow Fe^{3+} + OH^{-}$ ....(93)

$Fe^{2+} + HO_2^{\cdot} \rightarrow Fe^{3+} + HO_2^{-}$ .... (94)

$Fe^{3+} + HO_2^{\cdot} \rightarrow Fe^{2+} + O_2 + H^{+}$ ....(95)

The highly reactive free radicals can get deactivated by self-scavenging as well as by interaction with other radicals and/or H_2O_2

${}^{\cdot}OH + {}^{\cdot}OH \rightarrow H_2O_2$ ....(96)

${}^{\cdot}OH + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O$ .... (97)

$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2$ ....(98)

${}^{\cdot}OH + HO_2^{\cdot} \rightarrow H_2O + O_2$ ....(99)

In the absence of any organic substrate to be oxidized, H_2O_2 self-decomposes as in reactions (100) and (101).

$2\,H_2O_2 \rightarrow 2H_2O + O_2$ ....(100)

$H_2O_2 \rightarrow 2{}^{\cdot}OH$ ....(101)

In presence of organic molecules (R), such as PVC in the current instance, the degradation can take place as in reactions (102) – (104) or dimerization occurs as in reaction (105). Eventually mineralization takes place as in reaction (106).

${}^{\cdot}OH + R \rightarrow H_2O + R^{\cdot} \rightarrow$ (Partial mineralization + Colorless intermediates) ....(102)

$R^{\cdot} + Fe^{2+} \rightarrow R^{-} + Fe^{3+}$ ....(103)

$R^{\cdot} + Fe^{3+} \rightarrow R^{+} + Fe^{2+}$ ....(104)

$R^{\cdot} + R^{\cdot} \rightarrow RR$ ....(105)

$R^{\cdot}$ or R^{-} or R^{+} or RR + $^{\cdot}OH$, $HO_2^{\cdot}$, H_2O_2 etc. → intermediates

→ $CO_2 + H_2O$ + salts (mineralization) ....(106)

5.3.5 Effect of peroxydisulphate on the degradation

Our earlier studies have shown that peroxydisulphate (PDS) can also serve as an accelerator for the degradation of organic pollutants such as petrochemicals, plastics, pesticides and dyes [162]. In view of this, the effect of PDS on the photocatalytic degradation of PVC was investigated in the presence as well as absence of TiO_2. The results with increasing concentration of PDS are plotted in figure 5.10.

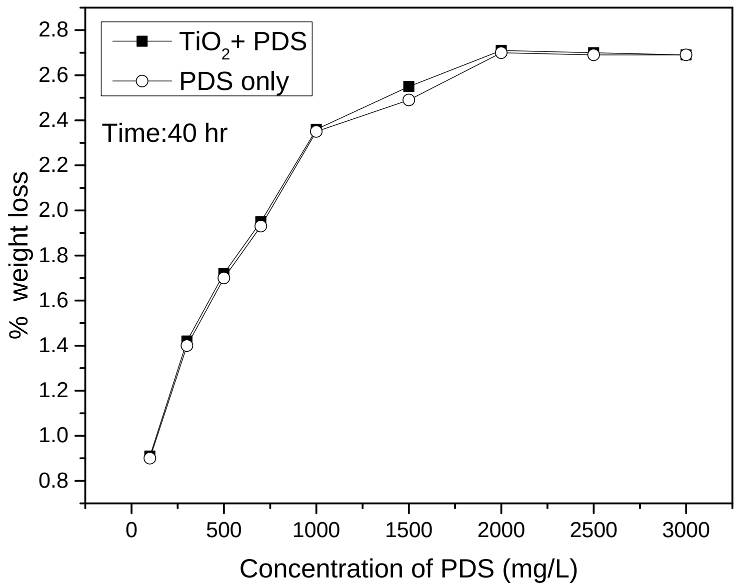


Figure 5.10: Effect of PDS on the photodegradation of PVC plastic with and without TiO_2

The degradation of PVC is enhanced by PDS. The effect is concentration dependent with higher concentration favouring increased degradation upto an optimum. The optimum concentration for PDS is 2000mg/L. Above this concentration degradation of PVC is stabilised. As seen from the data in figure 5.10, presence of combination of TiO_2 and PDS gives same degradation of PVC as in the presence of PDS. The comparative effect of TiO_2, PDS and TiO_2+PDS on the photodegradation of PVC, after longer times of UV irradiation is presented in figure 5.11.

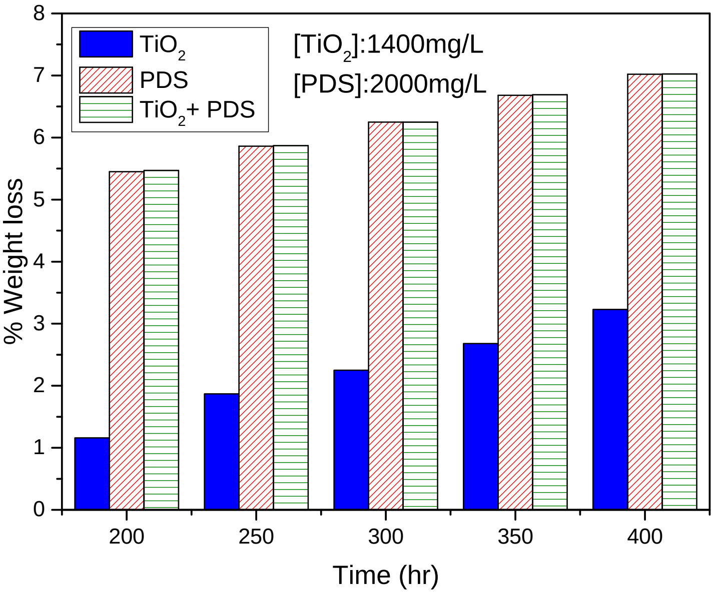


Figure 5.11: Comparative efficiency of TiO_2, PDS and TiO_2 + PDS on the photodegradation of PVC plastic

The results show that TiO_2 alone is much less efficient compared to PDS or TiO_2+PDS. Also PDS and (TiO_2+PDS) maintain comparable efficiency at all reaction times, ie, the relative efficiency of the oxidants is not affected by duration of irradiation. At the optimum concentration of

PDS, photolysis could achieve over 7% of PVC mineralisation in 400 hr time. During the same period the degradation effected by TiO_2 only is ~3.5%. Based on this result, it is seen that PDS alone is comparatively better for the degradation of PVC. The effect of time on the photodegradation of PVC in the presence optimised dosage (2000mg/L) of PDS is tested in detail and the results are plotted in figure 5.12.

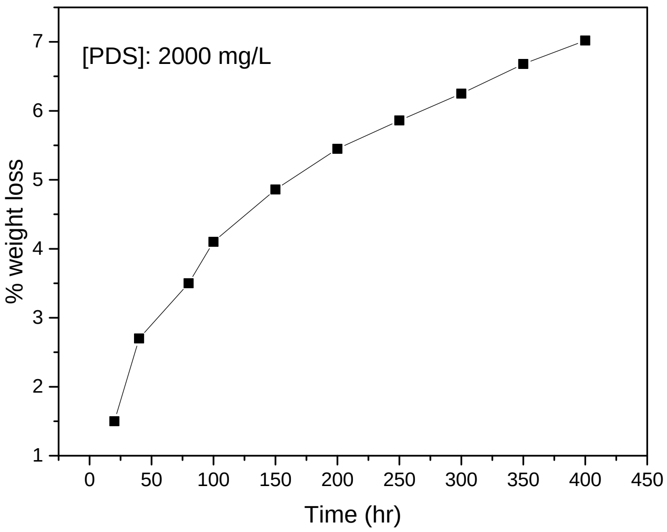


Figure 5.12: Effect of PDS on the degradation of PVC plastic

The degradation increases with time but the rate slows down towards the later stages as in the case of most photolytic degradation reactions.

Comparison of degradation in presence of other oxidants shows that PDS is a much better oxidant compared to H_2O_2 and Fenton reagent. At the optimized concentrations of the respective oxidants, PDS is at least three times more efficient than Fenton reagent and H_2O_2 as shown in figure 5.13.

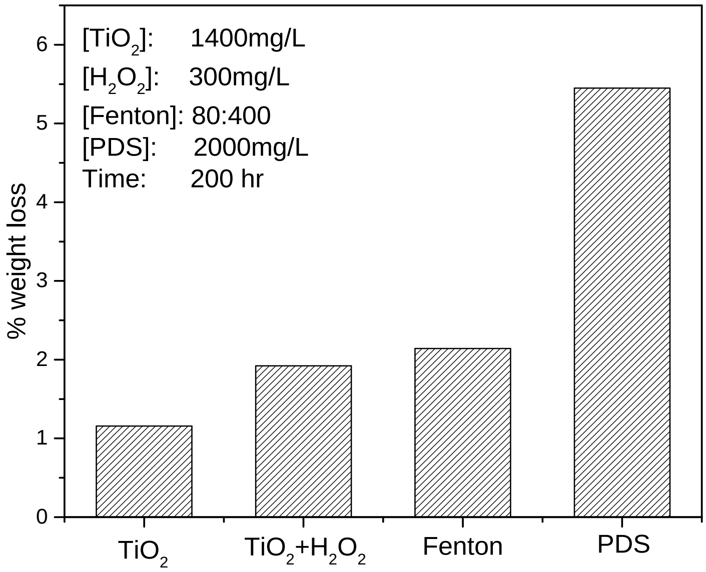
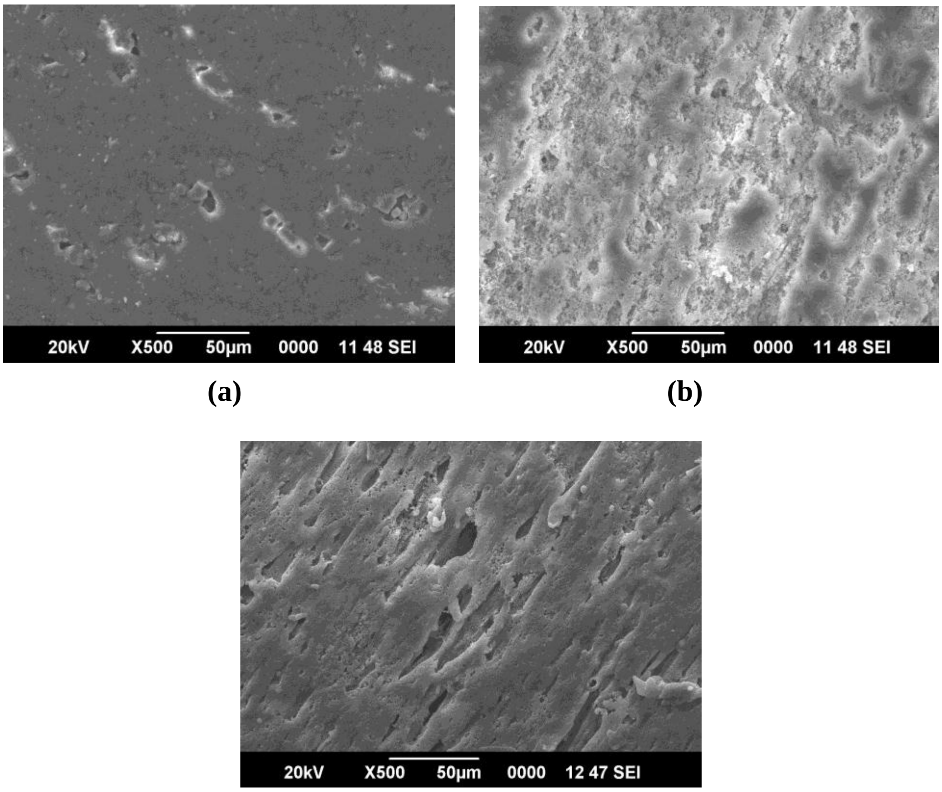


Figure 5.13: Comparative efficiency of TiO_2, TiO_2 + H_2O_2, Fenton reagent and PDS for the photodegradation of PVC plastic

Combination of methods ie, (TiO_2+H_2O_2), (TiO_2+Fenton), (PDS+H_2O_2) and (PDS+Fenton) do not lead to any significant enhancement in the degradation of PVC, over what has been achieved in presence of PDS only.

As irradiation progresses, the plastic sheet becomes thinner with localised cracks of various types and ruptured blisters. The photocatalytic degradation of PVC is further demonstrated from the surface morphology of the PVC sheet as seen from its SEM images. Figure 5.14 clearly illustrates that the surface morphology of plastic is severely changed and the technique is effective for the degradation of recalcitrant plastics.

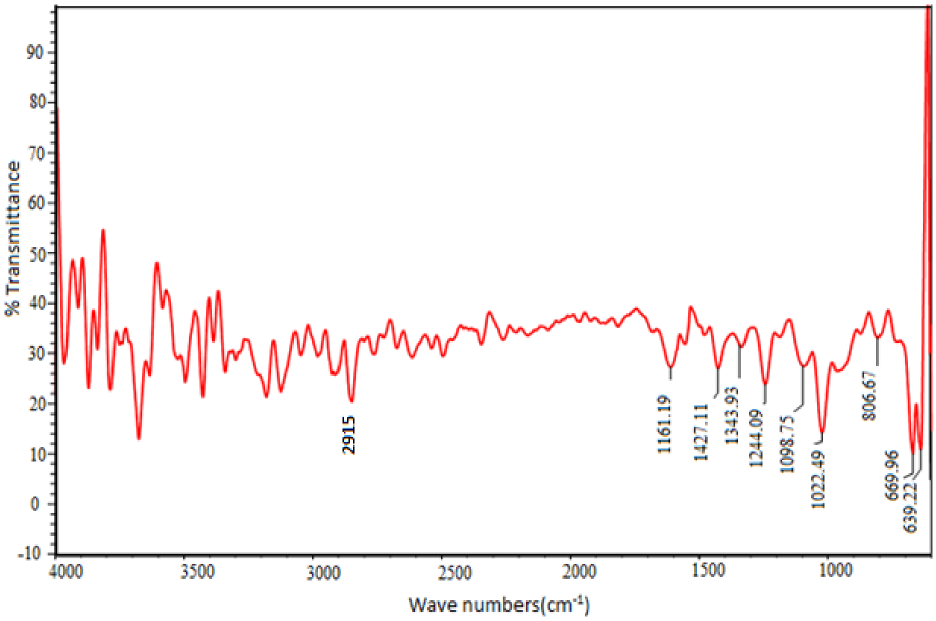


(a) (b)

(c)

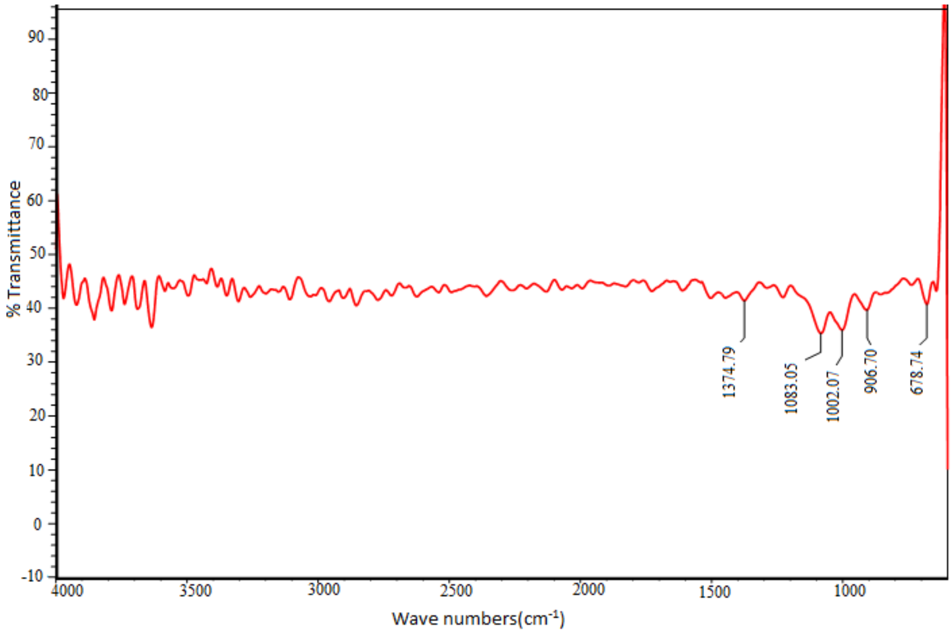
Figure 5.14: SEM images of PVC plastic (a) before, (b) after photolytic treatment using PDS (2000 mg/L), Time: 400 hr and (c) after photolytic treatment using FR (FS: H_2O_2; 80:400 mg/L), Time: 400 hr

The FTIR spectra of the PVC sheet before and after treatment with PDS are shown in figure 5.15 (a) and (b).



(a) Untreated PVC

Typical bands at 2915, 1343, 1244 and 639cm^{-1} which can be attributed to ν-CH$_2$ and ν-CH (vibrational absorption), δ-CH$_2$ and δ-CH (rotational absorption) and ν_{c-c} (vibrational absorption) respectively are quite evident in the spectra of PVC sheet before treatment. Many of these bands became weak after the photocatalytic treatment indicating degradation.



(b) Treated PVC

Figure 5.15: FTIR spectra of PVC (a) untreated and (b) treated under UV for 400hrs with PDS

The IR spectra clearly shows variation in the chemistry of PVC plastic after photolytic degradation, as seen from the appearance of extra bands. Similarly, many of the transmission bands typical of PVC in the range of 620-4000cm^{-1} in PVC disappear on photolytic degradation.

It has been proven earlier that PDS is not an effective oxidant of organic compounds under visible light or diffused light [203]. This is reconfirmed again by conducting PVC degradation experiments under identical conditions in the dark, diffused light and UV light. The results show that the degradation is maximum in the presence of UV light (figure 5.16).

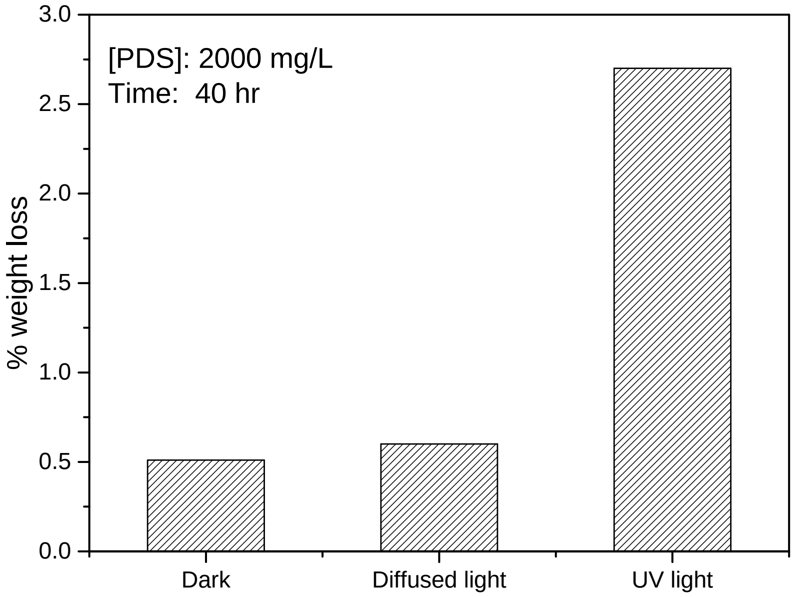


Figure 5.16: Efficiency of PDS on the degradation of PVC plastic at different conditions

In presence of semiconductor mediated photocatalysis PDS is known to enhance the degradation of organic pollutants by trapping the photo-produced electrons, thereby preventing the unproductive electron-hole recombination. In the absence of catalyst also, PDS can lead to the generation of more reactive free radicals and oxidising species such as ·OH and $SO_4^{-\cdot}$. The oxidation rate of intermediate compounds can be enhanced and the decrease in O_2 in the system during the degradation can be compensated by the PDS.

The mechanism of PVC degradation promoted by PDS may be proposed as follows:

(R = PVC in this case)

$S_2O_8{}^{2-} \rightarrow 2\ SO_4^{-}\cdot$ .... (107)

$S_2O_8{}^{2-} + R \rightarrow 2\ SO_4^{-}\cdot\ + R\cdot$ ....(108)

$SO_4^{-}\cdot + H_2O \rightarrow\ SO_4{}^{2-} + H^{+} + \cdot OH$ ....(109)

$SO_4^{-}\cdot\ + R \rightarrow\ R^{\cdot}\ +$ Products ....(110)

$\cdot OH + R \rightarrow$ Intermediates $\rightarrow$ Products ....(111)

$SO_4^{-}\cdot\ + R\cdot \rightarrow$ Chain termination ....(112)

$SO_4^{-}\cdot\ + \cdot OH \rightarrow$ Chain termination ....(113)

$R\cdot + \cdot OH \rightarrow$ Chain termination ....(114)

$2\ SO_4^{-}\cdot \rightarrow S_2O_8{}^{2-}$ (Chain termination)..(115)

$2\,\cdot OH \rightarrow H_2O_2$ ....(116)

$2\ R\cdot \rightarrow$ Chain termination..(117)

R· will breakdown after further interactions with the reactive free radicals eventually resulting in the mineralisation of PVC.

The absence of even simple additive effect in the simultaneous presence of PDS and TiO_2 was surprising. However this may be explained as follows based on the general mechanism of semiconductor photocatalysis. Schematic diagram illustrating the mechanism of photocatalysis is given in figure 5.17.

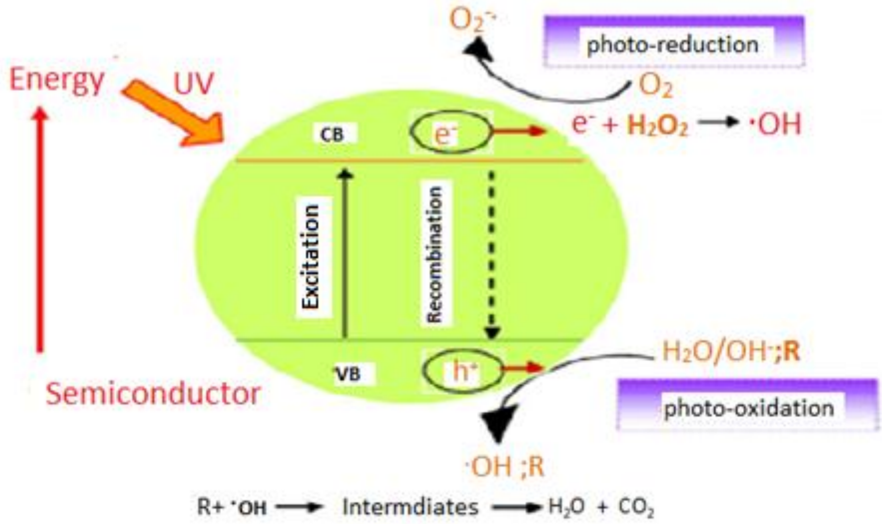


Figure 5.17: Schematic diagram illustrating the principle of semiconductor photocatalysis [194]

When a semiconductor is irradiated with photons of energy equal to or greater than its band gap energy (3.2 eV in the case of TiO_2 as well as ZnO) the photons are absorbed and electron-hole pairs are created [108,112]. These electrons and holes can either recombine or migrate towards the surface participating in several redox reactions eventually leading to the formation of Reactive Oxygen Species (ROS) such as $^{\cdot}OH$ radicals and H_2O_2. These transitory ROS can initiate and promote a number of reactions which end up in complete mineralisation of the pollutants into harmless products such as CO_2, water and salts as follows:

SC (Semiconductor) + $h\nu \rightarrow h^+ + e^-$ ....(118)

$h^+ + e^- \rightarrow$ Heat (Recombination) ....(119)

$h^+ + OH^- \rightarrow {}^{\cdot}OH$ ....(120)

$h^+ + H_2O \rightarrow {}^{\cdot}OH + H^+$ ....(121)

Scavenging of conduction band electrons

$e^{-} + O_2 \rightarrow O_2^{-\cdot}$ ....(122)

Formation of multiple peroxide species

$H^{+} + O_2^{-\cdot} \rightarrow HO_2^{\cdot}$ ....(123)

$HO_2^{\cdot} + e^{-} + H^{+} \rightarrow H_2O_2$ ....(124)

PVC + ROS (H_2O_2, $O_2^{-\cdot}$, $HO_2^{\cdot}$, $^{\cdot}OH$ etc) → Intermediates

→ H_2O + CO_2 + Salts ..(125)

In the case of PVC, HCl is one of the by-products of the degradation. The formation of Cl^{-} is verified experimentally after 400 hr of irradiation when ~7% of PVC has degraded, by using standard $AgNO_3$ method. However, the formation of HCl is not reflected in any significant decrease in pH, probably because the acid is getting converted to the potassium salt, by reaction with PDS or other potassium compounds in the system. Since Cl^{-} ions are known to inhibit the photocatalytic activity of many semiconductor oxides, the inability of TiO_2 to enhance the degradation promoted by PDS may be attributed at least partially to this. However results presented in section 5.3.6 show that Cl^{-} has practically no effect on the PDS promoted degradation of PVC. It is possible that the insitu formed Cl^{-} may be more active and can hence interact with the catalyst more effectively thereby inhibiting the reactions leading to the degradation of PVC. Other factors to be considered in this context are related to the interactions involving PDS.

$TiO_2 \rightarrow h^{+} + e^{-}$ ....(126)

$S_2O_8^{2-} + e^{-} \rightarrow SO_4^{2-} + SO_4^{-\bullet}$ ....(127)

$SO_4^{2-} + h^{+} \rightarrow SO_4^{-\bullet}$ ....(128)

Thus in presence of TiO_2, both SO_4^{2-} and $SO_4^{-\cdot}$ are formed from $S_2O_8^{2-}$ during irradiation. The former is known to inhibit many photocatalytic degradation reactions promoted by photoactivated TiO_2 [204]. $SO_4^{-\cdot}$ is a highly reactive oxidant and hence the inhibition by SO_4^{2-} can be more than compensated. However, it is also possible that the highly reactive $SO_4^{-\cdot}$ interacts with $S_2O_8^{2-}$ in the bulk as well as on the surface.

$$S_2O_8^{2-} + SO_4^{-\cdot} \rightarrow SO_4^{2-} + S_2O_8^{-} \quad \text{...(129)}$$

This results in the formation of less reactive $S_2O_8^{-}$ as well as SO_4^{2-} which can function as inhibitors.

The net effect of all these contradictory and complimentary interactions taking place on the surface as well as in the bulk is that the degradation in presence of (TiO_2+ PDS) is more or less same as that in presence of PDS only and the photocatalytic activity of TiO_2 is neutralised.

The intermediates may go through many reactions before eventual mineralization. The two highly reactive free radical species ($^{\cdot}OH$ and $SO_4^{-\cdot}$) formed from PDS together can more than compensate for the inhibiting factors, if any, caused by the SO_4^{2-} and Cl^{-} anions.

It is logical to assume that the cavities inside the plastic strip also expand with irradiation. The degradation is faster in the beginning and then slows down with time. The initial faster rate can be attributed to the interaction of reactive oxygen species and/other oxidising species with adjacent polymer chains leading to the degradation. These molecules of the intermediates have to be etched away so that the interaction with reactive free radicals and consequent degradation can continue. It is also possible that the degradation is initiated by photons attacking the polymer to create excited state followed by chain scission, branching, cross linking and oxidation. The chemical oxygen demand (COD) and biological oxygen demand (BOD) of the water in which the plastic sample was suspended were found to be nil indicating complete mineralisation of pollutants. At the same time the reaction media contains Cl^- as indicated by the formation of AgCl precipitate when treated with $AgNO_3$.

These results clearly illustrate that even highly recalcitrant materials such as PVC plastic can be mineralised by photolysis under suitably optimized conditions and in presence of oxidants.

PVC is also known to undergo degradation under UV irradiation. Impurities or defects present in the plastic sheet can initiate the degradation. Photolysis of PVC will start with the cleavage of C-Cl bond resulting in the generation of PVC radical.

$$\mathrm{PVC} + h\nu \rightarrow \mathrm{PVC}^{\bullet} \quad \text{..........} \quad (130)$$

Once these carbon centered radicals are formed in the polymer chain, they can interact successively with themselves or with reactive oxygen species (ROS) resulting in the formation of carboxyl, carbonyl or hydroxyl groups. Eventually they all get mineralized to CO_2 and H_2O.

$$\mathrm{PVC}^{\bullet} + \mathrm{ROS} \rightarrow CO_2 + H_2O + \mathrm{HCl} \quad \text{..........} \quad (131)$$

However these are much slower compared to the PDS or PDS/TiO2 promoted UV degradation of PVC.

5.3.6 Effect of anions and cations

The degradation of PVC results in the formation of chloride ions. Similarly, use of oxidants such as PDS results in the formation of SO_4^{2-} ions. The anions may influence the efficiency of photo/photocatalytic processes as has been demonstrated in many earlier studies [170]. Hence the effect of a series of anions which are likely to be present in the environment/water/soil with which the PVC plastic is likely to be in contact when littered, is investigated. Detailed studies were conducted to find the effect of anions and cations on the photocatalytic degradation of PVC plastic under the optimized conditions of other parameters. The effect of various anions on the photodegradation of PVC is shown in figure 5.18. Results show that presence of anions and cations at least in the concentration range studied here does not influence the photocatalytic degradation of PVC plastic. The cation is kept as same; ie Na^+, in all these cases.

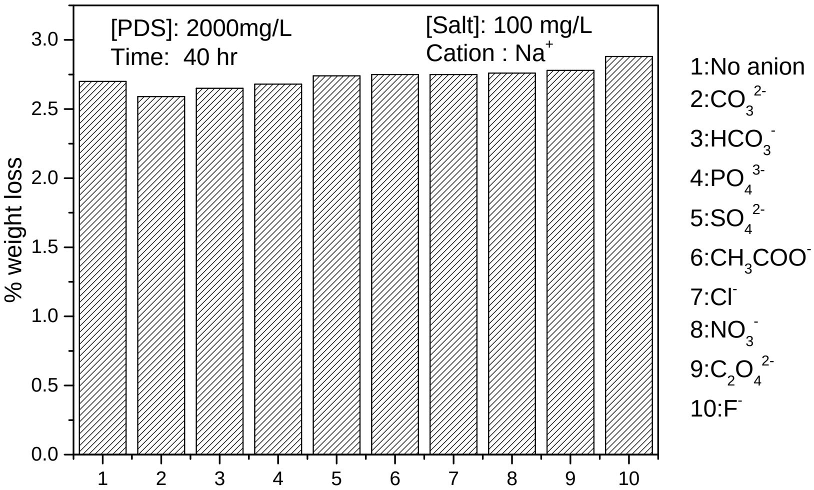


Figure 5.18: Effect of anions on the PDS promoted photocatalytic degradation of PVC

Study of the effect of various cations on the photocatalytic degradation shows that the degradation is practically unaffected in the presence of those cations (figure 5.19). In all these cases, the anion is kept the same; ie Cl^- .

The results show that K^+ has slight enhancing effect. Similar results with K^+ cation has been reported earlier also [205].

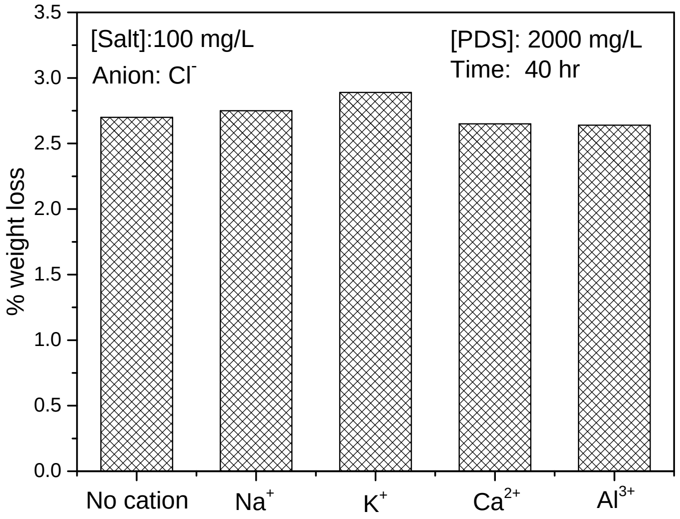


Figure 5.19: Effect of cations on the photocatalytic degradation of PVC in presence of PDS

If K^+ as a cation has enhancing effect on the photocatalytic degradation of PVC, the same should be reflected in the case of PDS also ie PDS with K^+ as cation ($K_2S_2O_8$) must be a better promoter compared to that with Na^+ ie, ($Na_2S_2O_8$). The degradation efficiencies of $Na_2S_2O_8$ and $K_2S_2O_8$ are compared and the results are shown in figure 5.20. The results clearly show that K^+ as the cation has a positive role in enhancing the degradation of PVC under photolysis.

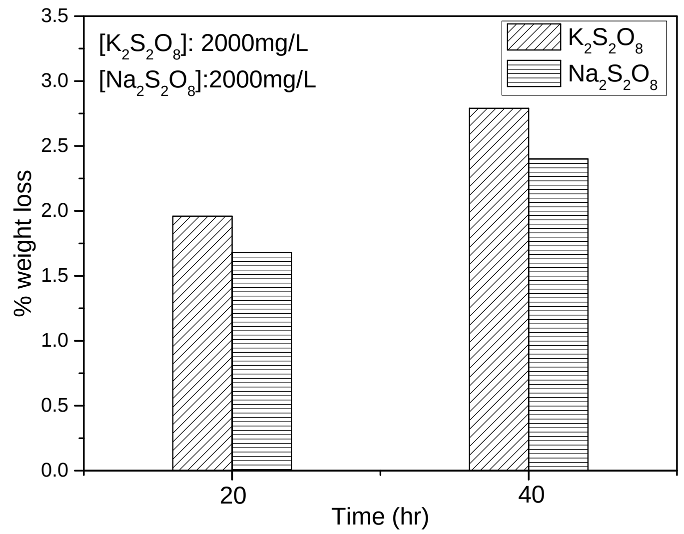


Figure 5.20: Comparative efficiency of $K_2S_2O_8$ and $Na_2S_2O_8$ for the Photodegradation of PVC

The effect of cations on the photocatalytic degradation of organics has not been investigated in detail. Even those limited number of reports give conflicting results. Presence of the anions in the salt which have their own inconsistent effect on photolytic processes, depending on concentration, reaction time, light intensity etc is another factor which complicates the salt effect. Extensive investigations under carefully designed conditions, including delineation of anion effect is important in this context. Such an investigation is beyond the scope of the current study and is hence not undertaken in this context of application of photocatalysis in pollution control. However, the possibility of using the mild enhancing effect of $K^{+,}$ for increasing the efficiency of photodegradation is examined by adding KCl at different concentrations [figure 5.21]. The degradation increases moderately with increase in concentration of K^+ and stabilizes/decreases at higher concentration. The anion is chosen as Cl^- since, it does not have any inhibiting effect on the degradation [figure 5.18]. The mild increase is not due to Cl^-, as the enhancement is less in the presence of NaCl (figure 5.22). However, the eventual stabilization/decreasing trend may be due to Cl^- also, as seen from the similarity in the effect at higher concentration of KCl as well as NaCl.

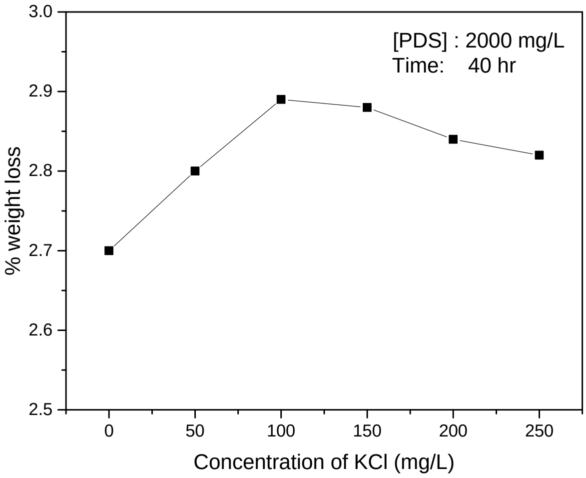


Figure 5.21: Effect of concentration of K^+ ions on the photocatalytic degradation of PVC in presence of PDS

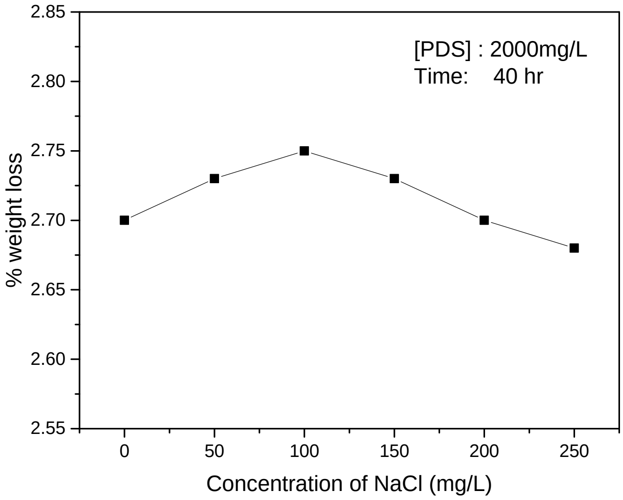


Figure 5.22: Effect of concentration of Na^+ ions on the photocatalytic degradation of PVC in presence of PDS

5.3.7 Effect of thickness of plastic sheet

One of the parameters which varies widely in the case of plastic sheets is their thickness. Hence the effect of thickness of the plastic sheet on the photocatalytic degradation was studied by taking PVC strips of different thickness. The experiment was done by taking three PVC samples of 1mm, 2mm and 3mm thickness keeping all other parameters constant. The results are presented in table 5.1. Irrespective of the thickness, the actual weight loss is more or less same.

Table 5.1: Effect of thickness of plastic sheet on the photodegradation of PVC plastic in presence of PDS [PDS]: 2000mg/L

Weight of PVC sample (g)	Thickness of PVC sample (mm)	Weight loss in 40 hr (g)
2.3333	1	0.063
4.5672	2	0.065
6.8923	3	0.064

The results show that as long as the surface area of the plastic sheet exposed to UV irradiation is the same the rate of degradation is independent of the thickness of the sheet. This observation is significant for the field application because, the shape/size of the plastic waste is immaterial in the efficiency of the process. Maximum exposure of the surface of the plastic films to the light irradiation is the critical factor.

5.3.8 Effect of combination of pollutants on the degradation of individual components

As PDS was found to be the best oxidiser for the degradation of both LDPE and PVC plastic, the effect of this oxidant on the photodegradation of the pollutants when they are together in the same reaction system was investigated by keeping the same optimum concentration of catalyst and oxidants as for individual components. The experiment was done in three sets. In all the three cases a suspension of 1400 mg/L TiO_2 and 2000 mg/L PDS was used. In the first experimental set up only LDPE strips and in the second case only PVC strips were suspended. Both LDPE and PVC strips were suspended together in the third system. The three sets were irradiated under identical conditions. The results are presented in figure 5.23. The rate of degradation is less in the case of both plastics when they are irradiated together. The effect of combination is less in the case of the relatively faster degrading LDPE. In the case of PVC plastic the degradation is inhibited more in the presence of LDPE. It is also observed that there is only slight increase in the degradation of PVC in the combination with time, in comparison to the system in which only PVC was there (figure 5.24).

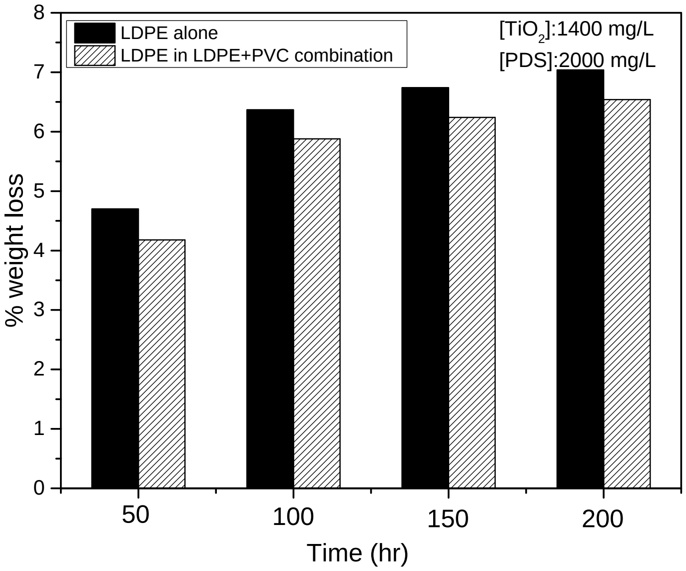


Figure 5.23: Comparative photodegradation of LDPE plastic individually and when in combination with PVC

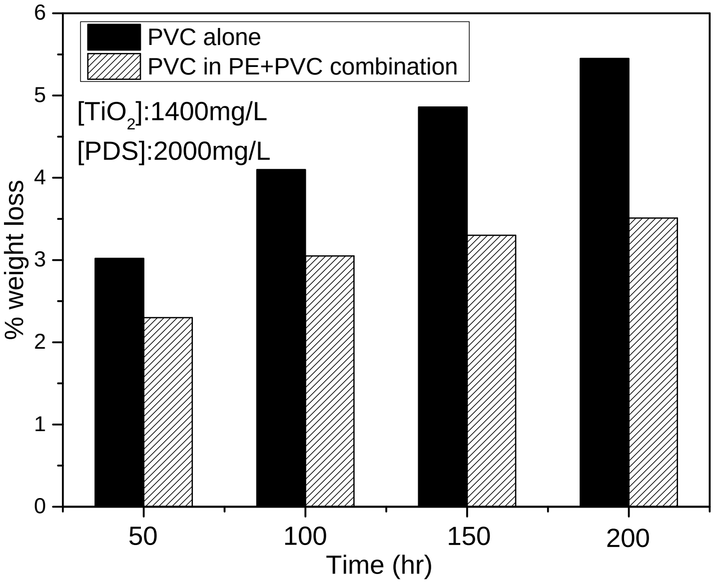


Figure 5.24: Comparative photodegradation of PVC plastic individually and when in combination with LDPE

TiO_2 as a photocatalyst has only negligible effect on the PDS induced degradation of PVC as demonstrated by earlier results. In view of the inhibition of PVC degradation in presence of LDPE, the possibility of augmenting the degradation of the former in the combination using varying amounts of TiO_2 as the photocatalyst is tested. Results are shown in figure 5.25 and 5.26. In the case of PVC plastic individually, the PDS induced degradation was unaffected in the presence of TiO_2. However in the combined system (of LDPE + PVC) the degradation of PVC is slightly enhanced in presence of TiO_2 (figure 5.25). As expected the enhancement is significant in the case of LDPE. It is possible that the multitude of free radicals present in the system including those formed from LDPE may be assisting the degradation of PVC in presence of TiO_2. However, increasing the dosage of TiO_2 beyond the earlier optimized quantity of 1400mg/L does not affect the degradation of PVC or LDPE (figure 5.26).

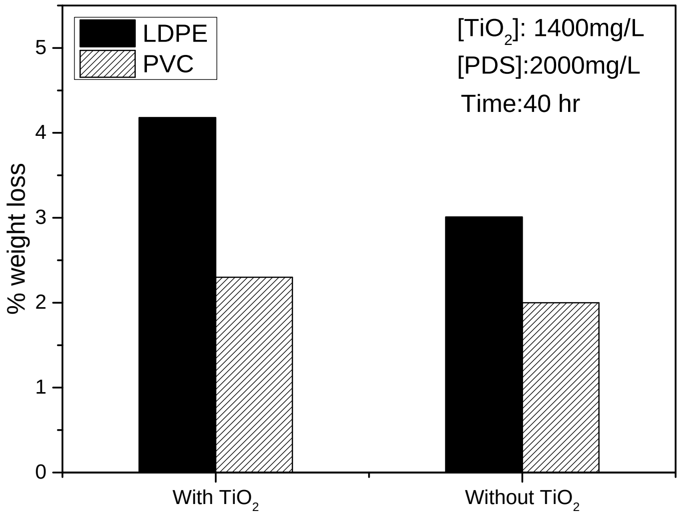


Figure 5.25: Effect of TiO$_2$ on the degradation of LDPE and PVC plastics when they are present together

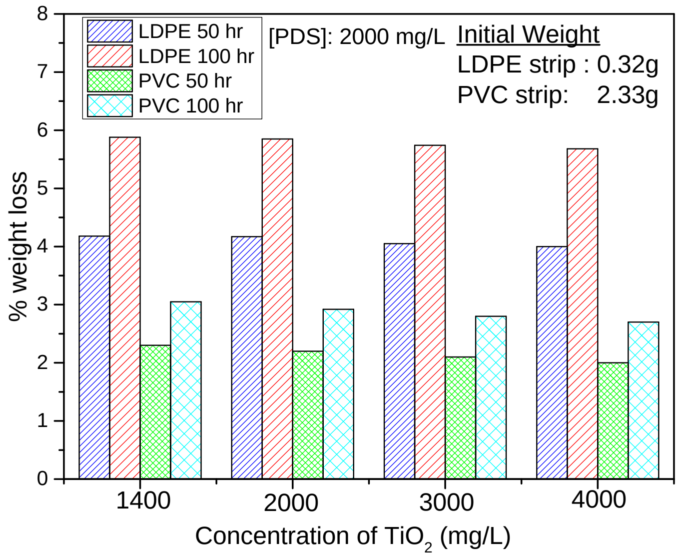


Figure 5.26: Effect of increase in concentration of TiO$_2$ on the photocatalytic degradation of LDPE and PVC plastics in combination

Hence it is clear that the optimum dosage of TiO_2 remains the same irrespective whether LDPE and PDS are present individually or in combination. An important observation is that the efficiency of TiO_2/PDS is reasonably sustained even when the plastic pollutants are combined together and irradiated. This will be important for the commercial application of the process where many different types of plastic pollutants of all sizes, shapes and chemistry must be treated economically.

5.3.9 Mechanism of the photolytic/photocatalytic degradation of polyvinyl chloride

Under UV irradiation, and in the presence of oxygen and moisture, PVC undergoes dehydrochlorination and peroxidation process with the formation of polyenes [206]. UV energy absorbed by plastics leads to the excitation by photons, which then create free radicals. These free radicals form hydroperoxides in the presence of oxygen and the process is often called photooxidation. In the absence of oxygen also there will be degradation due to the cross-linking process [207].

Various steps involved in the photooxidation of PVC can be described as follows [208-209]:

(1) Formation of polyene radical
(2) Formation of peroxy radical
(3) Formation of PVC radical
(4) Formation of γ-chloroalkyl peroxy radical
(5) Formation of hydroperoxide groups
(6) Formation of peroxide bridge
(7) Formation of alkoxy radicals

The reactions involved can be presented as in reactions (132)-(141).

$-(CH_2CHCl)- + h\nu \rightarrow -(CH_2{\bullet}CH)- + {\bullet}Cl$ ....(132)

(Formation of polyene and $^{\cdot}Cl$ radicals)

$-(CH_2{\bullet}CH)- + O_2 \rightarrow -(CH_2(OO{\bullet})CH)-$ ....(133)

(Scavenging of polyene radical by O_2 to form peroxy radical)

$-(CH_2(OO{\bullet})CH)- + -(CH_2CHCl)-$

$\rightarrow -(CH_2(OOH)CH)- + -({\bullet}CHCHCl)-$

$\rightarrow -(CH{=}CH)-$ ....(134)

(Formation of PVC radical by the interaction of PVC with peroxy radical)

$-(CH_2(OO{\bullet})CH)- + -(CH_2CHCl)-$

$\rightarrow -(CH_2(OOH)CH)- + -(CH_2{\bullet}CCl)- + O_2$

$\rightarrow -(CH_2C(OO{\bullet})Cl)-$ ....(135)

(Formation of ϒ-chloroalkyl peroxy radical)

$-(CH_2C(OO{\bullet})Cl)- + -(CH_2CHCl)-$

$\rightarrow -(CH_2C(OOH)Cl)- + -(CH_2{\bullet}CCl)-$ ....(136)

(Formation of hydroperoxide groups by hydrogen abstraction from PVC)

$2-(CH_2C(OO{\bullet})Cl)- \rightarrow -(CH_2CClOOCCl)-$ ....(137)

(Formation of peroxide bridge)

$-(CH_2C(OO{\bullet})Cl)- \rightarrow -(CH_2C(O{\bullet})Cl)-$ ....(138)

(Formation of alkoxy radicals)

$-(CH_2C(O{\bullet})Cl)- \rightarrow -(CH_2C(OH)Cl)- \rightarrow >C{=}O$ ....(139)

(Decomposition of alkoxy radical to the corresponding ketone)

$-(CH_2C(O\bullet)Cl)- \rightarrow\ >C=O$ ....(140)

(β–scission of alkoxy radical to form the corresponding ketone)

$-(CH_2C(O\bullet)Cl)- \rightarrow -(CH_2C(O)Cl)- + \bullet CH_2CH_2Cl \longrightarrow \bullet Cl\ -CHCH-$ [210].. (141)

(β–scission of alkoxy radical to form corresponding polyene)

Photolysis of PVC in the presence of O_2 leads to primary photochemical processes resulting in the formation of excited singlet polyenes. These excited states will then disappear by various routes including the allylic (C-Cl) bond cleavage with the formation of ($Cl^{\cdot}$) radical and polyene radical (eqn.132). The polyene radical which bears no Cl atom in the α -position is likely to be scavenged by O_2 to give peroxy radical (eqn.133). The peroxy radical reacts with the (CH_2) and (CH Cl) groups on PVC resulting in PVC radical (eqn.134). This is followed by the chain-dehydrochlorination of PVC (eqn.134). The peroxy radical attacks the (CH_2CHCl) group resulting in the formation of radical which possesses no labile β-chlorine (eqn.135) and it is likely to react with (O_2) to give a ϒ-chloroalkyl peroxy radical (eqn.135). The main oxidation products of PVC are expected to result primarily from various reactions of this radical. There are two major routes for the disappearances of the ϒ-chloroalkyl peroxy radical. The hydrogen abstraction from PVC with the formation of hydroperoxide groups (eqn.136) and the bimolecular interaction, leading to the formation of either a peroxide bridge (termination reaction, eqn.137) or the formation of alkoxy radicals (eqn.138). The most common reaction of alkoxy radicals is the hydrogen abstraction. The α –chloroalcohol formed by reaction of alkoxy radical with PVC is not stable and will rapidly decompose to the corresponding ketone, (eqn.139). Tertiary alkoxy radicals are also proved to be stabilized by β–scission. This process involves either (C-Cl) bond cleavage to form ketone or/and (C-C) bond cleavage to form polyene (eqn.140 and eqn.141) [211]. Thus it may be seen that both chlorinated volatile organic compounds as well as oxygenated compounds are formed. The bond energies of C-Cl and C-OH are almost the same [212]. Hence the formation of chlorinated and oxygenated products is controlled by the availability of $^{\cdot}Cl$ and $^{\cdot}OH$ radicals. In water matrix with excess of water molecules all around, generation of $^{\cdot}OH$ radicals will be prominent. These free radicals can compete with $^{\cdot}Cl$ in interacting with the PVC molecules and form different types of oxygenated compounds.

In addition to the above sequence of reactions, many other processes will be taking place in the photocatalytic system in presence of TiO_2. As seen in reaction (132) $^{\cdot}Cl$ free radicals are formed in the beginning of the process. Both photodegradation and photocatalytic degradation are possible in the system. $CHCl_3$, $COCl_2$ and CO_2 are reported from the photocatalytic degradation of PVC [213]. However, in the current study these compounds are not detected, probably because of the limitation of the analytical techniques used to measure small concentrations. Formation of these products shows that the photocatalytic degradation is an oxidation process. The mechanism of the process in presence of TiO_2 can be proposed as follows:

$$>TiOH^{+}\cdot + CHCl_3 \rightarrow TiOH_2^{+} + > \cdot CCl_3 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (142)$$

$$>Ti^{111}OH\cdot \; + > TiOH_2^{+} + O_2 \rightarrow Ti^{1V}OH^{+} + >TiOH_2 + \cdot O_2 \quad \ldots.(143)$$

$$\cdot CCl_3 + O_2 \rightarrow \cdot O_2CCl_3 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (144)$$

$2\ {\cdot}O_2CCl_3 \rightarrow 2{\cdot}OCCl_3 + O_2$ ....(145)

${\cdot}OCCl_3 + HO_2{\cdot} \rightarrow Cl_3COH + O_2$ ....(146)

$Cl_3COH \rightarrow Cl_2CO + H^+ + Cl^-$ ....(147)

$Cl_2CO + H_2O \rightarrow CO_2 + 2H^+ + 2Cl^-$ ....(148)

The general mechanism of photocatalysis involving the formation of reactive $^{\cdot}OH$ and other ROS is shown in figure 5.17, section-5.3.5. The highly reactive ROS can interact with PVC and various photogenerated radicals formed from it resulting in eventual degradation/mineralisation.

Thus eventually the recalcitrant polymer is irreversibly degraded to safer products. The mechanism of PVC degradation in presence of PDS, H_2O_2 and Fenton reagent is discussed in respective sections.

5.4 Conclusions

Semiconductor photocatalysis mediated by TiO_2 and/or peroxydisulphate is found to be a promising method for the safe removal of solid phase PVC plastic pollutants from the environment. Acidic pH enhances the degradation. However, due to economic and environmental concerns, this may not be a preferred option. Hence reaction parameters for optimum degradation efficiency were identified keeping pH at the natural harmless range of 5.5-7. Oxidants such as H_2O_2, Fenton reagent and peroxydisulphate (PDS) enhance the degradation. PDS is at least three times more efficient than the other oxidants. TiO_2 has no additional effect on the degradation of PVC plastic in the presence of Fenton reagent and PDS. Optimum concentration of PDS could achieve over 7% of PVC mineralisation in 400hr time. Complete mineralisation of PVC into CO_2, H_2O and salts are confirmed by the absence of any suspended matter as well as COD and TOC in water. The presence of salts (anions and cations) commonly present in water does not influence the photocatalytic degradation of PVC plastic. The degradation is not affected by the thickness of the PVC sample, as long as the light exposed surface area remains the same. Combination of LDPE and PVC in the same reaction system gives almost the same rate of degradation for both as in the case of systems with only individual components. However, in presence of TiO_2 photocatalyst, the degradation of PVC in the combination is more compared to the individual system. The study demonstrates that photocatalysis mediated by TiO_2 and/or peroxydisulphate offers good potential for the safer mineralisation of one of the worst environmental pollutant of the day, i.e. PVC plastics.

* * *

Chapter 6

SOLAR PHOTOLYSIS AND OTHER ADVANCED OXIDATION PROCESSES FOR THE DEGRADATION OF POLYETHYLENE AND POLYVINYL CHLORIDE PLASTICS

Contents

6.1 Introduction

The results presented in previous chapters point to the possibility of using photocatalysis as a viable technique for the degradation of plastic pollutants. The viability of the technique will be further enhanced if the abundant renewable sunlight is used as the energy source. The specific aim of the study in this chapter is to identify appropriate reaction conditions to harness solar energy for the effective degradation of plastic wastes which are accumulated in the environment, especially in residential households. Accordingly detailed investigations are made on the photocatalytic and photolytic degradation of plastics using sunlight as the energy source and TiO_2 as the catalyst.

Ultraviolet (UV) component of the solar radiation is known to be the main energy source in photocatalytic reactions including polymer degradation. The fraction of UV light with energy high enough (290–

400 nm, energy between 412–300 kJ/mol) to break chemical bonds is only about 4–6 % of the mean annual radiation falling on Earth [214]. In this context, the possibility of degradation of low density polyethylene (LDPE), high density polyethylene (HDPE) and PVC, which constitute the most commonly accumulated plastic waste in households as per the survey mentioned in Chapter-3, is studied using sunlight (SL) as the energy source. The effect of reaction parameters such as characteristics of the catalyst, presence of oxidisers, light intensity, temperature, time of irradiation, thickness of plastic sheet, presence of anions and cations etc is studied in detail. The ultimate reaction products of complete degradation/ mineralisation of plastic are CO_2, H_2O and salts depending on the chemistry of the material. The Total Organic Carbon (TOC) content in water (in which the plastic is suspended) is the parameter verified for complete mineralisation of plastic. Important factors that may affect the solar photodegradation of plastic can be summarised as in figure 6.1.

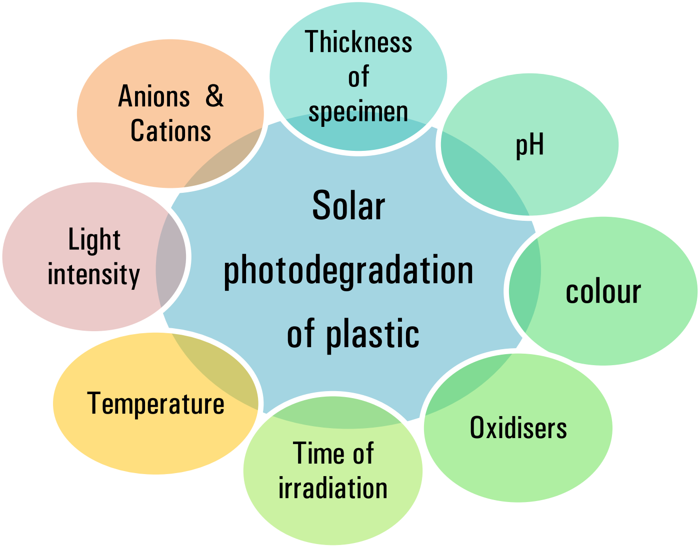


Figure 6.1: Factors affecting solar photodegradation of plastics

6.2 Materials and Methods

6.2.1 Materials

The sources of various materials used, their characteristics etc are the same as provided in Chapters 4&5. Here also the thickness of the specimen used was 41 micron for polyethylene (PE) and 1mm for PVC unless indicated otherwise.

6.2.2 Experimental set up

Typical plastic strips made from used carry bags and PVC pipes were used for the study. LDPE strips from carry bags used for the study were of circular shape of about 5cm diameter and PVC strips from pipes were rectangular of about 1cm breadth and 5cm length. They were cut in defined sizes, washed thoroughly, dried and then fully immersed in aqueous suspension of TiO_2. The irradiation under sunlight was done from 1000-1600 hr on sunny days. The experiments were carried out in 500ml glass beakers and the contents were frequently stirred. After specific intervals, the plastic strips were taken out, washed well with distilled water to remove sticking particles of catalyst, if any, and dried at room temperature in mild air flow until constant weight is reached. The weight loss, visible decrease in thickness, increased crumbling and periodic SEM imaging were used as the parameters to identify destruction of the samples used.

The experimental set up is shown in figure 6.2. The beakers containing plastic strips immersed in TiO_2-water suspension in which the plastic strips are immersed are placed in a plastic tray containing cooling water. The water in the plastic tray is periodically replaced to maintain the temperature of the suspension at the required temperature ± 2°C.

Figure 6.2: Solar experimental set up

Solar experiments were performed by placing the reactor assembly on the roof top of our laboratory at Kochi, Kerala, India (9^0 57’ 51” N, 76^0 16’ 59” E) during sunny days in February-May 2015 and 2016. Average solar light intensity during the experiment was 1.25×10^5 Lux, as calculated from the measurements using LT-Lutron LX-101A digital Lux meter.

6.3 Results and Discussion

The catalyst was characterized as explained in Chapter 4, section 4.2.

6.3.1 Effect of catalyst dosage

Optimization studies on catalyst dosage showed that the degradation increases with increase in loading and reaches an optimum at 3000 mg/L for both LDPE & PVC plastic (figure 6.3). Beyond the optimum loading, the light photon absorption coefficient decreases radially and the degradation slows down. Various other parameters that contribute to the optimum in the catalyst dosage in photocatalytic system have been explained in Chapters 4 and 5 (sections: 4.4 and 5.3).

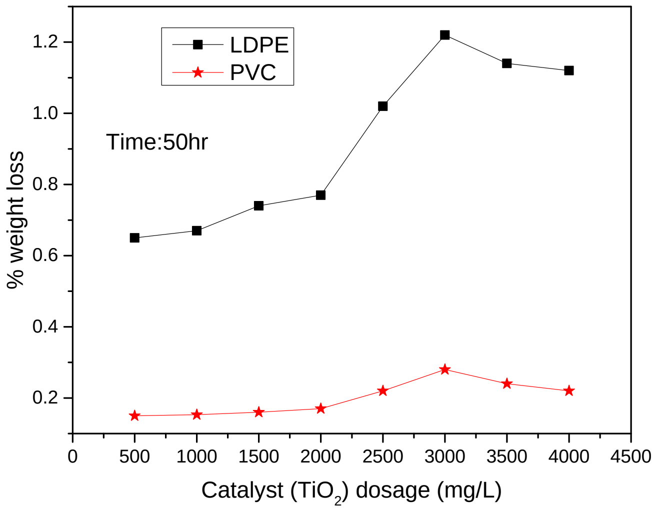


Figure 6.3: Effect of TiO_2 loading on the solar photocatalytic degradation of LDPE and PVC

The optimum dosage of TiO_2 is 3000 mg/L, in the case of degradation of both LDPE and PVC. However, the optimum dosage was only 1400 mg/L with UV irradiation as the energy source under similar experimental conditions. The higher optimum dosage of TiO_2 in the case of sunlight irradiation shows that more catalyst is needed to harness solar energy efficiently. This is natural since TiO_2 is more active in the UV region of the sunlight which is ~ 4-6% only.

6.3.2 Effect of recycling catalyst

The experiments to find the possibility of using catalyst repeatedly were done with fresh TiO_2 as well as TiO_2 used for 100 hr, 200 hr and 300 hr. The results are shown in figure 6.4 and 6.5.

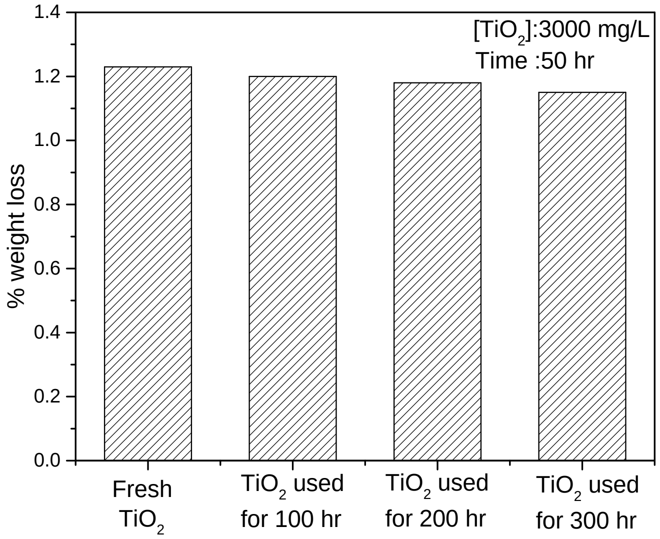


Figure 6.4: Efficiency of recycled catalyst for the photocatalytic degradation of LDPE plastic

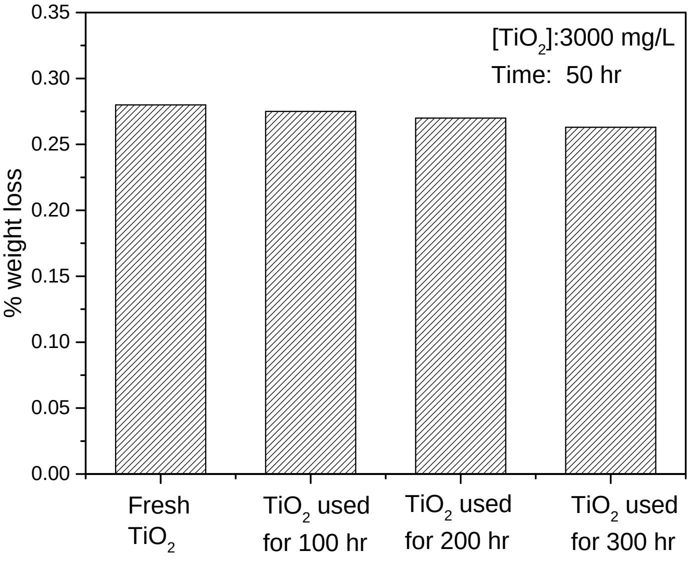


Figure 6.5: Efficiency of recycled catalyst for the photocatalytic degradation of PVC plastic

It is seen that the used TiO_2 can be recycled as solar photocatalyst many times without much loss of activity. As experimentally verified and reported in Chapters 4&5 (section 4.4.3 and 5.3.2) even though acidic pH favours photocatalytic degradation of LDPE and PVC plastic in presence of TiO_2, an extra neutralisation step will be required in this case which will make the process uneconomical and environmentally unfavourable for commercial applications. Hence, neutral pH which is also favourable for reasonable rate of degradation is chosen for further studies.

6.3.3 Effect of oxidizers on the degradation

As concluded from Chapters 4 and 5, oxidants such as H_2O_2 and PDS are good oxidisers for enhancing the degradation of LDPE and PVC. In view of these, the effect of these oxidants on the sunlight induced degradation of LDPE and PVC plastic is investigated in detail.

6.3.3.1 Effect of H_2O_2 on the degradation

The effect of concentration of the H_2O_2 on TiO_2 mediated degradation of LDPE and PVC are shown in figure 6.6. In the case of LDPE, increase in concentration of the H_2O_2 increases the degradation fairly steeply in the beginning upto ~500mg/L and stabilises thereafter. In the case of PVC also the increase in degradation is steep initially. Thereafter it is relatively slower and 500mg/L may be considered as optimised concentration. The pH of the system is not affected much by the addition of H_2O_2 in this range (upto 1500mg/L) and hence the increase in the degradation cannot be attributed to pH effect.

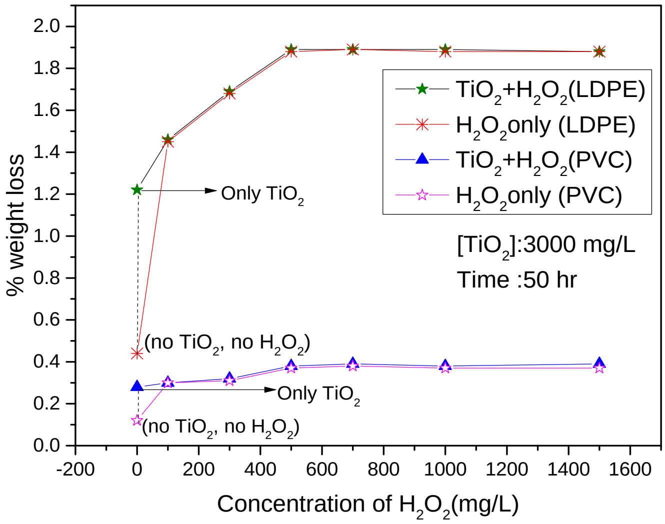


Figure 6.6: Effect of H_2O_2 on the solar degradation of LDPE and PVC plastic with and without TiO_2

The results show that (TiO_2 + H_2O_2) is only as effective as H_2O_2 for the solar degradation of LDPE and PVC plastics. The effect of increase in the concentration of H_2O_2 beyond the optimum is practically 'nil' in both cases showing that at high concentration of H_2O_2, the $^{\cdot}OH$ radicals formed in the system (from H_2O_2 as well as the photoactivation of TiO_2) will interact more with the more reactive H_2O_2 and then only with the recalcitrant plastic. Hence (TiO_2 + H_2O_2) is not a viable option for the solar degradation of plastic, at least under the experimental conditions used.

6.3.3.2 Effect of peroxydisulphate (PDS) on the solar degradation

The oxidant PDS, has been successfully tested as an enhancer for the degradation of LDPE and PVC plastics under AOTs as demonstrated in the earlier chapters. In the current study, the possibility of using PDS as the accelerator for the sunlight induced degradation of LDPE and PVC plastics is examined. The comparative degradation of LDPE and PVC plastic under solar irradiation in presence of TiO_2 as well as TiO_2/PDS is shown in figure 6.7. The optimised dosage of TiO_2 is used and the concentration of PDS is varied to arrive at an optimum efficiency. The degradation increases steeply with increase in concentration of the oxidant upto 1000 mg/L and levels off thereafter. Also in both cases TiO_2 does not have any effect on the photodegrdation of the plastics in presence of PDS as in the case of another oxidant H_2O_2, as demonstrated earlier.

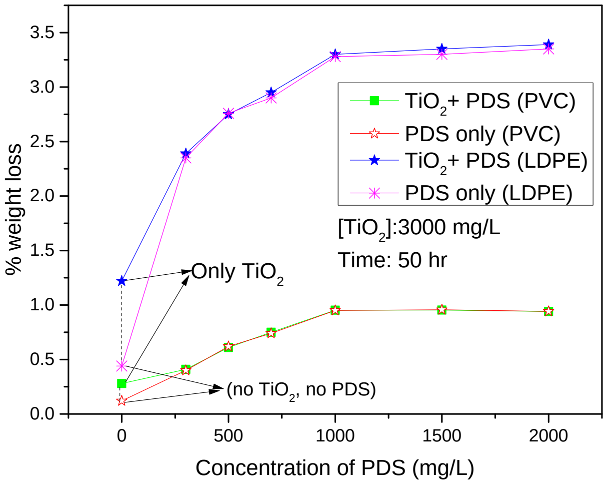


Figure 6.7: Effect of PDS for the solar degradation of LDPE and PVC plastics with and without TiO_2

The pH of the system varies from ~ 6 to ~ 4.5 in presence of PDS. The pH effect on the degradation of LDPE and PVC under UV (Chapters 4 and 5, sections 4.4.3 and 5.3.2) shows that the degradation does not vary much in this range. Hence the enhancement in presence of PDS cannot be attributed to any change in pH.

The effect of optimised quantity of PDS on the solar degradation of LDPE and PVC plastic is shown in figure 6.8. As in the case of UV irradiation reported in Chapter 4, LDPE plastic gets degraded much faster under sunlight/PDS, compared to PVC plastic.

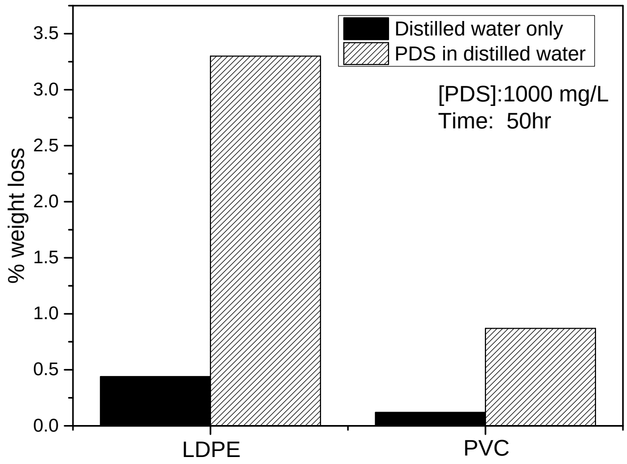


Figure 6.8: Solar degradation of LDPE and PVC plastic with and without PDS

Visual observations as well as photographs of the plastic strips before and after the solar irradiation in presence of PDS illustrate that the surface morphology of plastic has significantly changed. The plastic sheet becomes thinner, crumbles and becomes brittle in the case of LDPE plastic and becomes thinner and softer in the case of PVC plastic. The photograph of crumbled LDPE plastic is shown in figure 6.9. It is not so visually evident in the case of the harder and thicker PVC and hence a direct photograph is not taken. However, the surface of the plastic becomes rough and uneven, as can be felt by physical touching. SEM image of PVC sheet before and after photodegradation is shown in Chapter 5 (figure 5.14).

(a) **(b)**

Figure 6.9: LDPE plastic samples (a) before and (b) after irradiation

The degradation of plastic can lead to the formation of both soluble and insoluble intermediates before they get mineralised. However the intermediates are not detected in water (in which plastic samples are suspended) indicating that they are getting degraded faster than the parent plastic. Absence of TOC in water in which the plastic strip was suspended confirms the complete mineralisation. The photodegradation of LDPE plastic in presence of PDS with and without TiO_2 in terms of weight loss at different times of irradiation is shown in figure 6.10. The degradation in presence of PDS continues without decrease in rate for longer periods. Combination of TiO_2 and PDS, is only as effective as PDS only as shown earlier and is hence not tested at different times. The efficiency of ~10% degradation (figure 6.10) of LDPE in 400hrs is one of the highest reported so far in solar photolysis for such plastics. Hence this technique can be considered as a potentially inexpensive safer technology for the disposal of LDPE plastics.

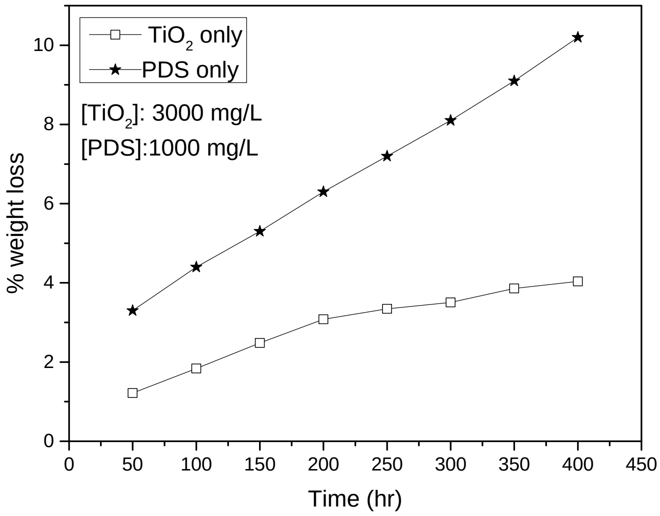


Figure 6.10: Effect of PDS on the solar degradation of LDPE plastic

Similarly results of solar degradation of PVC with and without catalyst at different times of irradiation are shown in figure 6.11.

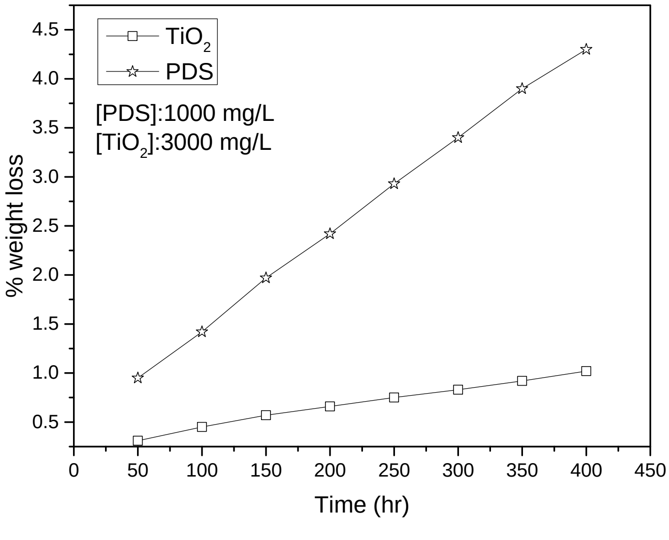


Figure 6.11: Effect of PDS on the solar degradation of PVC plastic

The degradation is ~4.5% in presence of PDS in 400 hr. Comparative degradation of both LDPE and PVC strips in presence of UV light and sunlight under respective optimised conditions is shown in figure 6.12. In both cases, the degradation is more under UV than under sunlight. The relative increase in degradation in the case of LDPE under UV/TiO_2/PDS is ~ 25% (from ~10% under sunlight to ~12.5% under UV/TiO_2/PDS) and 75% in the case of PVC (from ~4% under PDS/sunlight to ~7% under UV/PDS).

Direct comparison of the results under UV irradiation (reported in previous chapters) and solar irradiation may not be quite appropriate since the conditions are different. Under UV irradiation, maximum degradation in the case of LDPE is seen in presence of (PDS+TiO_2) while under solar irradiation TiO_2 has no effect on PDS initiated degradation. In the case of PVC, TiO_2 has no effect on PDS initiated degradation under UV as well as sunlight.

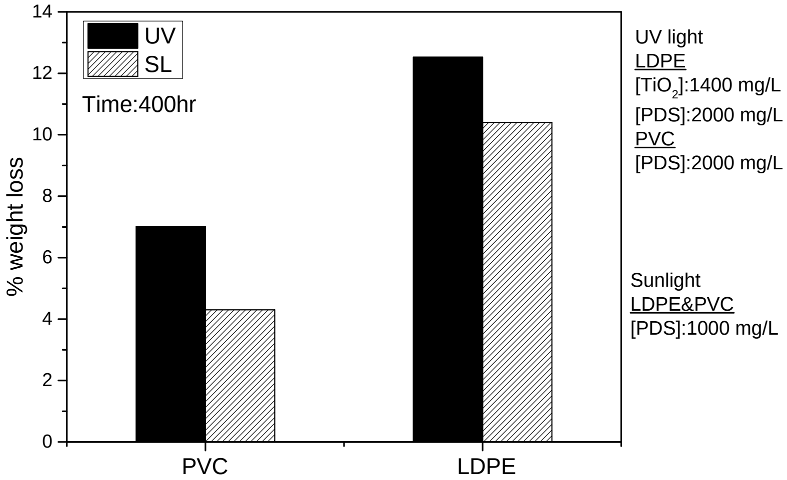


Figure 6.12: Comparative effect of UV and sunlight on PDS initiated degradation of LDPE and PVC plastic

Hence it is concluded that in the case of both LDPE and PVC plastic, solar irradiation is not as efficient as UV irradiation with or without catalyst. However since sunlight is natural, renewable and more economical with reasonable efficiency, further studies are made under solar irradiation only.

6.3.4 Use of Fenton reagent for the solar degradation of plastics

As mentioned in Chapters 4 and 5, Fenton reagent which is a mixture of $FeSO_4$ [FS] and H_2O_2, is an enhancer of the degradation of plastics. So the effect of Fenton reagent on the solar degradation of LDPE and PVC plastics is investigated in detail. The efficiency of degradation of LDPE at various ratios of FS and H_2O_2 is evaluated by keeping the concentration of the former constant and varying that of the latter. The optimum ratio of FS/H_2O_2 (mg/L) is identified as 1:8 in the case of LDPE as shown in figure 6.13. As in the case of PDS, in this case also, addition of TiO_2 does not cause any change in the rate of degradation.

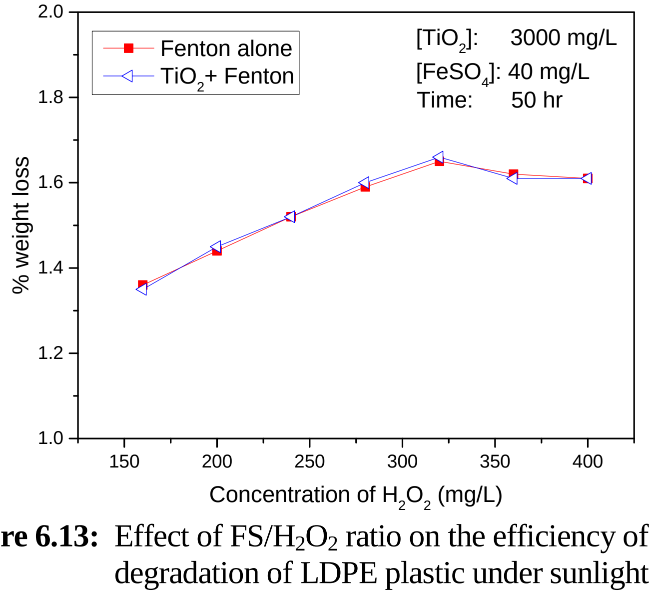


Figure 6.13: Effect of FS/H_2O_2 ratio on the efficiency of Fenton degradation of LDPE plastic under sunlight

The effect of concentration of the Fenton reagent (FR) in the optimum ratio (FS/H_2O_2=1:8) on the degradation of LDPE is examined. The degradation increases with increase in quantity of FR and reaches an optimum when the quantity is 80:640 (FS:H_2O_2). This is shown in figure 6.14. Beyond the optimum, the degradation is stabilised.

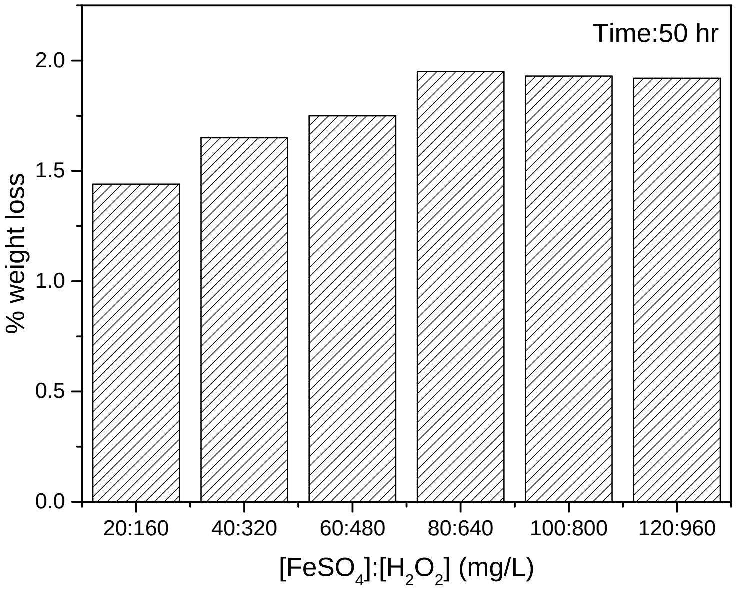


Figure 6.14: Effect of concentration of Fenton reagent on the rate of degradation of LDPE plastic

In the case of PVC, optimum ratio FS:H_2O_2 (mg/L) is identified as 1:6 as shown in figure 6.15. In this case also, the effect of TiO_2 is only marginal.

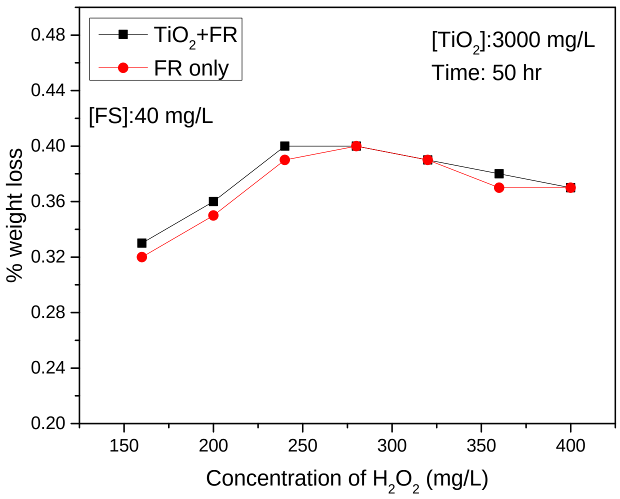


Figure 6.15: Effect of FS/H_2O_2 ratio on the efficiency of Fenton degradation of PVC plastic under sunlight

Study on the effect of concentration of the Fenton reagent at the optimum ratio of the components (FS/H_2O_2 = 1:6) on the degradation of PVC shows that the degradation reached an optimum when the quantity is 40:240 (FS:H_2O_2).This is shown in figure 6.16.

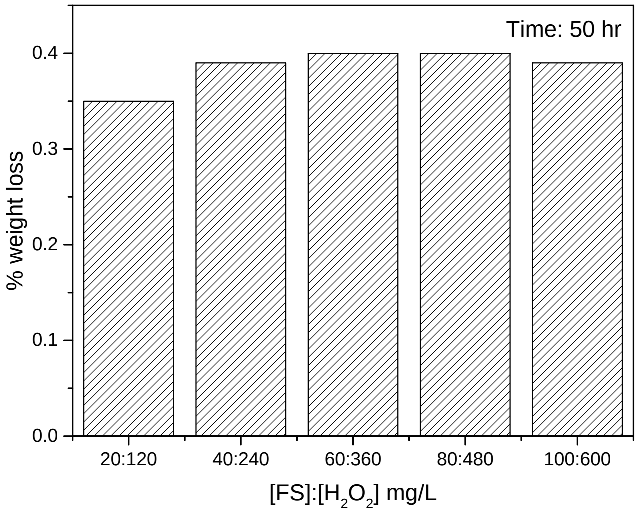


Figure 6.16: Effect of concentration of Fenton reagent on the rate of degradation of PVC plastic

The sunlight induced photocatalytic degradation of LDPE and PVC is tested in the presence of H_2O_2, FR (with optimum FS: H_2O_2 ratio) and PDS and the results are compared in figure 6.17 and figure 6.18.

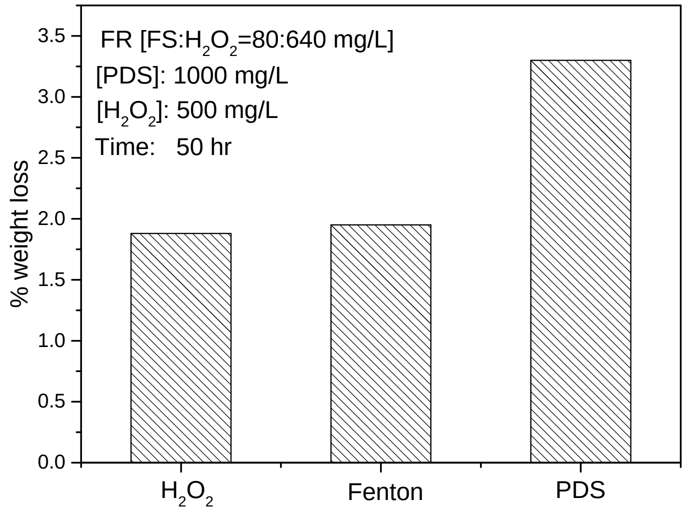


Figure 6.17: Comparative efficiency of H_2O_2, Fenton reagent and PDS for the solar degradation of LDPE

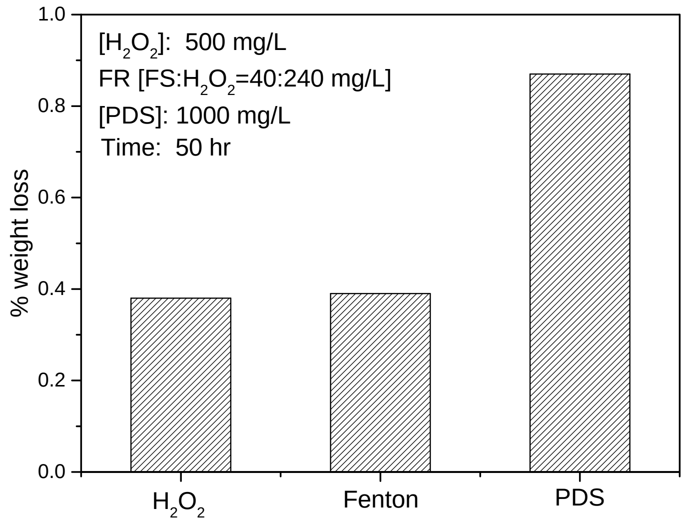


Figure 6.18: Comparative efficiency of H_2O_2, Fenton reagent and PDS for the solar degradation of PVC

It is seen that PDS is the most efficient among the tested oxidants for the solar degradation in the case of both LDPE and PVC plastics. Hence further studies are conducted with PDS only as the oxidant.

6.3.5 Effect of temperature

The effect of temperature on the solar photodegradation of LDPE and PVC plastics under the best reaction conditions (PDS/SL) was studied. The experiment is carried out in reactors containing LDPE and PVC strips suspended in water. The concentration of PDS was 1000mg/L (optimised concentration for both LDPE and PVC plastics). The reactors/beakers containing the samples were placed in a water bath. The required temperature was maintained by adjusting the temperature of water in the water bath suitably. The results are shown in figures 6.19 and 6.20.

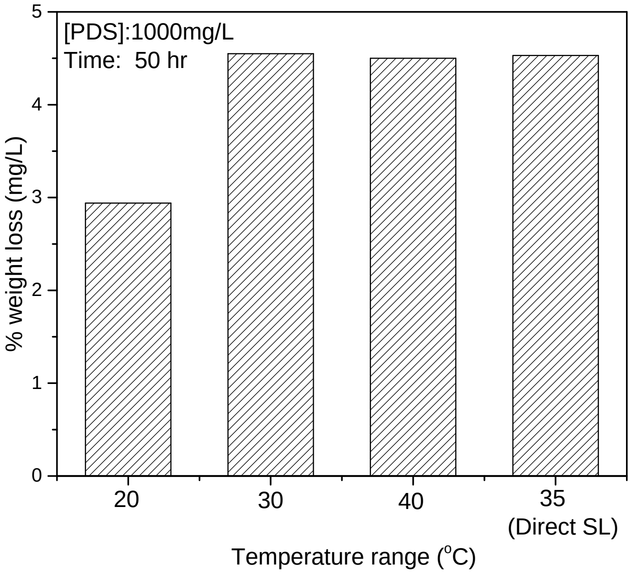


Figure 6.19: Effect of temperature on the solar degradation of LDPE plastic in presence of PDS

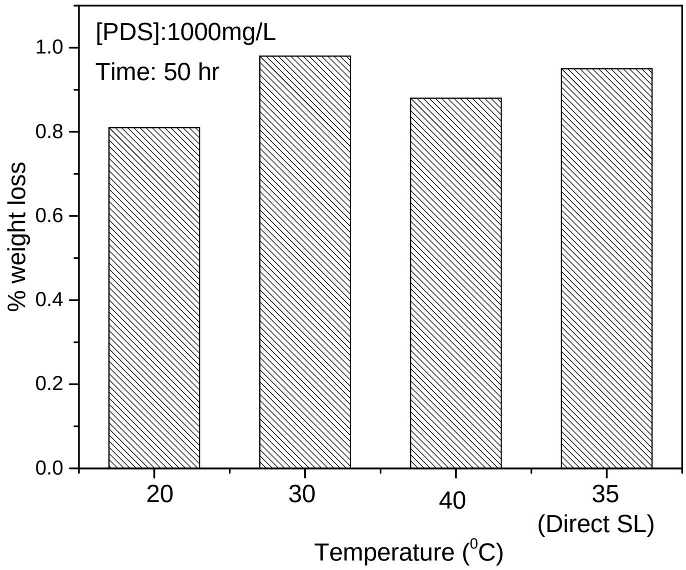


Figure 6.20: Effect of temperature on the solar degradation of PVC plastic in presence of PDS

In the case of both LDPE and PVC, optimum temperature for better degradation was found to be ~ 30°C. The extent of degradation under natural sunlight without any temperature adjustment of the reaction system also is shown (direct sunlight). In this case the temperature varied from 30-40^{0}C. The solar degradation of plastic is comparable with and without temperature adjustment in the range 30-40°C in the case of both LDPE and PVC. Hence, it is not necessary to artificially adjust the temperature for enhancing the degradation at least in the range 30-40°C.

6.3.6 Effect of anions and cations

The effect of a series of anions and cations which are likely to be present in the environment/water/soil with which the plastics are likely to be in contact is investigated. Study of the effect of these ions on the solar degradation is important in the context of commercial application of the method. Hence the effect of added anions and cations in water, in which the LDPE and PVC plastic were suspended, on the degradation was investigated under the optimized conditions of PDS/sunlight.

The effect of some of the common anions on the solar degradation of LDPE and PVC plastics in presence of PDS is studied. The concentration of the chosen anions is kept at 100mg/L. The cation in all cases is Na^+.

The results are shown in figure 6.21 and figure 6.23.

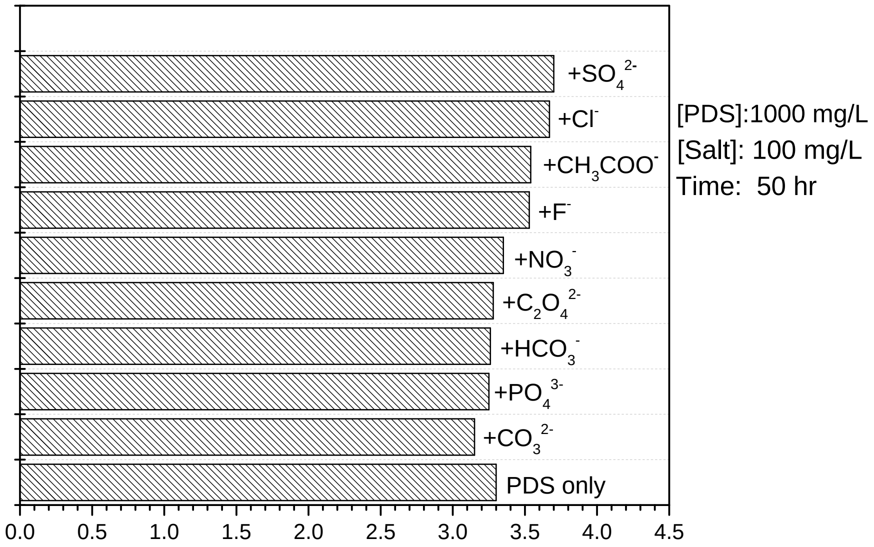


Figure 6.21: Effect of anions on the solar degradation of LDPE plastic in presence of PDS

The effect of anions is not much significant. SO_4^{2-}, Cl^-, CH_3COO^- and F^- have shown slight enhancement while CO_3^{2-}, PO_4^{3-} and HCO_3^- show slight inhibition. In order to further verify the extent of enhancement or inhibition, the effect of concentration of two selected anions, ie, SO_4^{2-} (enhancer) and CO_3^{2-} (inhibitor) on the degradation of the plastic is studied. The results are shown in figure 6.22.

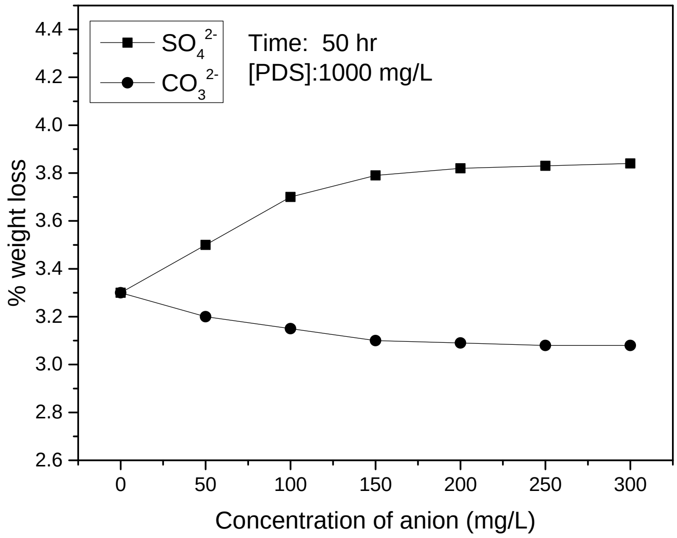


Figure 6.22: Effect of sulphate and carbonate ions on the solar degradation of LDPE in presence of PDS

The degradation of LDPE is increasing with increase in concentration of SO_4^{2-} and stabilises at 150-200 mg/L. In the case of CO_3^{2-}, the inhibition is not varying much with its concentration. Hence the general conclusion; ie 'SO_4^{2-}, Cl^-, CH_3COO^- and F^- enhance the degradation of LDPE moderately' is applicable only in the range of concentration used in the study and cannot be generalised for all concentrations and reaction times.

In the case of PVC plastic (figure 6.23), CO_3^{2-} and HCO_3^- inhibit the degradation. F^- and PO_4^{3-} also inhibit the degradation mildly. Other anions do not have any significant effect.

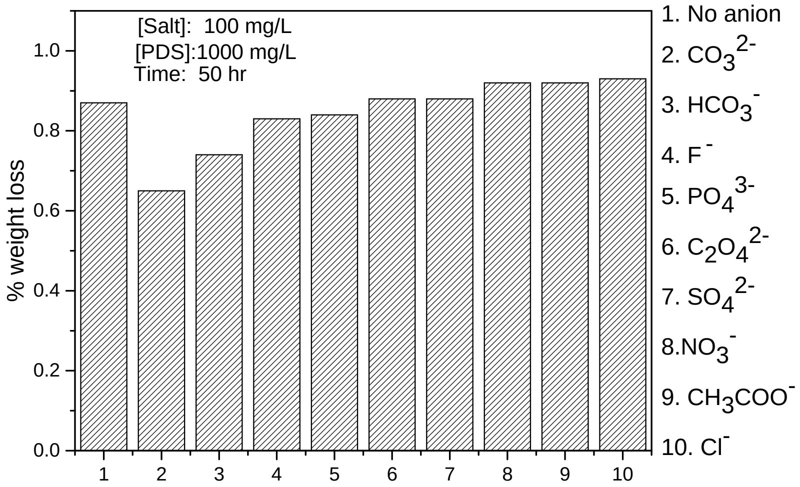


Figure 6.23: Effect of anions on the solar degradation of PVC plastic in presence of $K_2S_2O_8$

As observed in the case of the degradation of plastics under UV irradiation, in the presence of a powerful oxidant like PDS, the effect of anions is not significant under sunlight also. Only strong inhibitors like CO_3^{2-} and HCO_3^- have moderate effect in presence of PDS. Hence it may be inferred that PDS is an efficient enhancer for the photodegradation of plastic even in natural water containing a variety of anionic contaminants.

Any study on the effect of anions has to naturally include the effect of corresponding cations also. Hence, the effect of certain cations on the solar degradation of LDPE and PVC plastics is tested keeping the anion same, ie, Cl^-. This anion is chosen because it has only negligible effect by itself on the degradation of the two types of plastics. The results are shown in figure 6.24 and figure 6.25. The concentration of the salt is kept same at 100 mg/L.

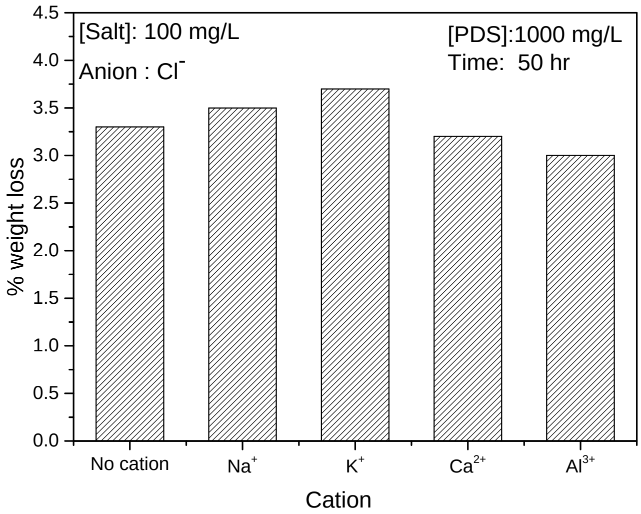


Figure 6.24: Effect of cations on the solar degradation of LDPE plastic in presence of PDS

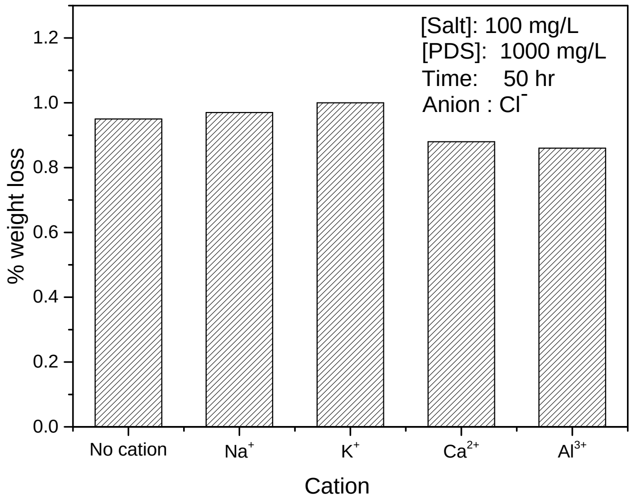


Figure 6.25: Effect of cations on the solar degradation of PVC plastic in presence of PDS

In the case of LDPE plastic, Na^+ and K^+ ions have moderate enhancing effect. Ca^{2+} has no effect while Al^{3+} is a mild inhibitor. The results are fairly the same in the case of PVC plastic too. In order to further verify the extent of enhancement or inhibition, the effect of two selected cations, ie, K^+ (enhancer) and Al^{3+} (inhibitor) on the degradation of LDPE plastic is tested. The results are shown in figure 6.26.

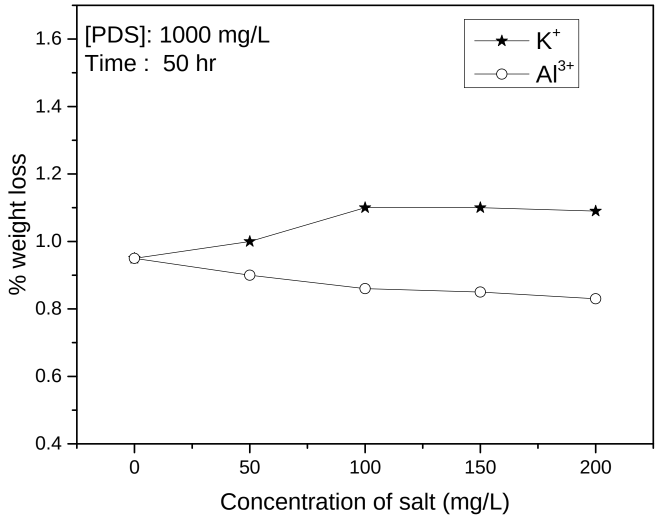


Figure 6.26: Effect of K^+ and Al^{3+} on the solar degradation of LDPE plastic in presence of PDS

The degradation of LDPE increases with increase in concentration of K^+ and stabilises at 100-200mg/L. In the case of Al^{3+} the mild inhibition increases as the concentration increases at least in the study range. Hence the environment in which the plastics are littered, especially the chemistry of soil, water etc and the salts present in them, have moderate influence on the degradation of LDPE and PVC plastics.

6.3.7 Effect of humic acid

The effect of humic acid in water on the rate of degradation of LDPE and PVC plastics in presence of PDS is studied and the results are presented respectively in figures 6.27 and 6.28.

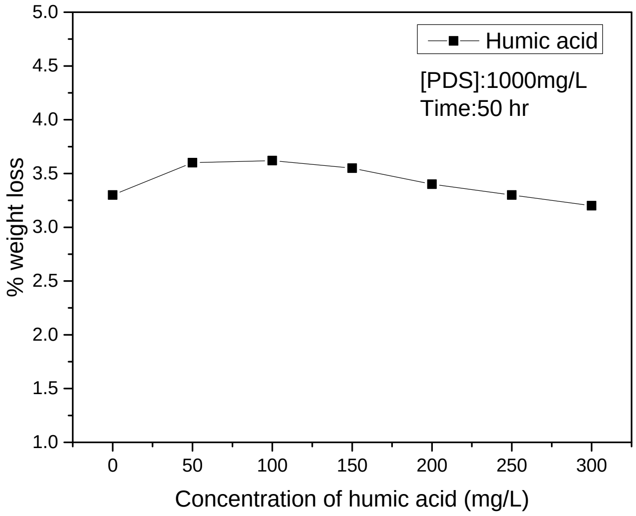


Figure 6.27: Effect of humic acid on the solar degradation of LDPE plastic in presence of PDS

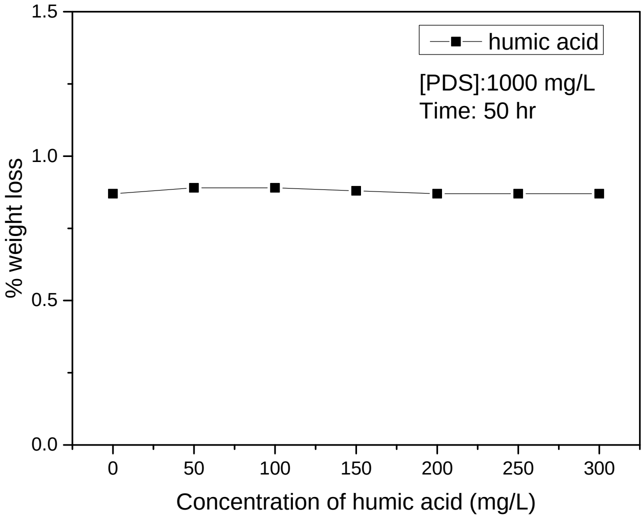


Figure 6.28: Effect of humic acid on the solar degradation of PVC plastic in presence of PDS

The study shows that the presence of humic acid at least in the concentration range of 0-300 mg/L has practically no effect on the PDS initiated solar degradation of both LDPE and PVC plastics.

6.3.8 Effect of diffused light/ direct light intensity

PDS functions as an oxidiser even in the dark for the degradation of LDPE and PVC. Under direct sunlight, the PDS induced degradation is enhanced considerably. Hence it is possible that the solar degradation can proceed even under diffused light or under shade as long as there is PDS. The possibility is checked quantitatively by conducting the experiments in dark, diffused light and direct sunlight, under otherwise identical conditions. The experiment is conducted by suspending LDPE and PVC strip samples in different beakers containing optimised concentration of PDS. One beaker is covered with black paper so as to maintain dark condition. Second one is kept inside the laboratory without covering (diffused light) and the third one is kept under direct sunlight. The results for LDPE and PVC are shown in figures 6.29 and 6.30 respectively.

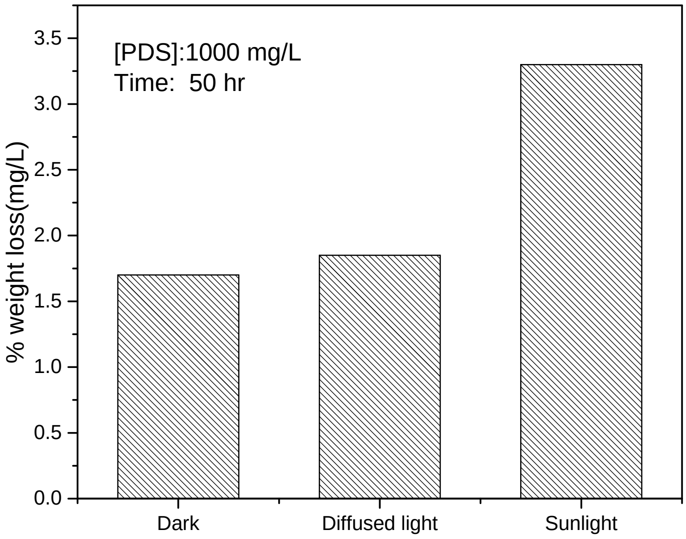


Figure 6.29: Degradation of LDPE at different light intensities

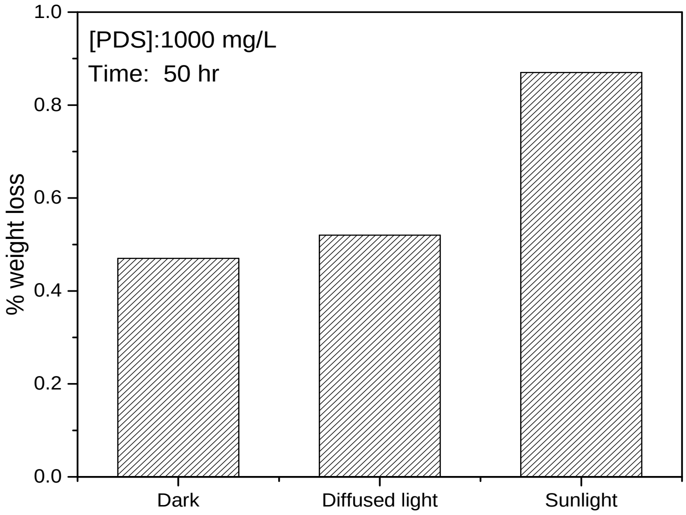


Figure 6.30: Solar degradation of PVC at different light intensities

Maximum degradation is observed in the presence of direct sunlight. The degradation is slow in the dark and diffused light indicating the role of intensity of light in the photodegradation of both LDPE and PVC plastics. However, any meaningful conclusion on the use of different light intensities for plastic samples degradation will require extended hours (days and weeks together) of study which is beyond the scope of this investigation.

6.3.9 Effect of size and thickness of the plastic strip on the degradation

Plastics come in different sizes, designs and shapes. These factors may also influence the rate of degradation. The effect of these parameters on the rate of degradation was studied by varying the thickness, length and breadth of samples under optimised conditions as explained earlier. The samples were kept in PDS suspension in direct sunlight for specified time period.

In order to study the effect of size and shape on the rate of degradation, plastic samples with different thickness, length and breadth were taken. The study shows that the light exposed surface area matters more for the degradation rate rather than the size and shape of the sample. The results of the study conducted by taking LDPE and PVC samples of same thickness but different length and breadth are shown in table 6.1 (a) and (b). Weight loss of the respective samples after 50 hr of exposure to sunlight is found to be proportional to the exposed surface area and the percentage degradation is more or less same.

Table 6.1 (a): The effect of exposed surface area on the rate of solar degradation of LDPE plastic
[PDS]: 1000 mg/L Time: 50 hr

Thickness of LDPE sample (microns)	Length of LDPE sample (cm)	Breadth of LDPE sample (cm)	Surface area (cm^2)	Initial weight of the strip(g)	Weight loss (g)	% degradation
41	5	5	25	0.4035	0.0133	3.296
41	5	10	50	0.8074	0.0255	3.158
41	10	10	100	1.6151	0.0522	3.232

Table 6.1(b): The effect of exposed surface area on the rate of solar degradation of PVC plastics
[PDS]: 1000 mg/L Time: 50 hr

Thickness of PVC sample (mm)	Length of PVC sample (cm)	Breadth of PVC sample (cm)	Surface area (cm^2)	Initial weight of the strip (g)	Weight loss (g)	% degradation
1	5	1	5	1.1263	0.0107	0.95
1	5	2	10	2.2727	0.0225	0.99
1	10	2	20	4.1170	0.0422	1.025

The results show that the weight loss and the degree of degradation of both types of plastic depend on the exposed surface area. The weight loss increases with increase in surface area, even though the % degradation is the same in all cases. Hence, design of bigger reactors/reactor ponds which can expose more surface of the plastic to the sunlight can enhance the degradation. This is further confirmed by the results presented in tables 6.2 (a) and (b). In this case, the study is conducted by taking samples of same thickness, length and breadth and hence same surface area. The weight loss and percentage degradation are found to be more or less the same in all the three cases for both LDPE and PVC plastics.

Table 6.2 (a): Confirmation of the importance of solar exposed surface for the degradation of LDPE plastic
[PDS]: 1000 mg/L Time: 50 hr

Thickness of LDPE sample (microns)	Length of LDPE sample (cm)	Breadth of LDPE sample (cm)	Surface area (cm^2)	Initial weight of the strip (g)	Weight loss (g)	% degradation
41	5	5	25	0.4035	0.0133	3.296
41	5	5	25	0.4034	0.0128	3.173
41	5	5	25	0.4034	0.0131	3.247

Table 6.2 (b): Confirmation of the importance of solar exposed surface for the degradation of PVC plastic
[PDS]: 1000 mg/L Time: 50 hr

Thickness of PVC sample (mm)	Length of PVC sample (cm)	Breadth of PVC sample (cm)	Surface area (cm^2)	Initial weight of the strip (g)	Weight loss (g)	% degradation
1	5	1	5	1.1263	0.0107	0.95
1	5	1	5	1.1313	0.0112	0.99
1	5	1	5	1.1086	0.0102	0.92

The above results show that the most important parameter for the solar degradation of plastic is the exposed surface area. This is further confirmed by varying the thickness of the plastic sheet. The experiment was done by taking three LDPE samples of thickness 31micron, 41micron and 51micron and PVC samples of thickness 1mm, 2mm and 3mm. The length and breadth of all the samples are kept the same. The results in tables 6.3 (a) and (b) show that the actual weight loss in all the cases is more or less the same, irrespective of the difference in thickness.

Table 6.3 (a): The effect of specimen thickness on the rate of degradation of LDPE plastic
[PDS]: 1000 mg/L Time: 50 hr

Thickness of LDPE sample (microns)	Length of LDPE sample (cm)	Breadth of LDPE sample (cm)	Surface area (cm^2)	Initial weight of the strip (g)	Weight loss (g)	% degradation
31	5	5	25	0.2966	0.0129	4.35
41	5	5	25	0.4035	0.0133	3.29
51	5	5	25	0.5454	0.0132	2.42

Table 6.3 (b): The effect of specimen thickness on the rate of degradation of PVC plastic
[PDS]: 1000 mg/L Time: 50 hr

Thickness of PVC sample (mm)	Length of PVC sample (cm)	Breadth of PVC sample (cm)	Surface area (cm^2)	Initial weight of the strip (g)	Weight loss (g)	% degradation
1	5	1	5	1.1263	0.0107	0.95
2	5	1	5	2.2592	0.0122	0. 54
3	5	1	5	3.2857	0.0115	0. 35

The results reconfirm the importance of exposed surface area. The weight loss is same irrespective of thickness, as long as the exposed surface area is the same. However, since the weight of the plastic strips were different the % weight loss will decrease with increase in thickness.

6.3.10 Effect of colour of plastic sheet on the degradation

Plastic products are available in different colours, shapes, designs and sizes. The colour of plastic sheet is found to have no special effect on the rate of degradation under UV light (Chapter 4, figure 4.38). The effect of colour on the solar degradation is also studied by taking LDPE samples of five different colours ie green, orange, red, white and yellow (figure 6.31).

Figure 6.31: samples of coloured LDPE sheets

All the samples are of 41microns thickness with other dimensions identical. The samples are suspended in 1000 mg/L PDS solution for 50 hours under direct sunlight. The results are presented in figure 6.32. The % weight loss remains the same for all plastic samples ie, ~ 3.2% in 50 hr. This shows that the colour has practically ‘no’ effect on the rate of degradation of LDPE.

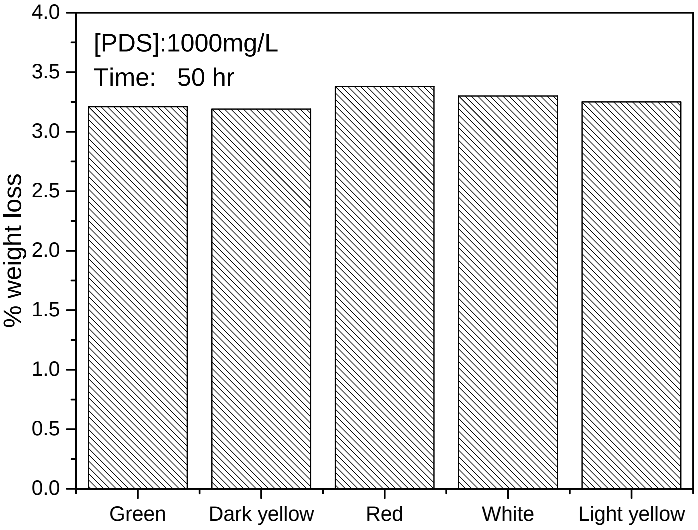


Figure 6.32: Effect of colour on the solar degradation of LDPE plastic in presence of PDS

6.3.11 Effect of combination of pollutants on the solar degradation

The survey results reported in Chapter 3 shows that the most accumulated plastic wastes in households are LDPE, HDPE and PVC. Hence a study of the solar degradation of different types of plastics when they are present together in the same environment is important and is undertaken here. The optimisation parameters arrived at in the case of LDPE have been extended to the combination. The experiment is carried out using LDPE, HDPE and PVC samples which are cleaned, washed and dried. One set of all three samples are then suspended in 1L of 1000mg/L PDS solution in the same reactor. In another experiment, identical samples of each of the above three types of plastic are suspended individually in three identical reactors. All samples (individual as well as the combination) are irradiated under sunlight under identical conditions.

Care has been taken to ensure that all samples either individually or in combination get direct sunlight fairly equally. The results are presented in figure 6.33 which show that, the degradation of all types of plastic strips are fairly the same, irrespective of whether they are irradiated individually or in combination. In the case of LDPE which is relatively a faster degrading plastic, the degradation is slightly less in presence of HDPE and PVC. However, since the degradation of slow degrading HDPE or PVC is not affected by the combination, it may be stated that the degradation of each one will proceed, practically unaffected by the presence of another. The results show that PDS-promoted solar photolysis can be used for the degradation of different types of plastics in the same reaction system, which is important for the commercial application of the process.

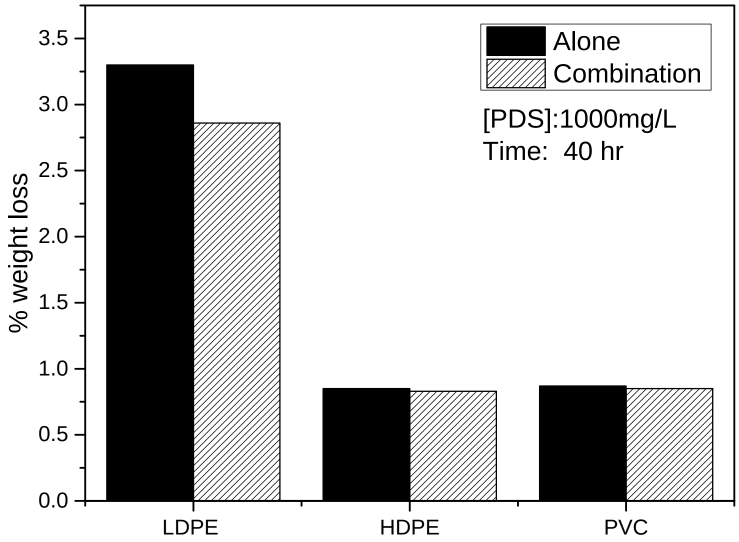


Figure 6.33: Comparison of solar degradation LDPE, HDPE and PVC Individually and in combination, under identical conditions

All the above experiments were conducted using distilled water as the medium for suspending the plastic. However for commercial application of solar photolysis, use of distilled water as the suspension medium may not be a viable option. Hence the rate of degradation of this combination of plastic pollutant in different types of water samples was studied. Five typical water samples ie (1) distilled water,(2) rain water, (3) well water, (4) municipal supply water and (5) sea water were selected for the study. In order to carry out the experiment, five different glass tanks of identical dimensions, ie, 30cm breadth, 75 cm length and 20cm height were specially designed and fabricated (figure 6.34).

Figure 6.34: Experimental set up for comparing the degradation of plastics in different types of water.

PDS solution of concentration 1000mg/L was prepared in each of the water samples. LDPE, HDPE and PVC plastic waste sheets were collected, washed, dried and then cut into small pieces. The plastic samples (one piece each of LDPE, HDPE and three small pieces of PVC) are then suspended in 1 litre of the PDS solution in individual glass tanks and are irradiated by direct sunlight. Relevant characteristics of the water samples which may influence the degradation of the plastics are analysed and summarised in table 6.4. Estimation of the hardness in various water samples is done by the EDTA method. Chloride was estimated by by Mohrs method, dissolved oxygen was estimated by Winklers method, Phosphate, Sulphate and Nitrate were estimated by spectrophotometry and turbidity was determined using a Nephelo-turbidity meter.

Table 6.4: Comparison of properties of various water samples

Water sample	**pH**	**Total Hardness (mg/L)**	**Chloride (mg/L)**	**Dissolved oxygen (mg/L)**	**Phosphate (mg/L)**	**Nitrate (mg/L)**	**Sulphate (mg/L)**	**Turbidity (NTU)**
Distilled water	6.8	Nil	Nil	8.2	< 0.1	< 1.0	< 2.0	Nil
Well water	6.5	5.74	16.5	8.1	< 0.1	< 1.0	< 2.0	Nil
Rain water (during S-W monsoon in the month of June)	6.7	Nil	Nil	8.7	< 0.1	< 1.0	< 2.0	Nil
Municipal Supply water from Chalakudy municipality	6.2	19.9	22.6	8.2	< 0.1	< 1.0	< 2.0	0.5
Sea water	8.2	7700	22500	7	4	10	5320	2.0

In another set of experiments, respective plastic strips were suspended individually in identical reactors in different types of water matrix and subjected to solar irradiation under identical conditions.

The degradation of LDPE, HDPE and PVC in different types of water matrix are shown in figures 6.35, 6.36 and 6.37.

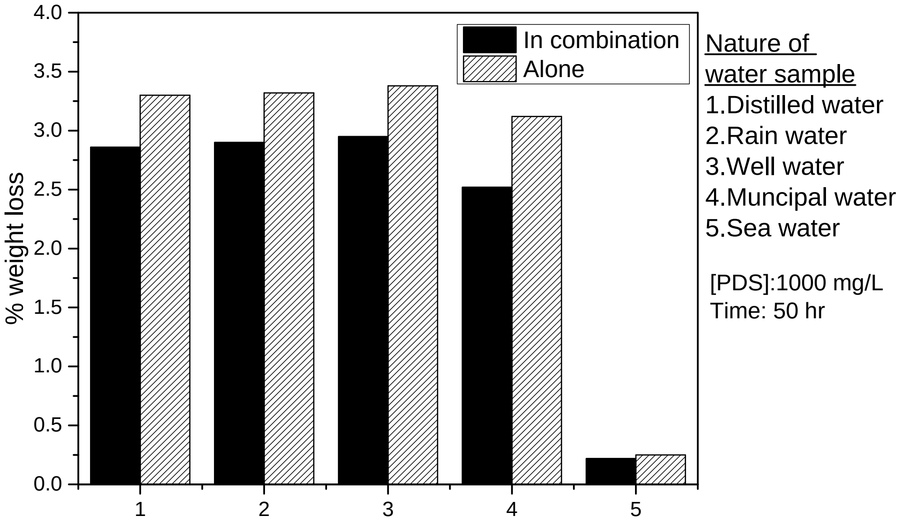


Figure 6.35: Solar degradation of LDPE (when present individually as well as in combination) in different types of water matrix

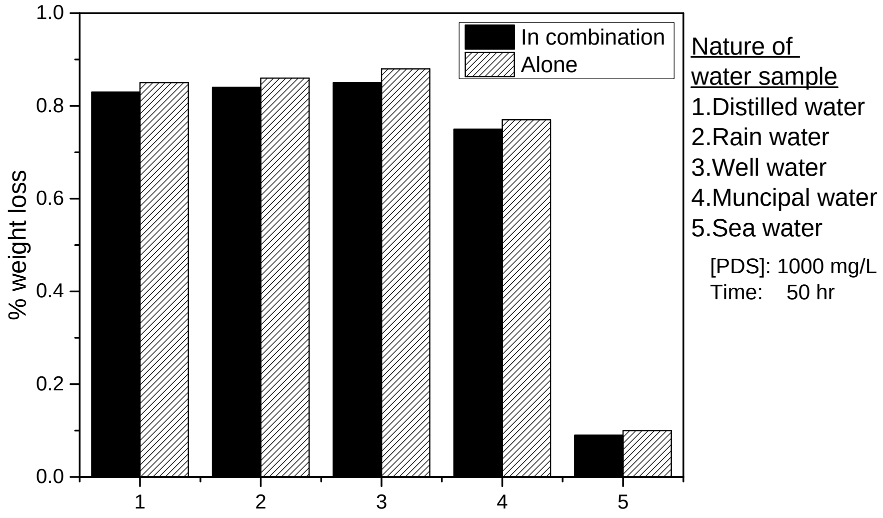


Figure 6.36: Solar degradation of HDPE (when present individually as well as in combination) in different types of water matrix

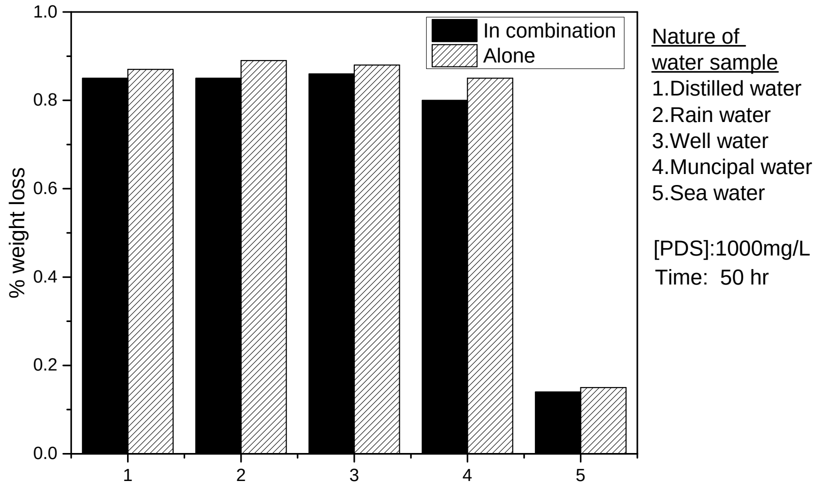


Figure 6.37: Solar degradation of PVC (when present individually as well as in combination) in different types of water matrix

Almost the same extent of degradation was observed in distilled, rain and well waters. Slightly lower degradation was observed in municipal supply water. The decreased rate in municipal supply water may be because of the presence of more hardness causing salts added to make the water safer and potable compared to distilled, rain and well water. Study on the effect of cations on the degradation rate (figures 6.24 and 6.25) shows that the presence of calcium and aluminium ions inhibits the rate of degradation. So it is natural that in municipal water which contains naturally present as well as externally added salts(for purification), the degradation of plastic will be slower. The degradation is slightly lower in the case of LDPE, when it is in combination with other slow degrading plastics such as HDPE and PVC, compared to the case when it is the only pollutant with total access to the oxidant and the solar illumination. This effect is irrespective of the nature of water matrix. However, the degradation proceeds fairly smoothly in the case of combination also thereby confirming that PDS induced photolysis can be considered as a potential method for the degradation and removal of different types of plastic pollutants from nature. In the case of all the three plastic pollutant samples ie LDPE, HDPE and PVC, the least or almost nil degradation was observed in sea water. As explained earlier this is due to the high concentration of Cl^- and SO_4^{2-} ions in sea water. These ions in moderate concentration have no effect while at high concentration they function as strong inhibitors in many photocatalytic processes. The mechanism is likely to be the same in this case also, even though the formation of the reactive species $SO_4^{-\cdot}$ will be slower under sunlight compared to UV. The mechanism of H_2O_2 and Fenton reagent enhanced degradation of plastic is also discussed in detail in the previous chapter.

The study indicates how severe and long lasting can be the plastic pollution caused by the improper disposal and consequent accumulation of large amount of plastic waste in marine water bodies. Marine plastic pollutants are mainly composed of plastic bags, food containers and packaging materials. In the ocean, plastic debris injures and kills fish, seabirds and marine mammals as a result of ingestion, starvation, suffocation, infection, drowning, and entanglement. Marine plastic pollution has impacted at least 267 species worldwide, including 86% of all sea turtle species, 44% of all seabird species and 43% of all marine mammal species [215]. The problem is further aggravated by the presence of persistent organic pollutants (POPs) in the marine environment. The POPs can attach to the surface of plastic debris and as a result floating plastics in the oceans accumulate pollutants and transport them through ocean currents. The mechanism of PDS induced enhancement of the degradation of pollutants has been discussed in section 4.4.17, Chapter 4.

6.4 Conclusions

Solar photolysis accelerated by peroxydisulphate is a promising technique for the safe disposal of LDPE, HDPE and PVC plastic pollutants. Optimized concentration of peroxydisulphate could achieve ~10 % of plastic destruction in the case of LDPE and ~4.5% degradation in the case of PVC in 400hr time. In the presence of a powerful oxidant like PDS, the effect of many anions and cations which are inhibitors of many photolytic processes is not significant. However anions such as CO_3^{2-} and PO_4^{3-} and cations such as Ca^{2+}, Mg^{2+} and Al^{3+} can inhibit their degradation moderately. The exposed surface area of the pollutant plastic is the most important parameter that determines the efficiency of solar degradation. The thickness, size, shape and colour of the sample are not that critical. The degradation is extremely slow in sea water which is probably due to the presence of a number of salts and a high concentration of chlorides which can inhibit photolysis. The data from the study clearly reiterates that it is absolutely important to prevent plastic pollution, especially the pollution of oceans and other water bodies. The hazards of plastic ingestions in marine organisms are well documented and all concerned agencies are alerted. However, individuals also have a very important role to play in this respect.

The slower degradation in municipal water compared to rain water is attributed to the presence of externally added hardness causing salts of Al, Ca, Mg etc which also inhibit the degradation.

Once scaled up and optimized further, PDS induced photolysis offers good potential for the safer mineralisation of one of the worst environmental pollutants of the day, i.e. plastics.

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Chapter 7

SUMMARY AND CONCLUSIONS

The main objective of the current study is to examine the suitability of AOPs for the removal of plastic wastes including plastic bags, pipes and other similar products of daily use from the environment. Photocatalysis, photolysis and Fenton reaction are the AOPs subjected to the investigation. The semiconductor oxides tested as catalysts are ZnO and TiO_2. The plastic pollutants subjected to the investigation are low density and high density polyethylene (LDPE and HDPE) carry bags and PVC pipes. The oxidants tested include H_2O_2, peroxydisulphate (PDS), Fenton reagent and their combination. The catalysts were characterized by standard wet analytical, adsorption and instrumentation techniques. The degradation of plastic was verified by weight loss, change in texture and morphology, SEM, IR spectroscopy etc and the TOC/COD of the reaction medium (water). The parameters subjected to detailed investigation and finally identified as relevant for optimum efficiency of the process include catalyst dosage, pH, presence of other contaminants, presence of oxidants, dissolved oxygen, size, shape and exposed surface area of pollutant plastic samples, catalyst life cycle etc.

Relevant findings of the study and the conclusions are as follows:

1) Precursor to this investigation was the evaluation of the plastic waste generated in a typical middle class semi urban community in the state of Kerala, by direct verification and survey among the families. The study showed that an average of ~1 kg of plastic waste/month/household is generated even in a typical middle class/lower middle class community. The quantity of plastic waste generated in these households was proportional to the income of the household and the number of family members. Biggest contribution to plastic pollution in terms of volume and spread comes from lighter 'carry bags'. Extremely light plastic carry bags, another major contributor to plastic pollution, may look less in terms of weight but is more in volume and number. Further, this type of plastics is dispersed over larger area causing major pollution hazards. An encouraging observation is that the culture of reuse of plastic bags is slowly picking up. The survey showed that concerted efforts are needed by government agencies/NGOs/community leaders to create more awareness among the public on the need for reduction in plastic waste and its safe disposal.

2) Photocatalyst TiO_2 and TiO_2-oxidant combinations are very efficient for the UV induced degradation and complete mineralization of LDPE plastic pollutants from the environment. The efficiency of different processes is in the order TiO_2-PDS > TiO_2-Fenton > TiO_2-H_2O_2 > TiO_2 > ZnO. The rate of degradation is dependent on a number of factors including the catalyst loading, pH, presence of other contaminants such as salts and humic materials in water, dissolved O_2

etc. The ultimate degradation products were CO_2 and H_2O in the case of LDPE. The Total Organic Carbon (TOC) content and Chemical Oxygen Demand (COD) of water in which the plastic is suspended for the experiment is 'nil' even after continued irradiation and significant weight loss to plastic. Hence the intermediates formed from the plastic are getting mineralised efficiently. Optimum combination of peroxydisulphate and TiO_2 could achieve over 12% of LDPE mineralisation in 400 hr time. Presence of anions and cations in water influence the phocatalytic degradation of LDPE plastic moderately. The degradation is extremely slow in sea water which is probably due to the presence of a number of salts which can deactivate catalyst.

3) Semiconductor photocatalysis mediated by TiO_2 and/or PDS is found to be a promising method for the safe removal of solid phase PVC plastic pollutants from the environment. Oxidants such as H_2O_2, Fenton reagent and PDS enhance the degradation. PDS is at least three times more efficient than the other oxidants. TiO_2 was found to have no additional effect on the degradation of PVC plastic in the presence of Fenton reagent and PDS. Optimum concentration of PDS could achieve over 7% of PVC mineralisation in 400 hr time. Complete mineralisation of PVC into CO_2, H_2O and salts is confirmed by the absence of any suspended matter or COD and TOC in water. The presence of anions and cations influences the photocatalytic degradation of PVC plastic only mildly. Combination of LDPE and PVC in the same reaction system gives almost the same rate of degradation for respective components as in the case where they are treated individually.

4) The above encouraging results on the degradation of LDPE and PVC plastics under UV irradiation prompted to extrapolate the study into the application of solar irradiation. Thus it is found that solar photolysis accelerated by PDS is a promising technique for the safe disposal of LDPE, HDPE and PVC plastic pollutants. Optimized concentration of PDS could achieve ~10 % of plastic degradation in the case of LDPE and ~4.5% degradation in the case of PVC in 400 hr time. In the presence of a powerful oxidant like PDS, the effect of many anions and cations (which are inhibitors of many photolytic processes) is not significant. However anions such as CO_3^{2-} and PO_4^{3-} and cations such as Ca^{2+}, Mg^{2+} and Al^{3+} which are strong inhibitors of most photolytic/photocatalytic processes, can inhibit the degradation of plastics also moderately. The exposed surface area of the pollutant plastic is the most important parameter that determines the efficiency of solar degradation. The degradation is extremely slow in sea water which is probably due to the presence of a number of salts and high concentration of chlorides which can inhibit photolysis by obstructing the penetration of light and trapping of insitu formed reactive free radicals.

In summary, the study demonstrates conclusively that photocatalysis/ photolysis has the potential to be used as an effective AOP for the irreversible removal of plastic pollutants from the environment. The main advantage is that the technique is environment-friendly without the use of any toxic or hazardous additives or complicated processes. It does not require any expensive equipment/instruments either. The possibility of using solar energy as the source of activation for the catalyst, oxidant and the components makes the process economically also attractive. However, as of now, the process is not efficient enough to be used on a large scale and further refinements are needed. Once scaled up and optimized further, PDS induced TiO_2 mediated photocatalysis/photolysis can be a potentially viable technique for the safe mineralisation of one of the worst environmental pollutants of the day, i.e. plastics.

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ANNEXURES

Annexure I

List of Abbreviations and Symbols

µm	micro meter
BPA	Bisphenol A
PVC	Polyvinyl chloride
PE	Polyethylene
PS	Polystyrene
PP	Polypropylene
IARC	International Agency for Research on Cancer
PET	Polyethlene Terephthalate
POP	Persistent Organic Pollutant
GIF	Gastrointestinal Fluids
AOP	Advanced Oxidation Process
AOT	Advanced Oxidation Technology
COD	Chemical Oxygen Demand
BOD	Biological Oxygen Demand
TOC	Total Organic Carbon
UV	Ultra Violet
US	Ultra Sound
VB	Valence Band
CB	Conduction Band
ROS	Reactive Oxygen Species
CuPc	Copper Phthalocyanine
TiO_2	Titanium Dioxide
ZnO	Zinc Oxide
SEM	Scanning Electron Microscopy
BiOI	Bismuth Oxyiodide
HPW	Tungstophosphoric acid
PPy	Polypyrrole
GPC	Gel Permeation Chromatography

AFM	Atomic Fluorescence Microscopy
LCD	Liquid Crystal Display
PDS	Peroxydisulfate
FR	Fenton reagent
FS	Ferrous Sulphate
LDPE	Low Density Polyethylene
LLDPE	Linear Low Density Polyethylene
HDPE	High Density Polyethylene
UHMWPE	Ultrahigh Molecular Weight Polyethylene
BET	Brunauer–Emmett–Teller
TEM	Transmission Electron Microscopy
XRD	X-ray Diffraction
FTIR	Fourier Transform Infra Red
PEP	Polyethylene Plastic
PZC	Point of Zero Charge
EDAX	Energy Dispersive X-Ray Analysis
SL	Sunlight
mg/L	milligram per Litre

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Annexure II

Questionnaire

Maximum points: 75

Name: …………………………………………………………………………..

Age (optional) : ………………………………………………………………

No. of members in the family: ………………………………………………..

Age group of members: <5 ..…. 5-30 …. 30-60 …… >60 ……

Educational qualification of the head of the family (optional): …………………..

Occupation: ……………………………………………………………………….

Family income (p.m.)(optional): >100,000 …. 50,000-100,000 …. 20,000-50,000 ….. <20,000 …..

Location of residence: Panchayat / Municipality / Corporation

1. Are you aware of plastic/plastic products? Y:75 / N:0
2. Do you use plastic products? Y :75/ N:0
3. If so, how often? Regularly:46/ Occasionally:21/ Rarely:8/ Never
4. Have you heard of polyethylene plastic? Y:65/ N:10
5. Have you heard of PVC plastic? Y :74/ N:1
6. Are you aware of ecological problems associated with plastic/plastic products? Y:73/ N:2
7. What kinds of plastic products do you use?

   Carry bags:66/ Bottles:66/ Sheets:24/ Toys:29 / Others:12
8. Do you think the use of plastic is more convenient for you?

   Y :54/ N:21

9. Do you think that the use of plastic can affect your health?

   Y :73/N:2

10. Does plastic pollute the land?

    Y:73/ N:2

11. Does plastic pollute the water?

    Y :72/ N: 3

12. Does plastic pollute the air?

    Y :72/ N:3

13. How do you dispose of the plastic material?

    Throwaway:14/ Bury:10/ Burn:33/ Collected by Others:34/ Other:1

14. Do you reuse plastic products?

    Y:36/ N:39

15. If so how much? <20%:15/ 20%:11/ 50%:12/ 75%:1/ 100%:0

16. When collecting garbage, do you collect the plastic items separately?

    Y :53/ N:22

17. Does the plastic content of a product influence your selection to buy any item? Y :35/ N:40

18. When buying toys for kids do you consider the material from which they are made? Y :44/ N:31

19. Do you know how plastic is made? Y :42/ N:33

20. Do you insist on packing items in separate plastic bags in the shop?
    Y :18/ N:57

21. Do you deliberately avoid getting new plastic bags each time you shop?
    Y:47/ N:28
22. Do you carry your own carry bags to the shop?
    Always:13/ Often:18/ Sometimes:41/ Hardly:3
23. Which is the most common plastic item that gets accumulated in your home?
    Carry bags:56/ Grocery covers:18/ Bakery covers :10/ Other:1
24. Have you ever thought of reducing the plastic waste?
    Y:64/ N:11
25. If so how? Recycling:23/ Alternatives:40/ Disposal:17/ Others:3
26. If the answer is disposal what is the method used?
    Dumping:5/ Burying:4/ Burning:15/ Others:8
27. Do you think recycling can help to reduce the problem of plastic pollution?
    Y:59/ N:16
28. Have you heard that plastic can cause deadly diseases like cancer?
    Y:66/ N:9
29. Do you make your family members aware of the danger of plastic material? Y :59/ N:16
30. Do the family members tell you to reduce / eliminate the use of plastic?
    Y :49/N:26
31. Are you aware of the substitutes for plastic bags?
    Y:60/ N:15
32. What are the common type of plastics you have heard of?
    PE:39/ PVC:65/ PET:19/ Others:6
33. Do you burn the plastic bags and bottles along with other wastes in your house? Y:30/N:45

34. Have you experienced any foul odor while burning plastic? Y:64/ N:11

35. Did you experience any discomfort from the fumes of burning plastic?

    Y:63/ N:12

36. What type of discomfort?

    Watering of eyes:5/ Breathing difficulty:53/ Cough:19/ Other:7

37. Have you seen animals eating plastic? Y:29/ N:46

38. If so did you try to dissuade them? Y:25/ N:50

39. If the animals eat plastic bags, will it be harmful? Y:71/ N:4

40. Is plastic reuse economical ? Y :60/ N:15

41. Have you seen plastic dumped in water bodies? Y :63/ N:12

42. What happens to the dumped plastic at the end?

    Pollute water:49/ Eaten up by aquatic life:15/ Make water toxic:32/ Other:4

43. Are you aware of any skin problems or allergies caused by plastic?

    Y :50/ N:25

44. Do you believe that plastic dust can cause eye-sore? Y:54/ N:21

45. Do you have a plastic collection system in your place? Y :24/ N:51

46. Is it OK to dispose of plastic waste by burying? Y:12/ N:63

47. If not why do you think so? It causes:

    Soil Pollution:60/ Water Pollution:19/ Other Problems:19

48. Have you ever felt that plastic has been a threat to people? Y :66/N:9

49. Do you think you can manage without plastic of any kind? Y:36/ N:39

50. Do you recommend banning of plastic altogether? Y:23/ N:52

51. Do you think it is possible to have a world without plastic products?

    Y:31/ N:44

52. What should the government do to reduce plastic use?

    Create awareness:42/ Strict rules:40/ Complete ban:17 / Strict punishments:14/ Others:8

53. What can individuals do to reduce plastic waste?

    Avoid Plastic Items:33/ Reuse Plastic Items:37/ Avoid Unscientific Disposal:29/ Others:2

54. Do you know how much plastic waste is generated in your home? Y:36/ N:39

55. If yes, how much/month? >2000g:3/ 1000-2000g:6/ 500-1000g:10/ <500g:19

56. Is there any avoidable item in this which you can do without?

    Y:58/ N:17

57. If so which item? Carry Bags:47/ Grocery Covers:32/ Bakery Covers:24 / Others:5

58. Can you take a decision to reduce your plastic use progressively?

    Y:71/N:4

59. Do you think the new supermarket culture leads to increased use of plastic?

    Y :69/ N:6

60. Do you think adoption of modern life style leads to increase in plastic use?

    Y :66/ N:9

61. If so do you recommend going back to the old customs? Y:44/N:31

62. Have you attended any awareness program about the ill effects of plastic?

    Y :19/ N:56

63. Has any such awareness program been conducted in your locality?

    Y :13/ N:62

64. If yes which agency has conducted the program?

    Government authorities:5/ Regional institutions:1/ Non government organizations:7/ Others:0

65. Are you willing to be a volunteer in your locality to create awareness on plastic? Y:64/N:11

66. What incentive do you need for this?

    Money:1/ Appreciation:32/ Awards:3/ Other:28

67. *Have you any suggestions to solve the problem caused by plastic or any other related issue? (One sentence to one page is OK)

67 * optional

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