PHOTOCATALYTIC DEGRADATION OF TITANIA EMBEDDED PET UNDER SALINE CONDITIONS

By

SABA IFTIKHAR

NUST201362299MSCEE65213F

A thesis submitted in partial fulfillment of the requirements for the degree of

Master of Science

In

Environmental Science

Institute of Environmental Sciences and Engineering (IESE)

School of Civil and Environmental Engineering (SCEE)

National University of Sciences and Technology (NUST)

Islamabad, Pakistan

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Has been found satisfactory for the requirements of the degree of

Master of Science in Environmental Science

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DEDICATION

I DEDICATE THIS THESIS TO MY BELOVED PARENT, MY HUSBAND & MY TEACHERS

FOR THEIR HELP & SUSTENANCE THROUGHOUT MY RESEARCH & MY LIFE

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I am very grateful to Al-Mighty ALLAH, Who create everything in this Universe and provides us the ability to learn about His Universe. He says the mankind to explore the Universe, where there are extraordinary things to learn about. I am first of all very thankful to Al-Mighty ALLAH for giving me the courage, energy to do this task, which would be impossible without the help of Almighty ALLAH. Countless salutations are upon the "Holy Prophet Muhammad (Sallallah-o-Alaih-Wassalam)", the city of knowledge who has guided his "Umma" to seek knowledge from cradle to grave.

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TABLE OF CONTENTS

LIST OF ABBREVIATIONS

AOPs	Advanced oxidation processes
As	Arsenic
e^-	Electron
EDS	Energy Dispersive Spectroscopy
eV	Electron Volt
FTIR	Fourier Transform Infrared
FWHM	Full width of a diffraction line at half of maximum intensity
GPR	General Purpose Reagent
h^+	Hole
IESE	Institute of Environmental Sciences and Engineering
LI	Liquid Impregnation
MARPOL	Marine Pollution
NPs	Nano-particles
PET	Polyethylene Terephthalate
$PET\text{-}TiO_2$	Polyethylene Terephthalate and Titanium Dioxide Composite
POPs	Persistent Organic Pollutants
SEM	Scanning Electron Microscopy
TiO_2	Titanium Dioxide
TPA	Terephthalate Acid
UNEP	United Nations Environment Program
UV	Ultra Violet
XRD	X - Ray Diffraction
λ	Wavelength

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Marine plastic pollution is one of the major environmental concern now a days due to its elevating rate universally. Titania nanoparticles are a reliable source of photocatalytic degradation of polymer and organic pollutants. Photocatalytic degradation of polyethylene terephthalate (PET) was investigated with different concentration of Titania nanoparticles under UV radiation, artificial light, and darkness immersed in artificial saline water. Titania nanoparticles were characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) techniques. Photocatalytic degradation of PET-Titania composite films were determined by monitoring weight reduction, SEM and FTIR spectroscopy. Maximum weight loss in saline conditions was observed in PET-Titania composite film (T-20) of 22.3% under UV irradiation in 10 days while maximum weight loss of 19.9% in 60 days under artificial light with 20% Titania was observed. Samples placed in darkness showed no weight reduction in 60 days. SEM images displayed small cavities in PET-Titania composite films after 60 days of photocatalytic degradation under artificial light. Results reveal that Titania embedded PET has the potential to degrade in saline conditions under irradiation without causing any further pollution.

INTRODUCTION

1.1 Background

Plastic a synthetic polymer is considered about 50-80% of the waste items floating on the ocean surface, beaches or trapped in the seabed extremely threatening the life of marine organism and ultimately human health by bioaccumulation and bio-magnifications through food chain. Plastic manufacture elevated 25-fold between 1960 and 2000 whereas reclamation persisted underneath 5%. Plastic holds 60–80% part of marine litter which is even elevated around 90–95% in some regions (Moore, 2008) which having highly significant effect on marine biota and polluting the marine environment.

Plastic litter can enter in the marine environment through land based sources about 80% of marine debris through wind blow from carelessly discarded waste or 65% from the downstream flow of water from river into sea, from cargo or passenger ships and fish industry which is throwing directly in the ocean (Derraik, 2002; Thail *et al*., 2013). Plastic debris effected more than 250 marine species world widely from crustaceans to epic mammals from impaction with debris and ingestion plastic materials which cause gastric rupture in mammals and presumed to be major cause of death after starvation (Stephanis *et al*., 2013). Plastic also adsorb the hydrophobic pollutants and when digested by marine organisms these toxic pollutants enter the food chain ultimately effect human health and also

threatening the marine biodiversity as hard plastic can also damage their digestive system. Plastic debris is an environmental concern as it is harmful for marine biota (Andrady, 2011; Wright *et al*., 2013).

Polyethylene terephthalate (PET) is one of the five major plastics which consist about 90% of plastic use universally (Zarfl and Matthies, 2010). It is the major constituent of mineral water, soft drinks and other beverages bottles. It is high persistent material and low degradation in natural environmental conditions and takes long time to degrade. Biological degradation of plastic is very low as it is resistance to degrade and requires unlimited time to degrade (Moore, 2008).

Photo degradation of PET bottles takes long time to degrade using UV radiations in natural sunlight on the basis of their composition, size and shapes as well physical factors like amount of sunlight, agitation, water chemistry, temperature and exposed surface area. Therefore, PET wastes requires environmental friendly degradation process under the ambient conditions (Zhao *et al*., 2008).

Polymer litter is treated mainly using physical and chemical methods but each has environmental concerns. One of motivated investigation for environmentalist is use of advanced oxidation processes (AOPs) for pollutants removal using photocatalytic properties of semiconductors e.g., TiO_2, Fe_2O_3, ZnO, ZnS and CdS which can be persuaded using higher energy photons to produce electron-hole pairs.

Among many inorganic chemicals, Anatase form of Titanium dioxide (TiO_2) is feasible semiconductor with high constancy, non-toxic, more competence and inexpensive in the nanocomposite synthesis (Shafaei *et al*., 2010). It has wide

applications in antimicrobial, antifouling and photovoltaic effects (Chen, *et al*., 2007). The Shafaei *et al*., (2010) results also showed TiO_2 as an effective photocatalyst from wastewater treatment to remove TPA which is a monomer of PET.

Photo-degradation is physical change which can be enhanced using Titania NPs in the composition of plastic bottle during manufacturing state as Titania has high degradation ability as a photo-catalyst (Kim *et al*., 2006; Asghar *et al*., 2011). Nano-composite polymer with well-dispersed Titania nanoparticles has better electro-optical, mechanical, and thermal properties of polymer (Chen, *et al*., 2007).

1.2 Objectives

The purpose of this research was to study photocatalytic degradation of PET using TiO_2 nanoparticles in the water of high salinity and to achieve this purpose:

➢ Titania embedded PET films with different concentration of Titania (1%, 5%, 10%, 15% and 20%) were prepared

➢ Degradation studies of PET films were conducted under ultraviolet radiation, artificial light and darkness in Saline water conditions.

➢ Comparative study of the different ratio of TiO_2 NPs for the photo catalytic degradation of PET under saline and distilled water conditions.

LITERATURE REVIEW

2.1 Marine Pollution

Marine waste is defined by UNEP, 2009 as

"Any persistent, manufactured or processed solid material discarded, disposed of or abandoned in the marine and coastal environment"

Marine environment can be polluted from many different sources, pathways and threats to marine life. It can be faced in many ways, from waste deposition, contamination, harvesting, overexploitation and exotic species to global climate change (Vikas and Dwarakish, 2015; Derraik, 2002).

The current and predicted risks associated with marine pollution, caused by human are multiple at a global scale posed by many different pollutants such as solid waste, chemicals, radioactive waste buried under water, human-induced sedimentation at coastal water, energy in the form of heat and noise, oil spills, biological and chemical pollutions.

The sources of marine litter can be land-based which includes municipal and industrial areas, sewage treatment plants, river discharge, legal and illegal dumpsites close to the shoreline, littering from coast and ship breaking yards etc. whereas marine based litter sources include fishing activities, aquaculture,

commercial and leisure shipping as well legal or illegal sea dumping (Tubau *et al.*, 2015).

Domestic Sewage or industrial effluents are released into the ocean through rivers, sewages or drainages. It contains polluting substances, certain toxic heavy metals and metalloids other than chemical nutrients which reduce oxygen levels with increasing the decay level of marine plants which ultimately results in deterioration of oceanic life itself (Vikas and Dwarakish, 2015).

Oil pollution is generally caused by oil discarding in ocean on daily basis from oil leakage, routine shipping or overflows in which about 12% oil enters the ocean due to oil spills while the rest come from shipping travel, overflows and discarding etc. Oil can cause devastating problems to local marine biota by forming thick layer on water that can suffocate marine faunas, can trap marine birds by lubricating their feathers and stopping them from flying and blocks sunlight required for photosynthetic floras (Vikas and Dwarakish, 2015).

World population growth and industrial production increasing waste generation rate proportionally and as well Inadequate anthropogenic waste management is the most deliberate departure of waste into the sea which is inducing negative impacts on such remote environments (Duhec *et al.*, 2015). Pollution has severe impacts on species and habitats in many areas and regions although the global marine ecosystem is quite resilient to single types of pollution of typical magnitudes. However, the long-term combined effects of different types of pollutants are effectively more severe (Wilhelmsson *et al.*, 2013). For example Micro-plastic concentrated with POPs can cause six times more severe damage to marine organisms as compared to from sea water whereas uptake of these micro-

5

plastic can cause physical damage as well chemical transfer in marine organisms (Wright *et al.*, 2013).

Anthropogenic marine debris most commonly encompasses plastics both in coastal waters (84.3%) and on shores (83%) with slightly different composition (Thiel *et al.*, 2013). Human induced pollution includes plastic which are non-degradable and becoming threat to marine life (Eriksen *et al.*, 2013). Plastic was found main marine litter in the region of Chilean continental coast and the Easter Island Ecoregion of Central South Pacific (SP) Ocean (Miranda-Urbina *et al.,* 2015). A study conducted in Northwestern Mediterranean Sea disclosed that plastic (72%) most dominant marine litter, lost fishing stuff (17%) while metal objects comprise 8% share coming from land sources predominantly (Tubau *et al.*, 2015). Albatross species in the southwest Atlantic and Fulmar, a biological indicators in southern North Sea shown increased amount of plastic materials in their digestive track (Jimenez *et al.*, 2015; Franeker and Law, 2015).

2.2 Plastic Pollution in Marine Environment

Plastics a synthetic polymer derived from petroleum is most common and persistent pollutant with its increasing production and low rates of recovery causing a net accumulation in coastal, surface water and in bottom sediments of marine environments worldwide (Thiel *et al.*, 2013). Marine habits contain plastic from beaches to the bottom sea and from the equator to the poles in the form of macro-plastic to micro-plastic throughout the world (Sul and Costa, 2014; Fischer *et al.*, 2015) which is the only substance which is illegal to dump in the ocean (Vikas and Dwarakish, 2015).

In early 1970s plastic litter was first observed in the marine ecosystem, since the widespread utilization of plastic in the half century oceans have become a dumping ground for human waste and becoming permanent part of marine environment (Sul and Costa, 2014). It is considered about 50-80% of the waste items freely moving on surface, beaches or descended to bottom of sea is plastic litter of different sizes, shapes and compositions (Driedger *et al*., 2015). Plastics can float on the sea surface and transfer from one place to other using sea current and wind to spread over long distances (Eriksen *et al.,* 2013; Juan *et al.,* 2014; Duhec *et al.,* 2015). Marine litter is now 60–80% plastic (Derraik, 2002; Eriksen *et al*., 2013; Tubau *et al.,* 2015), also found elevated to 90–95% (Moore, 2008). The survey conducted by Duhec *et al*., (2015) discovered that plastic was 96% in the marine debris.

2.2.1 Plastic in Oceanic Gyre

Plastic is the leading and prevalent part of marine litter which can transport over long distance due to lightweight and durability by water currents and wind to collect in hot spot zones distant from generated areas (Moore, 2008; O'Shea *et al*., 2014; Fischer *et al.,* 2015) known as oceanic gyres.

In 1999, the first large area of waste was discovered in the ocean gyres in the North Pacific called waste patch whereas the presence of equivalent waste patches in North Atlantic, the South Pacific, South Atlantic and Indian Ocean also has been confirmed (Oceaneye, 2013; Duhec *et al.,* 2015). Marine plastic pollution in South Pacific subtropical gyre (4489 km) was accomplished in March–April 2011 indicates 88 % plastic waste occupy near center with highest value of 396,342 particles km^{-2} while average plastic quantity was 26,898 particles km^{-2} throughout

this oceanic gyre with the average mass of 70.96 g km^{-2} (Eriksen *et al*., 2013) whereas in North Pacific Subtropical Gyre maximum concentration was found 32.76 particles m^3 and mass of 250 mg m^3 respectively have been recorded (Goldstein *et al*., 2012).

2.2.2 Origins of Marine Plastic

Plastic litter arrives to oceans through land based sources about 80% of marine debris through wind blow from carelessly discarded waste or from the downstream flow of water from river into sea while 20% from cargo or passenger ships and fish industry which is throwing directly in the ocean (Derraik, 2002; Andrady, 2011; Thail *et al.,* 2013; Wright *et al.,* 2013; Juan *et al.,* 2014; Duhec *et al.,* 2015). Plastic items like buoys and fishing tackle which may break over time and release fragments into the sea water and events like storms, tidal flooding, and shipping accidents may inject large quantities of plastic material into the oceans all at once. Coastal towns and industrial areas near shore symbolize a permanent cause of litter while tourism enhances litter production during summer months (Wright *et al.,* 2013; Tubau *et al*., 2015).

2.2.3 Micro-Plastics

Micro-plastics are recognized as an abundant component of marine waste globally with maximum concentrations reaching 100,000 particles per cubic meter besides the large floating plastic rubbish (Wright *et al*., 2013; Eriksen *et al.,* 2013). Ocean contain average micro-plastic about 18,500 pieces per square kilometer whereas from low concentrations of 3 particles per square meter in coastal waters of California to >1000 particles per square meter in coastal sediments of Malta which can have highly significant impact on marine biota and marine habitat (Oceaneye, 2013). According to Fischer and co-workers (2015) the amount of

micro-plastic vary among different areas from 60 pieces per square meter to highest concentrations of more than 2000 pieces per square meter of the Kuril–Kamchatka Trench area. According to review of Sul and Costa (2014), Micro-plastics are observed in each marine organism groups e.g. plankton samples, vertebrate and invertebrate ingestion, even with chemical pollutants and becoming an extreme threat to marine environment. According to findings of Jaun and coworkers (2014) micro-plastic concentration is exceeding more than 100 g of 1 kg of sediments with high pollution level in the Canary Current of Atlantic Ocean.

2.2.4 International Policies about Marine Plastic Pollution

After MARPOL Convention in 1973 and protocol in 1978, institutions and policies are formed in many countries to better understand and regulate Marine plastic pollution, which reflects public awareness of Ocean pollution; as plastic damping in oceans is prohibited now. However implementation is still very low due to improper waste management and weaknesses in regulation enforcement that need incorporating efforts among international environmental bodies, governments, non-governmental organizations, the private sector and the residents of coastal areas to reduce the amount of plastics and protect threatened marine species globally, which is still continue to be created, used up and discarded at an mounting rate (Juan *et al*., 2014; Carman *et al*., 2015).

2.3 Consequences of Occurrence of Plastic Litter in Marine Environment

Plastic pollution has environmental consequences including global hazards to shipping, fisheries and other oceanic activities, particularly, the lethal effects on marine biodiversity, which did not depend on sources of pollution whether land and

9

marine-based, their pedigrees may be local or distant (Juan *et al.*, 2014; Carman *et al.,* 2015).

2.3.1   Impact on Flora and Fauna

Plastic debris effected more than 250 marine species world widely from crustaceans to epic mammals (Wright *et al*., 2013; Fischer *et al*., 2015) while figure will likely increase as smaller organisms are considered. Macro-plastics pose a health risk to aquatic animals including fishes, reptiles, and seabirds because of possible entanglement, impaction with debris and ingestion plastic materials (Moore, 2008; Stephanis *et al*., 2013; Thiel *et al.,* 2013; Driedger *et al.,* 2015; Duhec *et al*., 2015; Fischer *et al.,* 2015). Plastic ingestion may cause internal bleeding, scrape and sores, as well as blockage of the digestive tract of organisms. It can even cause death from gastric rupture and starvation (Wright *et al.*, 2013; O'Shea *et al*., 2014; Duhec *et al*., 2015). Abandoned fish nets and other lost macro-plastic gear may trap marine animals that can be hurt, choke or suffocate (Duhec *et al*., 2015). Sperm whales in the Mediterranean Sea were examined by Stephanis and co-worker (2013). They found plastic materials in a huge quantity in body and believed that death was caused due to gastric rupture from impaction with debris.

Plastics degrade slowly in the environment and have long-term adverse ecological and economic impacts, including the dispersal of persistent organic pollutants and heavy metals which can disrupt endocrine functions and cause harmful developmental as hard plastic can also damage their digestive system and reproductive effects in marine organisms (Zarfl and Matthies, 2010; O'Shea *et al*., 2014; Driedger *et al*., 2015). The accumulation and transport of persistent, toxic and bio-accumulative chemicals with plastic do enhance their effect through bio-

magnification in food chain. Biodegradation of organic contaminants also confines by sorption to plastic which increases their persistence in the environment.

The oral ingestion of plastic-sorbed toxins enter to marine organisms directly additionally these toxic pollutants shown hazard in trophic transfer along aquatic food webs ultimately effect human health and also threatening the marine biodiversity (Andrady, 2011; Wright *et al.,* 2013; Sul and Costa, 2014; Driedger *et al.,* 2015). The ingestion of micro-plastics containing toxins and plastic-additives, like phthalates, polychlorinated biphenyls, endocrine disrupting chemicals and other harmful materials can be transfer into marine organisms (Zarfl and Matthies,2010; Fischer *et al.,* 2015).

Floating plastic can have influence on the species dispersal from their original habitat to foreign area where they may act as invasive species and also can impact on the indigenous inhabitants by establishing their genetically stable population (Fischer *et al*., 2015). Plastic can also transports potentially harmful, invasive organisms which can includes pathogens which results in suffocating and damaging to marine environment (Juan *et al*., 2014; Duhec *et al*., 2015). Inert litter can cause chemical and physical pollution, blanketing and suffocation on the seabed (Tubau *et al*., 2015).

Accumulation of plastic debris in bottom of sea can disrupt deposits, dislocate the fauna ultimately affect the structure and functioning of benthic microbial communities (Thiel *et al*., 2013; Driedger *et al.,* 2015). Coral reef can be damage due to use of fishing equipment through shallow reefs thereby compromising the reef structure (Duhec *et al.,* 2015).

2.3.2 Esthetic Impact

Recreational usage can discourage in coastal areas due to accumulation of plastic debris because tourists use beach hygiene as a leading feature (Driedger *et al.*, 2015) while waste piles decreases the appearance of the coastal environment.

2.3.3 Impact on Human Health

The direct effect on humans of consumption of sea food that ingested plastics is currently unknown, though it is obvious that human health might have injurious impact due to it. But the transport of persistent, toxic and bio-accumulative chemicals settling on plastics and ingested by animals has ultimate bio-magnification effect on humans at the end of the food chain.

2.3.4 Economic Impact

It is hard to assess the complete economic consequences of marine litter except some known effects such as: plastic debris can reduce revenue generation to coastal countries specifically small island states from tourism (Duhec *et al.*, 2015). It stances a hazard to divers and swimmers, and carry a risk of minor abrasion injuries or cuts to beach-goers. Macro-plastic litter can be a structural hazard to smaller marine vehicles and shipping vessels such as entangled propellers and burnt out water pumps (Driedger *et al.*, 2015).

2.4 Plastic Proliferation

Plastic annual production is increasing day by day reaching about 245 million tonne per year (Andrady, 2011; Sul and Costa, 2014) and showing no marks of reducing in the upcoming future because the plastic industry is generating an

immensity of new applications and products as plastics are lightweight, durable, strong and inexpensive (Vikas, and Dwarakish, 2015; Wang *et al.,* 2015). Plastic production has raised from 0.5 million tons per year in 1950 to 288 million tons in 2012 (Fischer *et al.,* 2015). The estimated production raised of plastic in 1960 to 2000 is about 25-fold whereas its recovery persisted less than 5% (Moore, 2008).

Plastic replaced for nearly every customary material at reduced cost and weight from textiles to metal as well offers qualities unfamiliar in naturally occurring substances. Plastic particles used in cosmetics and sandblasting fluids get into the wastewater and unable to remove in treatment plants. Plastic proliferation in all the domains of human activities, particularly elevating mismanage discard in developing countries associate the plastic pollution will increase in marine environment.

Plastic litter is erratically classified according to size, shape, origin and composition where size can be micro-plastic (less than 5 mm) or macro-plastic (larger than 5 mm). A wide range of shapes of Plastic are available such as pellets, films, strands and pieces. According to origin, plastic rubbish is classified as primary (original form) or secondary (remains or shards). The composition of plastic depends on the polymer type used which defines the density of debris. Low-density plastics remain submerged include polypropylene and polyethylene while high-density plastics can sink into the water include polyethylene terephthalate, polystyrene, and cellulose acetate. An assessment reveal 70% of plastic litter entering the oceans ultimately sink (Oceaneye, 2013; Driedger *et al*., 2015) due to increase in the density of plastic objects through degradation and fragmentation into smaller pieces (Fischer *et al*., 2015).

2.5 Plastic Degradation

Plastic waste is increasing at elevated rate which steered higher amount of plastics fired into the waste stream (Hamad *et al*., 2013). Environmental break down of plastic rubbish is through combination of photo and thermal-oxidative degradation by mechanical weathering, ultraviolet (UV) radiation and biodegradation but complete mineralization requires hundreds or thousands of years (Andrady, 2011; Driedger *et al*., 2015). Plastic is mainly recycled and reuse to minimize the environmental burden but still it is increasing day by day.

2.5.1 Natural

Plastic breakdowns in smaller pieces in natural sunlight using UV radiation but not degradable making it persistent to more access to marine organisms and increasing abundance of plastic rubbish in the ocean environment (Sul and Costa, 2014; Vikas and Dwarakish, 2015). Biological degradation of plastic is very low as it is resistance to degrade and requires unlimited time to degrade (Moore, 2008) which is even slower in the ocean due to cool hindrance (Andrady, 2000).

2.5.2 Artificial

Plastic waste is becoming environmental and social issue due to sharp increase in its production rate (Dimitrov *et al*., 2013). Plastic waste is mainly incinerated which produces hazardous byproducts including dioxins and ash which contains lead and cadmium (Zhang *et al*., 2010) or landfilled with municipal solid wastes which requires large capacity in landfill as well longer time period to degrade making it more expensive (Wang *et al*., 2015).

Pyrolysis and incineration with energy recovery are also used to dispose plastic waste but pyrolysis process requires high energy with high calorific value output products but emits air pollutants. Complex equipment and procedure required in incineration with energy recovery to eradicate hazardous byproducts before discharging to the surrounding environment. But still clean technology for safe disposal of plastic litter has become a vital concern due to its environmental effects and financial constrains (Wang *et al.,* 2015).

Recycling is considered an operational way now to minimize the negative impact of plastic waste because plastic materials can be melted and recovered without any major physico-chemical change in their properties or reuse as it is present for refilling purposes etc. or chemical recycling (Hamad *et al*., 2013). It is receiving attention as potential useful resource and better choice as compared to other options to handle plastic waste bases on social, economic and environmental issues (Zhang *et al*., 2010). However recycling plastic is still limited due to difficulties in separation of polymers as each type of plastic should be recycled alone to get good quality of recycled plastic because of their different melting points and chemical structures (Wang *et al*., 2015).

2.6   Polyethylene terephthalate (PET)

Polyethylene terephthalate (PET) is one of the five major plastics combine making 90% of plastic used generally worldwide (Zarfl and Matthies, 2010; Sul and Costa, 2014). It is a thermoplastic having two basic building blocks, ethylene glycol and terephthalic acid to form a polymer chain. It is a strong and inert material like glass that does not react with foods, non-corrosive, resistant to microbes and

biological degradation which is considered an important plastic type used from clothing to packaging (Gao *et al.*, 2013).

PET was first synthesized in 1940s in North America and named as "Dacron" in the form of new synthetic fiber. In fiber and fabric applications, it is known as Polyester, whereas for other application like containers and other packaging material, it is called PET or PET resin. PET films were created in 1950s used for video, photo and packaging films while strong, easily processed and blow-stretch molding PET bottles were developed in 1970s.

PET is considered vital for blow mold bottles used for packaging of mineral water, soft drinks and other beverages (Dimitrov *et al.*, 2013) because of its exceptional mechanical and physicochemical properties such as low weight, transparent, good barrier for water and oxygen, stability and low absorbency levels for gases and cheap as well (Dombre *et al.*, 2014; Ingrao *et al.*, 2014).

2.7 Degradation of PET Waste

Municipal solid waste comprise exponential amount of post-consumer PET due to extended usage of PET. However due to petroleum means used during production, it is difficult to degrade PET waste as it requires hundreds of years to degrade naturally causing plastic waste accretion (Ingrao *et al.*, 2014; Muller W. W., 2014). PET is denser than water having density of 1.38–1.41 and tend to sink in water (Driedger *et al.*, 2015) and breakdown into micro-plastic instead of degradation (Duhec *et al.*, 2015). It is high persistent material and low degradation in natural environmental conditions and takes long time to degrade.

Many physical, chemical, mechanical and thermal approaches have been developed to minimize post-consumer polymer waste (Caparanga *et al*., 2009; Hamad *et al*., 2013). Recycling is receiving significant consideration as effective and hygienic PET waste reclamation practice with environmental benefits universally. Recycling can be of two types: chemical breakdown, such as hydrolysis or glycolysis generating various monomers and mechanical, based on elaboration of pellets via extrusion plastic using washing and re-melting (Hamad *et al*., 2013; Ingrao *et al*., 2014).

PET depolymerization is another most used options to handle post-consumer PET through different processes like glycolysis, hydrolysis and alcoholysis. PET is converted into bis-(hydroxyethyl) terephthalate (BHET) using ethylene glycol depolymerizes in glycolysis process while terephthalate acid (TPA) is produced in the procedures of hydrolysis under acidic or basic conditions and the alcoholysis processes of PET yields dimethyl terephthalate (DMT) and diethyl terephthalate (DET) but each chemical practice have both merits and demerits (Favaro *et al*., 2013).

Many studies also providing a novel application to construction industry for using PET bottles as additive to traditional construction materials in different ways such as composite with concrete, fillings containing PET waste aggregates as a strengthening material for concrete and brick structures (Foti, 2013), eco-bricks (Taaffe *et al*., 2014) and recycled PET mortar with sand as soil reinforcement exhibited higher strength compared with single-sized mortar (Ge *et al.*, 2013). But again recollection of all post used PET waste bottle are not an easy trade and with immense growing quantity annually it is problematic economically.

According to Sarker and Rashid (2013) polyethylene terephthalate (PET) and low density polyethylene (LDPE) waste plastics can use for fuel production using Thermal degradation process (250-400ºC) but this requires further modification for use in refinery process and power plant for electricity generation as well for separation of wax produced as residue.

Regenerated PET resin from recycling process has reduced physical properties due to impurities (Chen *et al*., 2014). Recycled PET has deviations in decomposition mechanism due to change in their chemical and structural composition (Dimitrov *et al*., 2013). Comparison of virgin PET and 100% recycled PET done by Dombre and co-workers (2014) also confirmed difference in their thermal properties due to presence of impurities and shorter chains of polymer in recycled PET as well exhibit the heterogeneity in dispersion and size of crystals. They also found that recycled PET was not a good barrier for volatile organic compounds such as ethanol, isoamyl acetate and hexanol (Dombre *et al*., 2014). Generally it is considered one of five bottles of PET may be a nonfood bottle due to its secondary route for storage of several chemicals which can penetrate in recycled PET bottles (Dimitrov *et al*., 2013).

2.8 Polymeric Nanocomposites (PET)

Blending of organic polymer and inorganic nanoparticles produces nano-composites having significant influence on the properties and performance of polymer matrix. The polymer composites largely influence by type, size and shapes of nanoparticles. Different research studies over the past two decades identify the influence of nano-composites on thermal, fire retardancy, rheological, mechanical, catalytic, electrical, and optical properties of polymers. These polymeric nano-

composites are widely used as hybrid membranes, field-responsive constituents of electronic and optoelectronic devices, food packaging films, coating of chromatographs and catalysis in the fields of medical, biology and engineering etc. (Kango *et al*., 2013).

PET nanocomposite are mainly used for physical and thermal stabilities of PET under different studies or substrate to support nanoparticles. PET matrix can have homogeneous $CaCO_3$ nanoparticles dispersion below 5% wt. as well can increase thermal stability which can act as nucleating agent however up to 360°C no significant mass loss occurred (Gao *et al*., 2013).

TiO_2/PET system was developed using immobilization technique in the study of Fostier *et al*., (2008). In this study, PET bottles were used to provide support to TiO_2 for removing inorganic arsenic (As) from ground water and resulted in successful removal of 96% As in 2hrs under solar irradiation. TiO_2 photo-catalyst immobilized on PET bottles without using any expensive reagent showing a feasible choice to apply for removal of toxic organic and inorganic pollutants. The immobilized titania on the polymer may degrade polymer substrate during photo-oxidation that need further investigations (Singh *et al*., 2013). Rehan and co-worker (2013) also pledge immobilized technique for $AgI/AgCl/TiO_2$ on PET fabrics and found improvement in self-cleaning of nano-composite measured using methylene blue photo-degradation while antimicrobial properties were measured using Escherichia coli in UV and visible light.

2.9 Photo-degradation of PET

PET is not completely recycled and a large amount is randomly discarded into environment after a small portion of recovery which can slowly degrade under

UV portion of sunlight or other complex phisco-chemical process in the nature. Photo-degradation of PET takes long time to degrade using UVA-Vis photons and also heating due to the IR spectrum in sunlight on the basis of their composition, size and shapes as well physical factors like amount of sunlight, agitation, water chemistry, temperature and exposed surface area.

According to a study of oceanic pollution by Duhec and co-workers (2015), plastic surplus in different stages of decay from unspoiled plastic bottles showing very little photo-degradation to brittle form and as well fragmented plastic pellets. They also found micro-plastic (< 5 mm) arise from photochemical decay of large plastic materials.

When plastic enters in marine environment, it starts to degrade by UV solar radiation with thermal and/or chemical degradation afterward susceptible to further microbial action while light-induced oxidation is higher than other types of degradation which weakens the plastic and the material become brittle which breakdown into powdery fragments from ocean tides (Andrady, 2011; Sul and Costa, 2014).

Therefore, it is required to find a degradation process for PET wastes which can enhance degradation rate without forming any harmful yields under the ambient sunlight irradiation (Zhao *et al.,* 2008) in less time period.

2.10 Catalyst to Enhance Photo-degradation

Photo-catalyst is only the mediator to enhance the degradation process which combines light and oxygen (reactants) during oxidation reaction of photo-degradation process. A substance that absorbs UV, visible or infrared light and

change in the rate of a chemical reaction is called a photo-catalyst (Braslavsky, 2007).

Advanced oxidation processes (AOPs) have very attractive processing for photo-catalysis organic pollutants as compared to other physical and biological processes due to production of clean and harmless inorganic byproducts without any secondary waste product which is an environmentally sparkling approach (Leong $et\ al.,$ 2014).

AOPs can be initiated using primary oxidants similar to hydrogen peroxide or ozone, energy sources like UV light, ultrasonic and heat or using catalysts TiO_2, Fe_2O_3, ZnO, ZnS and CdS to generate hydroxyl radicals which is a strong oxidant to degrade toxic and rebellious pollutants into inorganic particles without producing secondary waste (Leong $et\ al.$, 2014).

Several semiconductors and their composites in the form of nanoparticles such as TiO_2, WO_3, BiOBr, $BiFeO_3$, CuS, and ZnO, Fe_2O_3, ZnS and CdS are accepted as photo-catalysts to enhance photo-degradation of different organic pollutants and disinfection by reducing their life time and for practical application without forming any harmful byproducts. These semiconductors generate electron-hole pairs by photons with a proper energy level due to their electronic structure (Twu $et\ al.$, 2015). These nanoparticles have ideal physical, optical, mechanical, magnetic and electronic properties and used in several fields as catalysis, waste water treatment, paints and medical treatments that arise clearly due to their nano-size (Kango $et\ al.$, 2013).

In these photo-catalysts Titanium dioxide (TiO_2) is widely used in many studies due to inexpensive, non-toxic, commercially available and chemically

stable and established Titania has high degradation ability as a photo-catalyst (Kim *et al*., 2006; Asghar *et al*., 2011; Leong *et al*., 2014; Twu *et al*., 2015).

2.11 Titania as a catalyst

Titanium dioxide (TiO_2) is mostly used photo-catalytic semi-conductor due to its exceptional assets such as photocatalytic properties, cheap, self-cleaning, conservational approachability and chemical constancy in decomposing various organic pollutants besides wide applications in deodorization, sterilization, antifouling, nano-medicine, skin care products, and photovoltaic effects (Chen *et al.,* 2007; Chimeh *et al*., 2013; Fisher *et al.,* 2013; Kango *et al*., 2013; Jiang *et al.,* 2014; Kadota *et al.,* 2014). It is one of the best semiconductor with high constancy, non-toxic, more efficiency, ease of mass production and inexpensive in the nano-composite synthesis (Shafaei *et al.,* 2010; Lei *et al.,* 2015; Twu *et al.,* 2015).

2.11.1 Factors Effecting TiO_2 Photo-catalyst

TiO_2 is very sensitive to surface morphology, particle size, crystallization and phase structure for its photocatalytic activity (Kadota *et al*., 2014; Jiang *et al.,* 2014). Its proficiency also depend on

> ➢ Pollutant concentration
>
> ➢ Amount and duration of light irradiance
>
> ➢ Preparation and thermal treatment

Anatase form indicate the highest photo-activity as compared to the other polymorphic rutile and brookite forms of Titanium dioxide (TiO_2) as degradation rate increases with the smaller particle size of nanoparticles (Jiang *et al*., 2014; Leong *et al*., 2014; Twu *et al*., 2015). Anatase, a metastable form of Titania shown

high quantity below 200℃ temperature in thin films formation (Twu *et al.*, 2015) while anatase crystalline form transformation requires about 400℃ temperature from amorphous (Ratova *et al.*, 2014). Whereas, khalil and co-worker (2013) found up to 500℃ pure anatase phase was stable.

Numerous studies conducted for Titania photocatalytic activity was shown highest by TiO_2 powder calcined at 600℃ with the maximum quantity of anatase and slight rutile as titania photocatalytic activity largely depends on the calcination temperature (Fisher *et al.*, 2013; Wang *et al.*, 2014). The surface area of TiO_2 largely effected by increase in calcination temperature (not more than 650℃) and duration (less time with high temperature) of thermal treatment (Sonawane and Dongare, 2006).

Nano-composite polymer with well-dispersed titania nanoparticles has better electro-optical, mechanical, and thermal properties of polymer (Chen, *et al.*, 2007) while other numerous methods like atomic layer deposition, film formation, dip-coating etc. are also effectively used for the addition of photocatalytic titania in polymeric substrates (Ratova *et al.*, 2014).

Jiang and co-worker indicate that photocatalytic activity of calcined titania at 500℃ is very much high for phenol removal (82%) in aqueous solution as compared to uncalcined titania (23%).

2.11.2 Degradation Mechanism Under TiO_2 Photo-catalyst

Photocatalytic activity of titania is triggered using UV radiation energy higher than band gap energy which eject electron from valance bond to conductance band and form positive hole here. These hole and electron pair participate in redox reaction at the surface of titania with water and oxygen where holes (h^+) react with

water molecule forming hydroxyl radical (OH·) while reacting with electrons, oxygen molecules (O_2) convert into superoxide radical anion (O^{2-}). These both radicals act as photo-degrader for organic pollutants (Fisher *et al*., 2013; Leong *et al*., 2014; Liang and Patel, 2014).

Fig. 1 Photocatalytic Degradation of Organic Pollutant
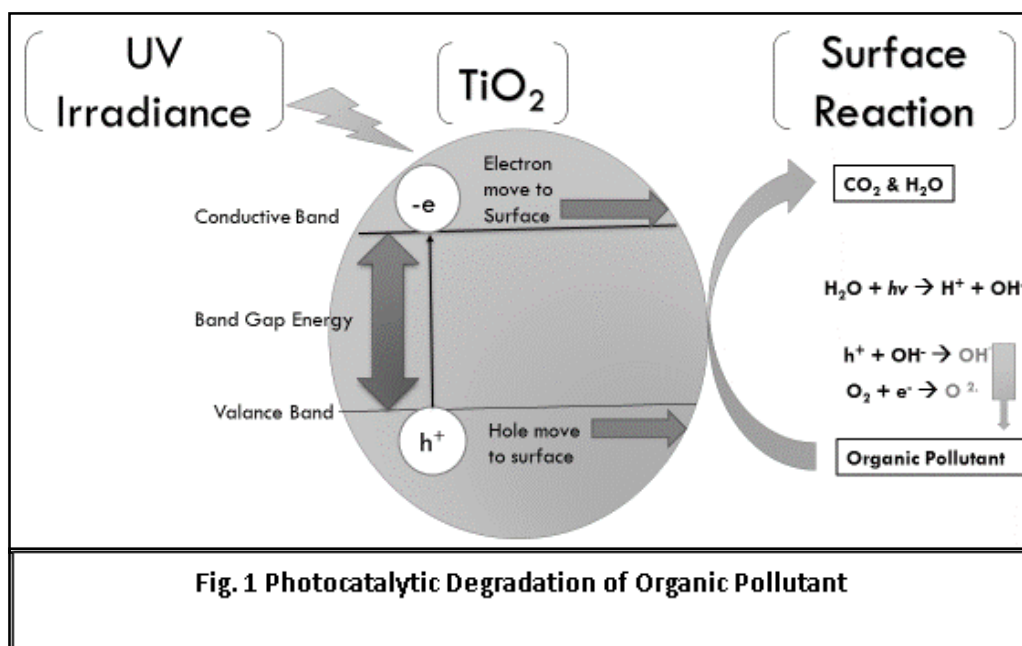
2.11.3 Degradation Studies of TiO₂ Photo-catalyst

Titania is widely used to observe degradation aptitudes for many pollutants which are unable or difficult to degrade naturally. Awadallah *et al.,* 2014 studied that TiO_2 incorporation with Ni (25%)–Al_2O_3 revealed improved decomposition of methane into hydrogen and carbon nanostructured materials as well stability of catalyst. Fisher and co-worker (2013) also found accelerated degradation rate of methylene blue under natural sunlight using doped and undoped TiO_2 films.

According to review by Leong and co-worker (2014), extensive use of TiO2 for manufacturing photocatalytic membranes used in wastewater treatment for pollutant removal and water purification applications for disinfection as this

process efficiently associates physical separation, organic degradation and anti-bacterial property together.

2.11.4 Polymer Degradation Using TiO$_2$ Photo-catalyst

Polymer nanocomposites is becoming vital in the field of polymers due to wide applications of polymer in daily life. Research on organic and inorganic nanocomposite materials can be nanoparticles, nano-layers or nanotubes are widely considered in recent years (Bikiaris, 2013). Metal oxide, Titania in a trifling quantity approximately 1-10% wt. can be used as a pro-degradant by incorporating into the polymers which can stimulate and fasten its photo-degradation process by generating reactive species during irradiation ($\lambda < 387$). Titania catalyst was used in the synthesis of polyethylene (PE) and poly(ethylene-co-octadecene) copolymer by in situ polymerization shown cavities of 50 μm during SEM analysis after 26 days as well higher degradation was observed with 5 wt. % of nanoparticle (Zapata *et al*., 2014).

Shafaei and co-workers (2010) found TiO$_2$ as an effective photo-catalyst when used as wastewater treatment for the removal of TPA, a monomer of PET. Alocoholysis of PET into dioctyl terephthalate (DOTP) using Ti(OC$_4$H$_9$)$_4$ catalyst resulted in 95% degradation of PET and corresponding produce 86.7% of DOTP while with 1% weight ratio of catalyst/PET show maximum PET degradation and produce DOTP but Ti(OC$_4$H$_9$)$_4$ is liquid and can cause difficulty to separate products (Chen *et al.,* 2014).

The photocatalytic activity of anatase under natural irradiation show remarkable degradation of 2,4-dichlorophenol (2,4-DCP) within few hours elucidates high potential to degrade organic pollutants (Leong *et al*., 2014). Lei and

co-worker (2015) studied the photo-degradation of the hindered amine modified aromatic polyamide dendrimer/polystyrene-grafted-TiO$_2$ hybrid photo-catalyst (PS-HADPG-TiO$_2$) films which showed excellent photo-stability for 0-250hr under solar irradiation and higher photodegradable efficiency for 600hr about 20% under the solar irradiation than the pure PS films about 1% and PS-TiO$_2$ films about 10% which provides a better way for developing highly efficient and controllable photodegradable plastics.

Result reported by different studies are challenging regarding increasing marine plastic pollution, natural photo-degradation as well usage and functioning of Titania nanoparticles for PET degradation under saline and natural sunlight conditions as polymer substrate may degrade during photo-oxidation that need further investigations (Singh *et al*., 2013) because most of the scientists used titania nanoparticles and polymer for secondary purposes which is resilient and inert semi-crystalline, thermoplastic material (Bikiaris, 2013).

MATERIALS & METHODS

3.1 MATERIALS

Polyethylene terephthalate (PET) pellets were obtained from local marketplace synthetic by QAPCO Petrochemical Corporation, Qatar. Analytical Grade sodium chloride (NaCl), sodium sulphate (Na_2SO_4), potassium chloride (KCl), sodium hydrogen carbonate ($NaHCO_3$), Magnesium chloride hexa hydrate ($MgCl_2.H_2O$), Calcium Chloride di-hydrate ($CaCl_2.2H_2O$), Xylene (Merck, Germany) and General Purpose Reagent (GPR) TiO_2 (Riedel-de Haen) without further refining were used in the research work.

3.2 SYNTHESIS

3.2.1 Titania Nanoparticles

Titania NPs were synthesized by using the Liquid Impregnation method (Sahoo *et al*., 2005) and calcination process (Sayilkan *et al*., 2005). Ensuing five steps were used to acquire crystalline form of titania with high photocatalytic abilities without forming agglomeration.

i)   Suspension

GPR Titania powder (25 gm) was added to 100 ml of distilled water in clean, dry 250 ml Pyrex beaker stirred with a homogenizer at 300 rpm for 24hr at room temperature for continues mixing to obtain a disperse solution of nanoparticles.

ii)   Settling

This dispersed solution was allowed to settle for 24hrs without disturbance to settle down the solid residue in particles form without cluster formation at room temperature.

iii)   Dehydrating

Complete water evaporation was carried out by placing this settled solid material into WTC Binder air oven at 105°C for 12 hours to get dry residue of titania.

iv)   Grinding

After drying TiO_2 was then allowed to cool down slowly at the room temperature and was crushed properly into fine powder using mortar and pestle to ensure no agglomeration.
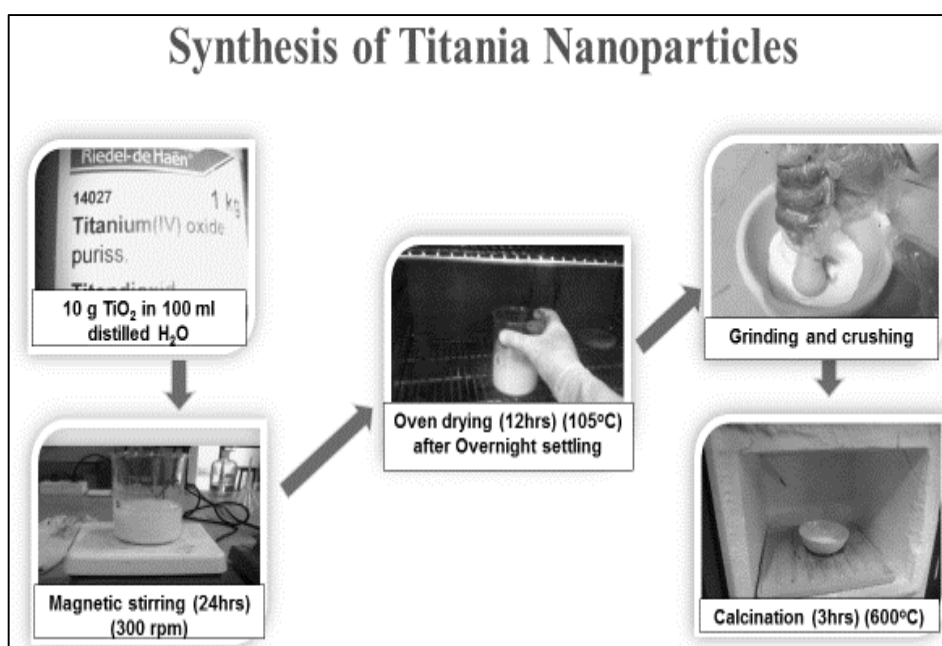

Figure 3.1: Synthesis of Titania Nanoparticles

v)   Calcination

NEY-525 SRIES II muffle furnace was used for calcite TiO_2 at high temperatures of $600^{\circ}C$ for 3hrs in a clean china dish which converted it from amorphous to crystalline form.

3.2.2 PET-TiO$_2$ Composite Films

Pure PET and PET-TiO$_2$ Composite Films were prepared using dissolution and solvent evaporation process, already tested by Asghar and co-workers (2011).

i)   PET Dissolution

PET pellets (1 gm) were dissolved in xylene (100 ml) at $170^{\circ}C$ under continue stirring at 360 rpm for 60 min to get clear solution.

ii)   Polymeric Nano-Composite Solution

Different concentrations, (1%, 5%, 10%, 15% and 20%) of TiO_2 NPs to the total quantity of PET were added to suspend uniformly in the above solution to get nano-composite polymeric solution and sonicator, was used to homogenies this solution.

iii)   PET-Titania films formation

PET films were obtained by pouring 20 ml above warm solution on clear, clean petri plates to get uniform film having radius of around 4 cm which were left undisturbed for 24 hours at room temperature to evaporate solvent and get dried films formation on glass plates.

iv) Film Separation

Films were placed in water bath at a temperature of 80°C for 15 mint to separate them from Petri plates easily. These films were used for further analysis.
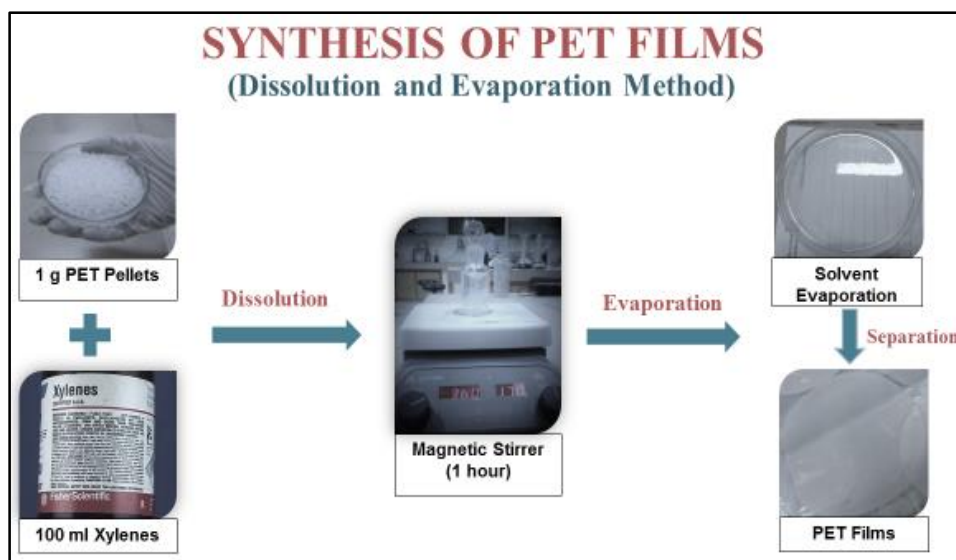

Figure 3.2: Synthesis of PET Films (Pure & Composite Films)

3.2.3 Synthesis of Artificial Sea Water

Artificial sea water was synthesized using USEPA (2007) method. Deionized water (EC: 0.002 dS/m) was used to dissolve the following salts one by one in clean Pyrex Volumetric flask (1litre) and mixed well. Sea water was store in plastic container for Prolonged application (> 2 month) to avoid contamination from glass.

i) Artificial Sea Water Composition

Seawater having a salinity of roughly 34,700 ppm was synthesized using 34.7 grams of reagent grade salts per one liter of water. Salts with the quantities are listed in Table: 3.1.

TABLE: 3.1. Reagent Salts Concentration for Synthesis of Artificial Sea Water

Compound	34.7 g/L Conc.
NaCl	23.555
Na_2SO_4	3.943
KCl	0.683
$NaHCO_3$	0.190
$MgCl_2.6H_2O$	10.641
$CaCl_2.2H_2O$	1.479

ii)   Preliminary Analysis of Artificial Sea Water

Artificial sea water was aerated (24 hours) for preliminary test to confirm its properties for further analysis. Average measured values of sea water at 24°C were respectively.

➤ pH : 8.1

➤ EC : 58 dS/m

➤ Salinity : 34.7 ‰

Spectrophotometer was used as a qualitative analytical technique by scanning UV and Visible spectrum (200-600 nm) of synthetic sea water to check λ-max (278 nm). Spectrum curve of synthetic sea water showed no absorbance of UV-Vis light required for photo-degradation so no hindrance in the photocatalytic degradation process of polymer.
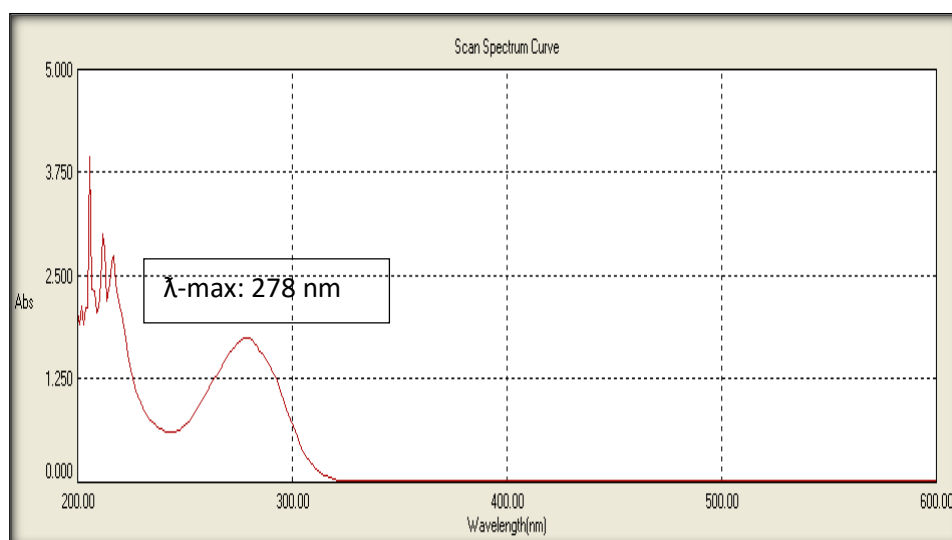
Figure 3.3: Spectrum Curve of Artificial Sea Water in the Range of 200-600 nm

3.3 EXPERIMENTATION

Photocatalytic degradation behavior of PET was studied using different parameters like light, duration, temperature, mixing and catalytic concentration under saline conditions.

3.3.1) Photocatalytic degradation using distinct light conditions and Catalyst concentration

Experiment was carried out using pure PET films and five types of PET-titania composite films (1%, 5%, 10%, 15% and 20% of PET wt.), practicing triplets of each film and find out better ambient air supportive concentration of catalyst under light conditions.
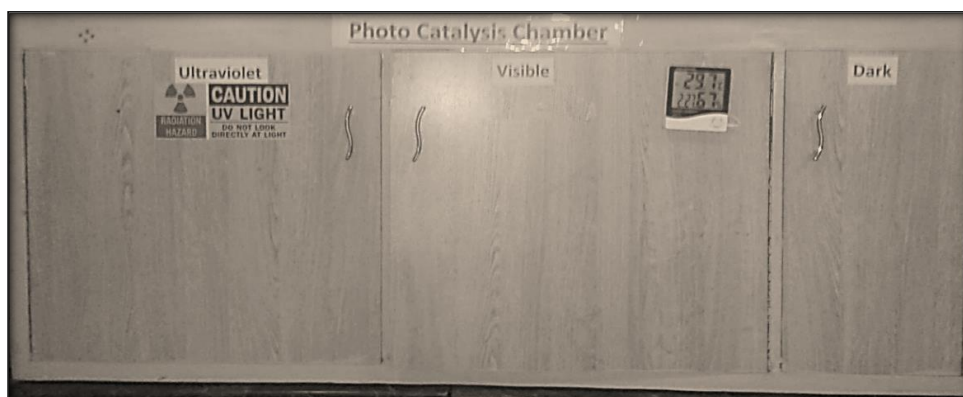
Fig.3.4 (a): Pictorial View of Experimental Chamber for Photocatalytic Degradation

i) Dark

Pure PET, PET-TiO$_2$ composite samples were added in sea water and placed in dark conditions to check effect of degradation due to saline conditions and catalyst without light as controlled environment to compare with photocatalytic degradation under natural and UV light sources.

ii) Artificial Fluorescence light

Compact Florescence Lamp (CFL 85 Watt - 5000k) was used as artificial light source for photo-degradation studies of PET-titania composite films as well pure PET films under induced saline conditions.

Figure 3.4 (b): Pictorial View of Artificial Light Setup for Photo-catalytic Degradation

iii) UV light

Samples were also irradiated under 6W UVL-56 ultraviolet lamp having wavelength of 365 nm inside saline water.

3.3.2) Batch Photo-reactor Experiments

Pyrex cylinder having 1.5 liter capacity were used to check the influence of temperature and mixing on the degradation rate of titania composite films under saline conditions. Samples added to Sea water were circulated at 400 rpm continuously to keep steady internal temperature in both batch reactors with diverse ranges, chiller as 4-7°C whereas warm as 37-40°C. These setups were irradiated using immersed UV lamps encapsulate in quartz tubes and vessel walls were covered using aluminum foil to elude radiation exposure.
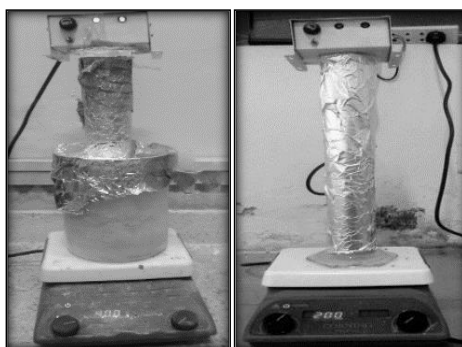

Fig. 3.5: a) Cold Temperature Photoreactor b) High Temperature Photoreactor

3.4 CHARACTERIZATION

Titania nano-particles and PET films (pure PET and PET-TiO$_2$ composite) were characterized using XRD, SEM, EDS, XRF, FTIR and percent Weight loss and described briefly here in the following topics:

3.4.1 X-ray Diffraction Analysis

Powder XRD is extensively used X-ray diffraction material characterization technique. Titania powder was analyzed using powder X-ray diffraction for determination of size of nano-particles and crystalline phase (Rehan *et al.*, 2013). The synthetic catalyst was examined at room temperature using XRD, JEOL JDX-II apparatus. The pattern was recorded using $CuK_{\alpha1}$ radiation (k = 0.1541 nm) and 2θ range from 20° to 80°.

Figure 3.6: XRD Working Principle
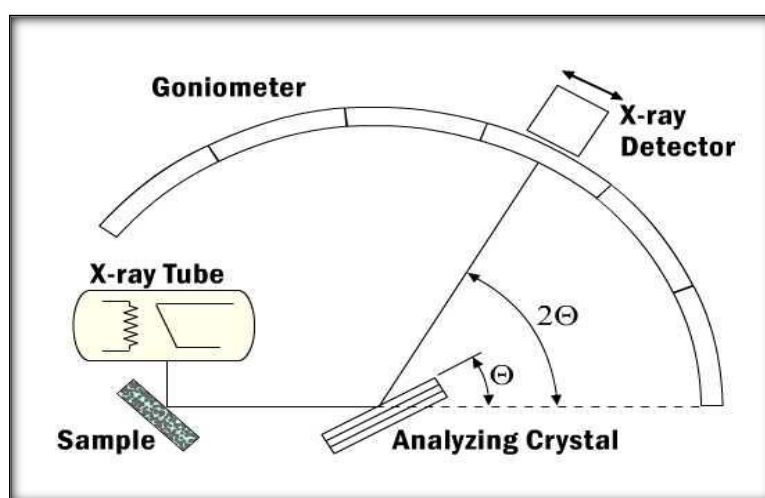
➤ **Size of Titania Particles**

Titania is generally used as a catalyst and requires size less than 100 nm to become nanomaterials. X-ray diffraction pattern was used to describe the crystallite size based on the Scherer equation (Theivasanthi and Alagar, 2013).

$$L = \frac{k\lambda}{\beta \cos\theta}$$

Where,

L = Average particle size

k= 0.9 (Constant for spherical particles)

$\lambda = 0.1540$ nm, X-ray wavelength (CuKα1)

β= Full width of a diffraction line at one half of maximum intensity (FWHM) radian

θ = the diffraction angle of crystal plane (hkl)

➤ **Phase Analysis**

Phase analysis was conducted by comparing the pattern of the titania nanoparticles with the reference pattern of all possible phases available in International Center for Diffraction Data (ICDD) using inorganic and organic spectra.

The locations and the intensities of the graph peaks were used for detecting the fundamental structure (or phase) of titania. This phase identification is important because the catalytic properties of titania are highly dependent on structure (Leong *et al*., 2014).

3.4.2 Scanning Electron Microscopy (SEM)

Scanning Electron microscope (SEM) is a convenient scientific instrument to examine objects at a higher magnification using resolution of less than 1 nm. The three-dimensional, high-resolution image of samples were obtained by scanning samples using focused beam of energetic electrons using scanning electron microscope (JEOL JSM-6460). The high-resolution, three-dimensional images produced by SEM based on following diagram.

➤ **Titania Nanoparticles**

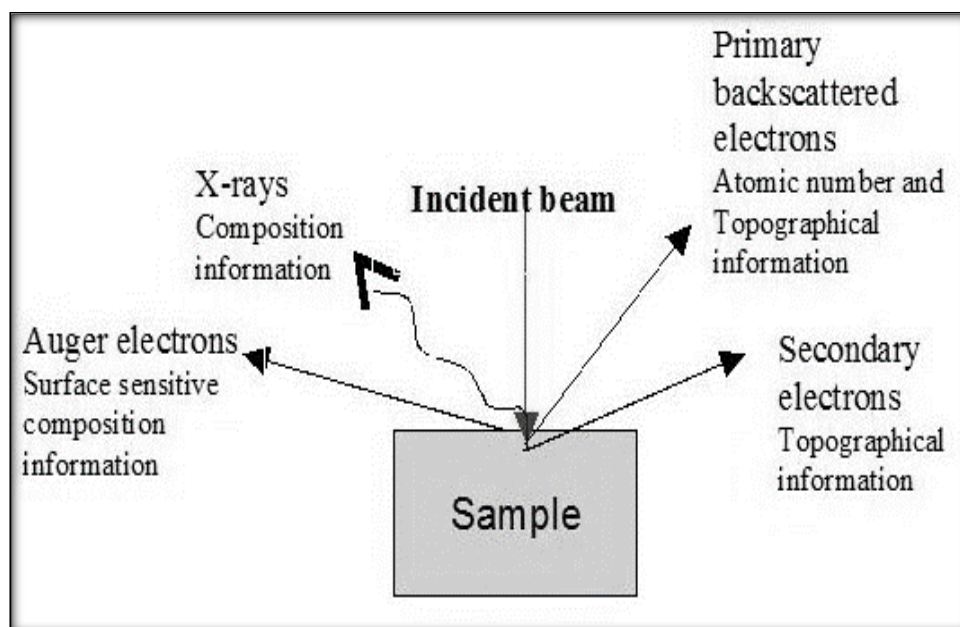Topography and surface morphology of titania nanoparticles were examined using SEM.

Figure 3.7: SEM working Principle

➤ **PET Films**

Changes in Surface morphology of pure PET and PET-TiO$_2$ composite films were explored with SEM after the 2 months irradiation exposure to observe photo-catalytic degradation and see its relation to the weight reduction.

3.4.3 Elemental Analysis

Elemental analysis of Titania nanoparticles and PET films (Pure and Composite) was done using EDS and XFR using working principle explained in figure 3.8. Above both works on the change in the movement and placement of electrons in the element by causing excitation process. This excitation is caused by hit electrons from lower orbits produce vacant positions while releasing energy

which further used by higher energy level electrons to occupy inner shell to cover the gap with releasing X-rays.
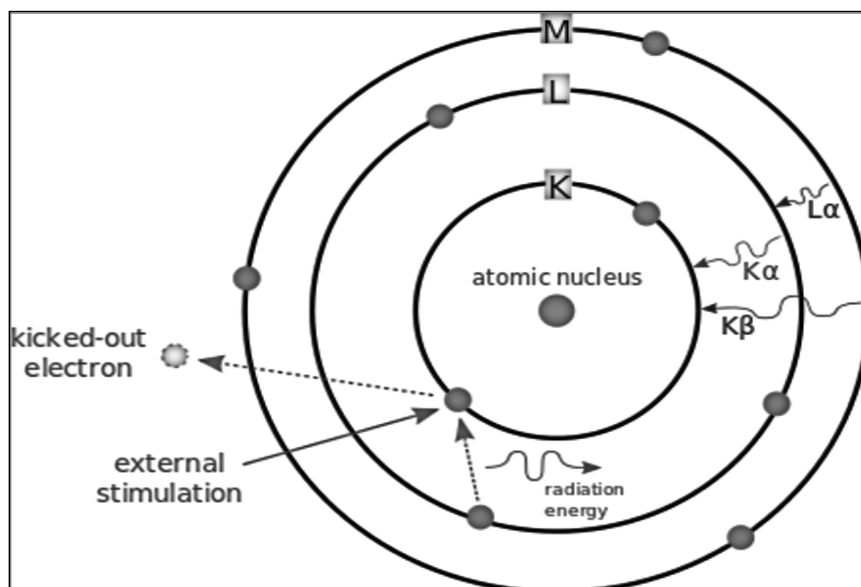

Figure 3.8: EDS & XRF working Principle

3.4.3.1 Energy Dispersive Spectroscopy (EDS)

Energy-dispersive spectroscopy (EDS, JEOL JSM 6490A), a chemical microanalysis technique was used to identify the elemental composition of Titania nanoparticles and PET films (Before and after photo-catalytic degradation) with SEM. EDS detects these definite, different atomic structure peaks on x-ray atomic spectrum produced by controlled beam of electron. It explains elemental composition while number of counts on the graph show the percentage composition of specific element.

3.4.3.2 X-Ray Fluorescence (XRF)

X-ray fluorescence (XRF) was used for chemical analysis of PET-Titania composite films after the photocatalytic degradation in saline water conditions to

check difference in their elements due to salt accumulation with different titania concentration. XRF is the emission of secondary x-ray from excited material by causing ionization with short-wavelength and high-energy X-rays or gamma rays.

3.4.4   Fourier Transform Infrared Analysis (FTIR)

Fourier Transform Infrared Spectroscopy is a useful technique used in chemistry to identify the presence of certain functional groups in the sample due to their absorbance of specific frequencies of Infrared radiation and compound identification. It is a technique used for the absorption of different IR frequencies by sample positioned in the path and result in the excitation of molecules from ground state to higher energy levels.

FTIR analysis of pure PET and PET-Titania composite films before and after irradiation exposure were conducted using Perkin Elmer Spectrum BX-II FTIR Spectrometer. The infrared spectrum was obtained by plotting percent transmittance against frequency with ranges from 4000 to 625cm^{-1}. Peaks of FTIR spectrum provides information about the photo-catalytic degradation of PET and formation of CO_2 which can be the ultimate product of the PET degradation.
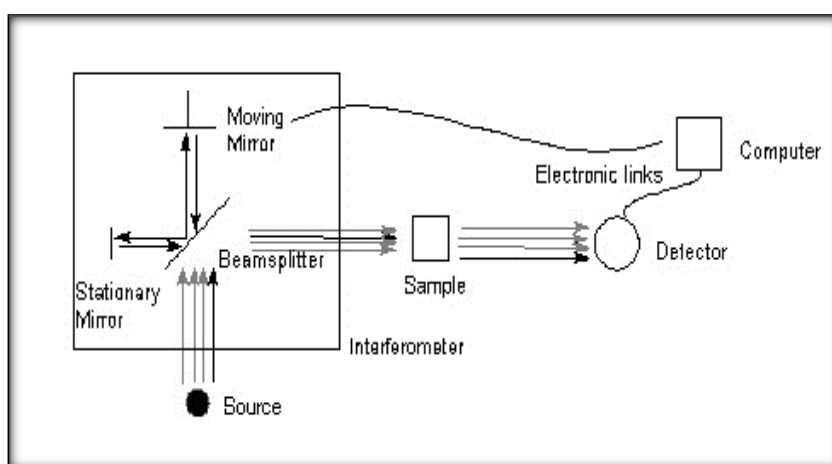

Fig 3.9: Working Principle of FTIR Spectroscopy

3.4.5   Weight Measurements

An analytical balance with 0.1mg sensitivity (BB Adam Instrument Company of AAA Series, model 160 LE) was used for all the measurements to a very high degree of precision and accuracy. The weighing balance is enclosed by transparent doors to avoid disturbance in operation.

Weight reduction (mg) was also measured to observe the photo-catalytic degradation of pure PET and PET-Titania composite films under UV, Artificial light and dark conditions. Weight reduction (%) was calculated as

$$\textbf{Weight Loss of Film (\%)} = (W_t - W_0) / W_0 * 100$$

Where; W_0: the initial weight of Film

W_t: the final weight of Film after time interval

RESULTS AND DISCUSSION

4.1 X-Ray Diffraction (XRD) Analysis of Titania Nanoparticles

XRD analysis was conducted to identify the crystalline structure and particle size of titania powder. Results are illustrated in the Fig. 4.1, 4.2 and table 4.1. Structural analysis of titania powder was performed at room temperature using range of diffraction angle 20°-80°.

XRD analysis confirmed that synthetic titania nanoparticles has crystalline size less than 100 nm which was an important factor in photocatalytic degradation of polymer as smaller particle size can quicker degradation rate (Jiang *et al*., 2014; Twu *et al*., 2015). The XRD spectra reveals that synthetic titania nanoparticles has crystalline anatase phase as peak positions match with those of the characteristic peaks of anatase titania (ICSD No. 01-084-1285) without any main corresponding peaks of rutile and brookite phases shown in fig 4.1.

Calcination temperature played an important role in crystal size with maximum quantity of anatase (94%) and slight rutile (6%) calcined at 600°C for 3 hours provided appropriate results revealed by Zhu *et al*., 2012Fisher *et al*., 2013; Wang *et al.*, 2014. The crystallite size of titania nanoparticles was measured as 43 nm using Scherer formula. Thomas *et al.,* 2013 found enhanced results of photocatalytic degradation of polyethylene using sol gel synthesized anatase form of TiO_2 nanoparticles (50 nm). From these results, it is concluded desired nanoparticles are successfully fabricated.
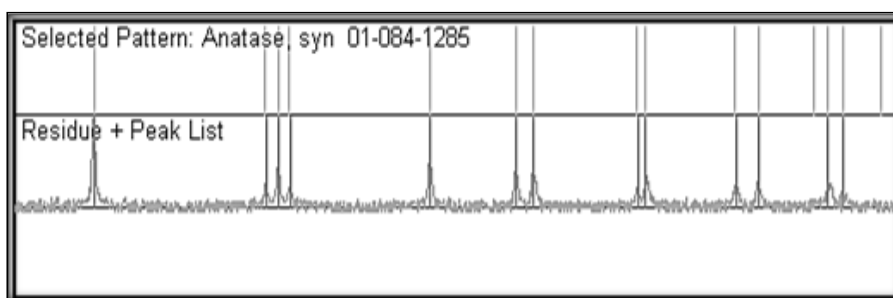
Figure 4.1: XRD Anatase Pattern of Synthetic and Reference

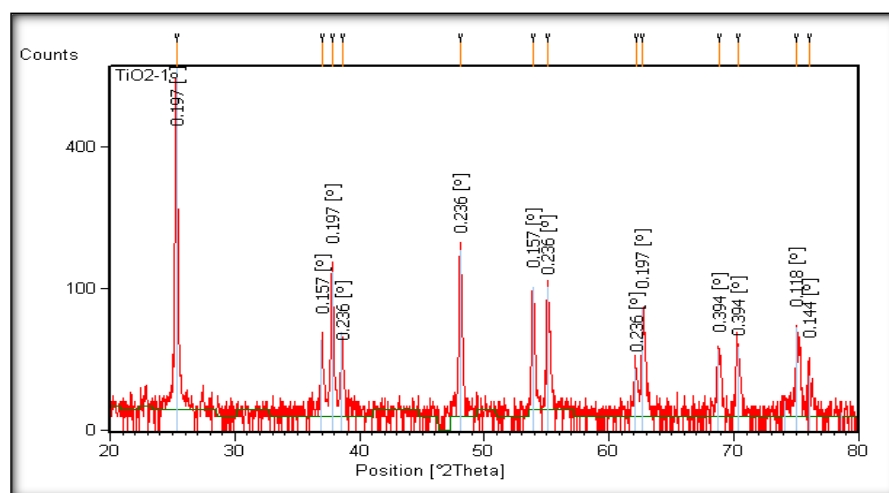**Figure 4.2**: XRD Pattern of Synthetic Titania Nanoparticles

Table 4.1. Prominent Peak Angles, Intensity and Spacing of TiO_2- Anatase Phase

Sr. No.	Angle (2Theta)	Intensity (%)	Spacing
1	25.30	100	3.52
2	37.80	18.8	2.37
3	48.03	24.6	1.89
4	53.89	15.2	1.69

4.2 Scanning Electron Microscopy (SEM) Analysis

4.2.1 Titania Nanoparticles

Surface morphology of titania nanoparticles was analyzed using JEOL JSM-6460 SEM at resolution of x 10,000 and x 20,000. These figures depict that structure of titania nanoparticles was spherical, porous and complex which can provide high surface area for photocatalytic degradation process while the average particle size of the titania nanoparticles shown Fig. 4.4 at 20,000 x magnification was found to be 70 nm.
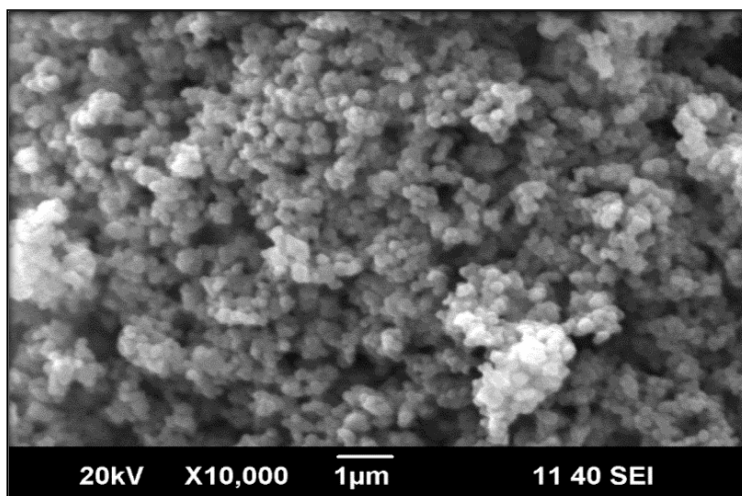

Figure 4.3: Pure TiO$_2$ Nanoparticles at X 10, 000 (SEM Image)
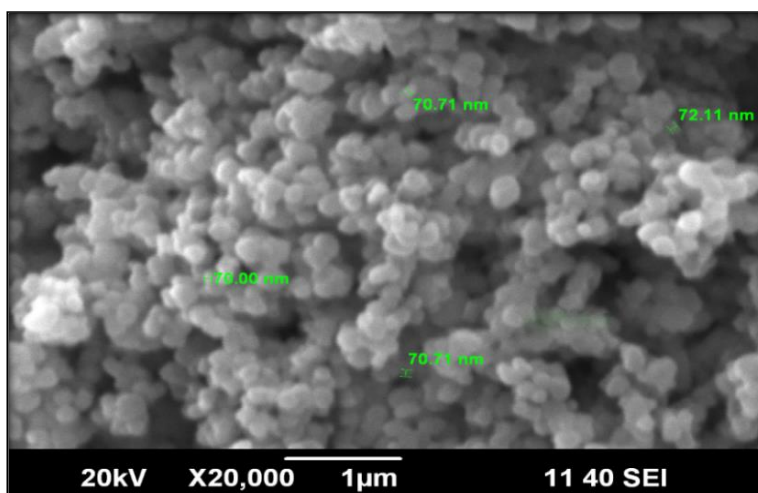
Figure 4.4: Pure TiO$_2$ Nanoparticles at X 20, 000 (SEM Image)

4.2.2 PET-Titania Composite Films

Morphological structure of PET and PET-Titania composite films were studied using JEOL JSM-6460 SEM at 10,000 magnification before and after artificial light irradiation (60 days). Surfaces of pure PET film and PET-Titania composite films were smoothly extended shown in Figures 4.5 (a, b) before irradiation and saline conditions but after photo-degradation exposure for 60 days under intensity of 3.38 mW/cm^2 in ambient air and saline water conditions random small cavities seemed on the structure of PET films which increased in size and number with the increasing concentration of titania (0-20 %).

(a)

(b)

(c)

(d)

(e) **(f)**

(g) **(h)**
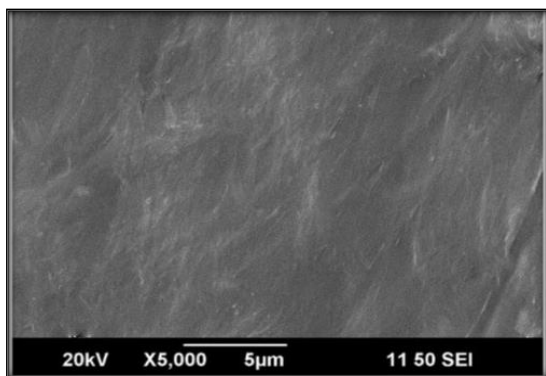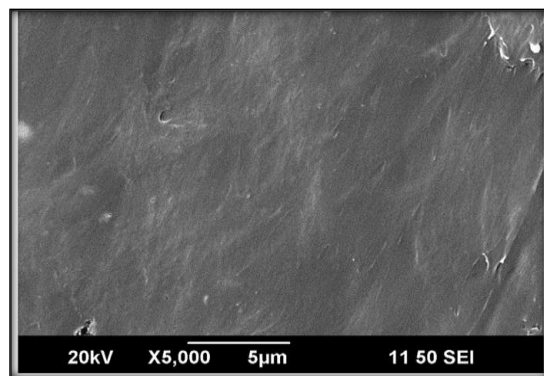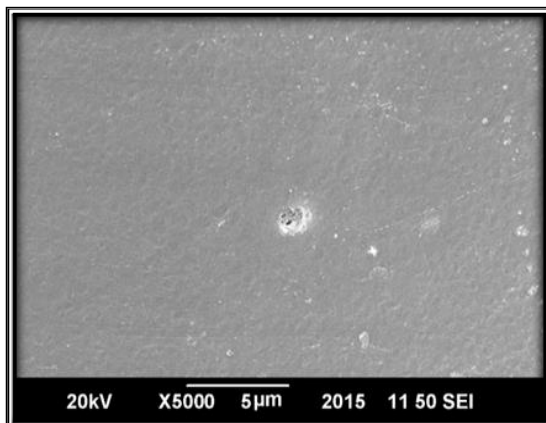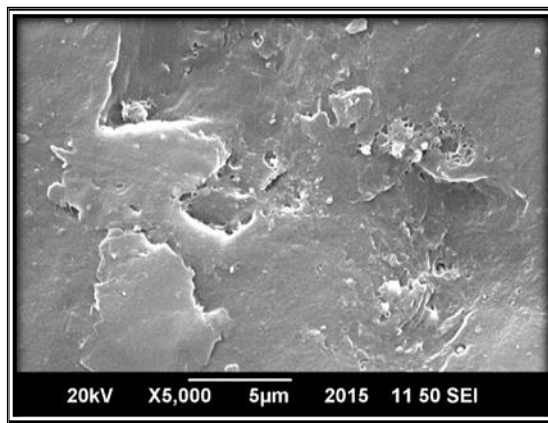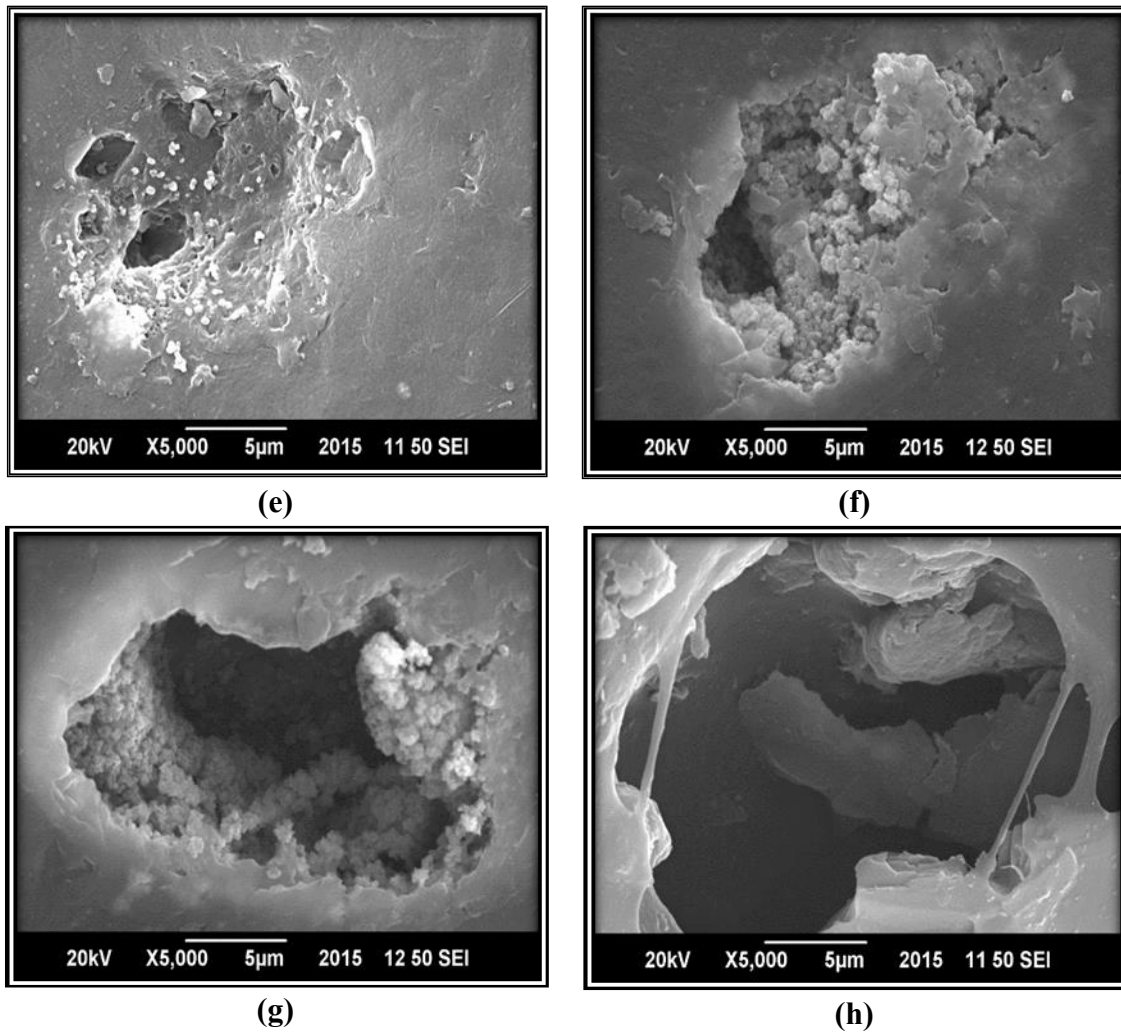
FIGURE 4.5: SEM Images (a) Pure PET Film before Radiation (b) PET-Titania Composite Film before Radiation (c) Pure PET Film after 60 days Radiation (d) 1% PET-Titania Composite (e) 5% PET-Titania Composite (f) 10% PET-Titania Composite (g) 15% PET-Titania Composite (h) 20% PET-Titania Composite

Figures 4.5 (a-h) are illustrating the texture of pure PET and PET composite films before and after irradiation with different concentration of Titania 0%, 1%, 5%, 10%, 15% and 20% respectively. After exposure small cavities appeared in pure PET film under irradiation and saline conditions while these cavities were continuously increasing with increasing amount of titania in film composition as results revealed by Shang *et al*., 2003. SEM results implied that photocatalytic properties of Titania help in PET degradation by generating the active oxygen species which diffuse through a finite distance to scratch out

the polymer surface. After irradiation for 60 days, the size of the cavities in the pure PET sample is much smaller (around 13 μm) as compared to PET-Titania composite films. On the other hand, the generated cavities of PET-Titania composite films show bigger sizes of holes (around than 60 μm). This type of surface degradation is also observed by Shang *et al*., 2003 and Thomas *et al*., 2013 from the spurting of volatile organics from polymer surfaces. SEM outcomes remained similar as results of weight loss and FTIR analysis presented in subsequent topics which support respectively to each other.

4.3 Energy Dispersive Spectroscopy (EDS) Analysis

4.3.1 Titania Nanoparticles

EDS was used to confirm elemental composition of titania nanoparticles before embedded in PET films illustrated in Fig.4.6 to check its purity. Relative elemental mass composition of titania nanoparticles are shown in Table 4.2. These outcomes confirmed that titania nanoparticles contain only titanium and oxygen elements with elemental composition of 58.3% and 41.7% respectively without any impurity.
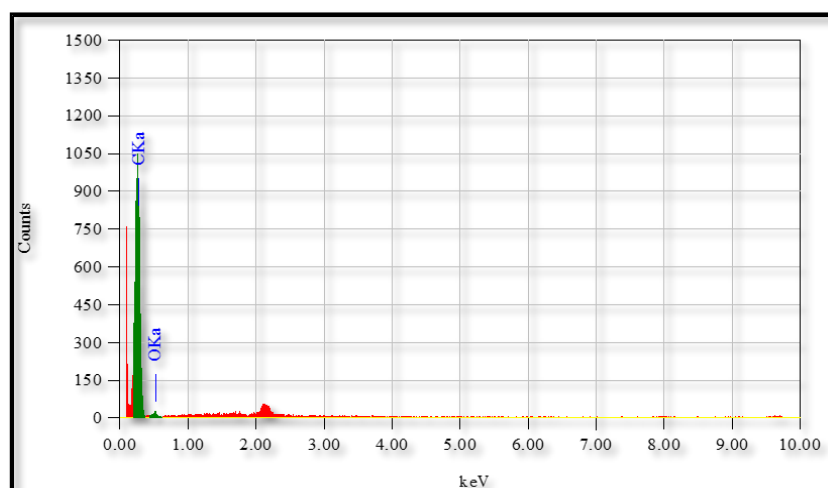
Figure 4.6: EDS spectrum of Titania nanoparticles

**Table 4.2:** Mass percentage of Titania nanoparticles

Titania Nanoparticles	Atom (%)	Expected (%)
Ti	58.29	60
O	41.71	40

4.3.2 PET-Titania Composite Films

PET films were also investigated using EDS to check any influence on elemental composition after retained for long time period (60 days) under irradiance and saline aqueous solution. Results shown that pure PET film did not accumulate any salt after experiment (fig.4.7) while PET-Titania composite films accumulate salts explained in fig. 4.8.
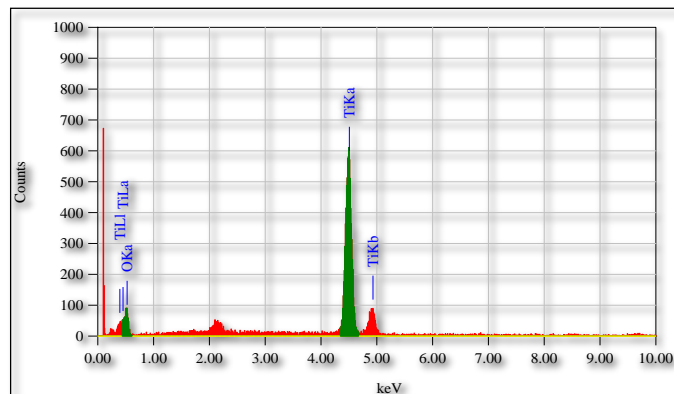
Figure 4. 7: EDS spectrum of Pure PET Film after Irradiance
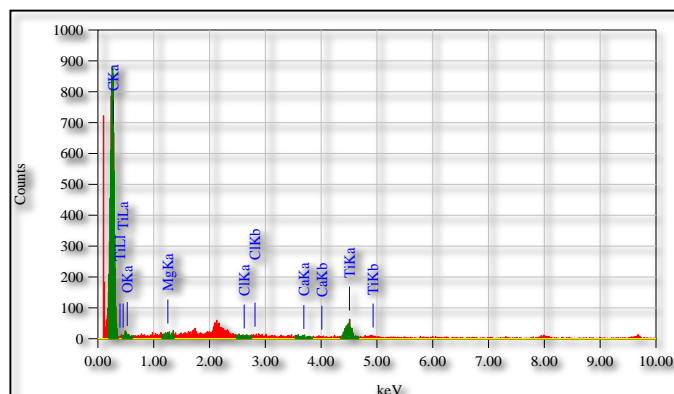
Figure 4. 8: EDS spectrum of PET-Titania Composite Film after Irradiance

Table 4.3 shows relative elemental composition of Pure PET and PET-Titania composite films in which PET-Titania composite films accumulate a small quantity of salts from sea water after film degradation process. It was observed that this accumulation has increasing trend with increase in the amount of titania can be due to film roughness as the presence of titania in higher amount. Increase in oxygen content and decrease in carbon content in degraded films with increasing mass of titania is also observed. These outcomes confirmed that higher quantity of titania nanoparticles in films can cause roughness and provided niche for salts to settle on film surface.

Table 4.3: Mass percentage of Pure PET and PET-Titania Composite Films

| PET Films (Titania %)	C (%)	O (%)	Ti (%)	Mg (%)	Ca (%)	Cl (%)
Ti-0	85.12	14.88	-	-	-	-
Ti-1	82.22	16.64	0.98	0.05	0.07	0.04
Ti-5	68.76	26.12	4.82	0.10	0.11	0.09
Ti-10	61.50	27.56	9.94	0.55	0.20	0.25
Ti-15	55.10	30.44	13.21	0.72	0.23	0.30
Ti-20	45.84	33.57	19.08	0.90	0.25	0.36

4.4 X-ray Fluorescence (XRF) Analysis

XRF analysis was used for spectro-chemical analysis of PET-titania composite films to confirm that these ions were accumulated in niche due to sea water. For this purpose Pure PET and PET-Titania composite films (20% Ti) were placed under UV light immersed in sea water as well distilled water (6 days). Results shown in fig. 4.9 and 4.10 confirmed that salt accumulated in higher amount in films which were immersed sea water while no salt ion was seen in films immersed in distilled water except Titania which was embedded in PET film.
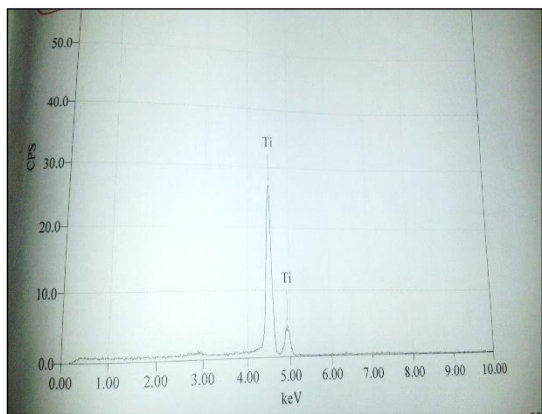
Figure 4.9: XRF spectrum of PET Film (T-20) after Irradiance in Distilled Water
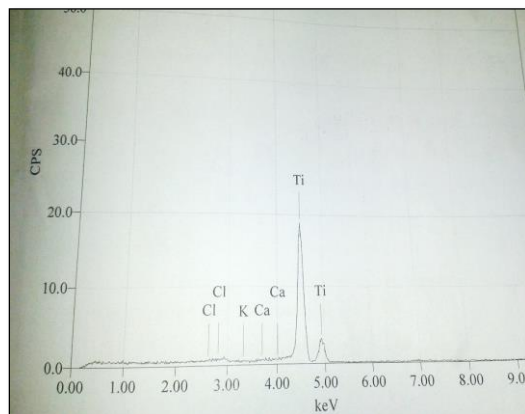
Figure 4.10: XRF spectrum of PET Film (T-20) after Irradiance in Sea Water

4.5 PET Films Degradation Studies using Weight Loss

Weight reduction is one of indicators associated with photo-catalytic degradation of PET films due to the loss of volatile products. It was conducted to check effect of light, water conditions, temperature and mixing on PET-Titania composite films.

4.5.1 Removal of Salts Accumulated on Films

As analysis done above shows high amount of salts (1-2%) which can influence on the weight measurements. PET films were immersed in distill water for 1 hour to remove salts before each time weight measurements. This time interval was fixed after trial and error process by providing immersing time from 15 mints to 2 hours.

Results presented that PET-Titania composite films with less amount of titania (T-0, T-1 and T-5) shown no difference in their weight before and after immersing in distill water for 1 hour. After one hour about 1-2% weight loss was observed in T-10, T-15 and T-20 but after that no weight loss was observed in films shown in the table 4.4.

Table 4.4: Weight Difference after immersing PET Films in distilled Water

Films with titania Percentage	Weight Direct from sea water	Weight after immersed in distilled water for 1hr	Percent Change in Weight
	mg	mg	%
T-0	12.9	12.9	0
T-1	10.8	10.8	0
T-5	11.7	11.7	0
T-10	10.8	10.7	0.9
T-15	10.9	10.7	1.8
T-20	15.2	14.9	2.0

4.5.2   Light Effect on Degradation of PET Films in Sea Water

PET-Titania composite films (T-0 to T-20) were prepared and immersed in sea water, irradiated separately under UV light, visible light as well placed in darkness as controlled experiment to check any influence caused by sea water to catalytic activity of titania without light. The detailed weight loss of PET-Titania composite films (T-0 to T-20) immersed in sea water under these three conditions are presented in fig.4.11.

Results shown here elucidates weight loss of PET films is continue increasing with increasing amount of titania concentration in both artificial and UV light irradiance. No weight reduction was noted in pure PET film and all the PET-TiO_2 composite films during 60 days under dark conditions. This shows that pure PET and PET-TiO_2 composite films remained stable and no degradation occurred under dark conditions in sea water except increases in the weight of films by accumulation of salts which was removed using above method.

On the other hand, pure PET films shown slight weight reduction in artificial light (1.27%) and UV light show photo degradation of 3.03% due to breakdown of organic chains of PET by the intense UV radiation. These results show some salt influence in photo-catalytic degradation of polymer as finding of Mehmood *et al*, 2015 show no degradation of pure PE degradation under 90 days influence of UV as well artificial light while these outcomes agree with the experimental result of Asghar *et al*., 2011 who found weight reduction of PE (3.32%) under UV while degradation (0.65%) was observed under artificial light.
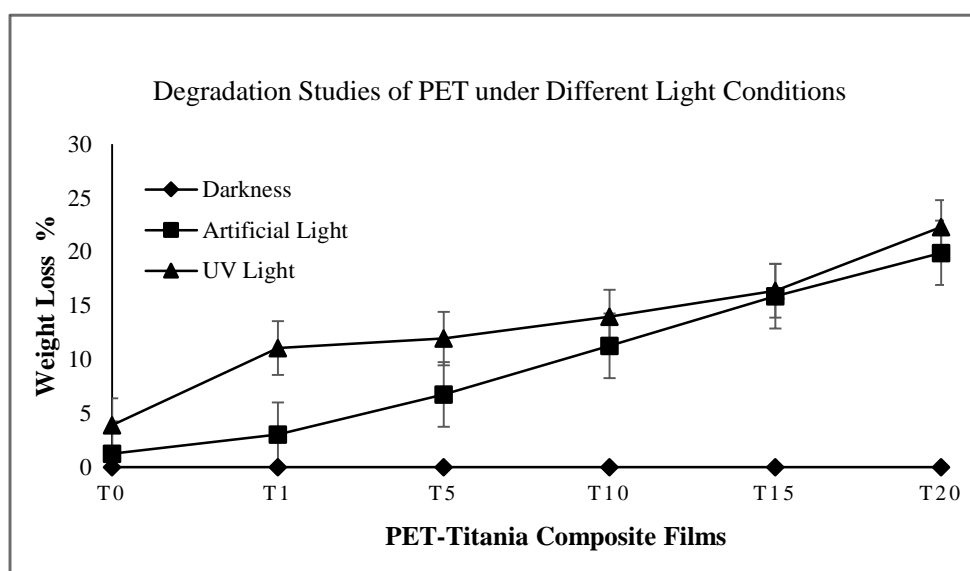
Figure 4.11: Comparative weight loss of PET Film after Irradiance in Sea Water

It was very encouraging to note that PET films can degrade equally under artificial light and UV light in sea water, however captivating six times more time period in artificial light (60 days) than UV light (10 days). It can be perceived that by increasing the amount of titania in the PET films, the weight loss under UV and artificial light had become almost same by providing more time to artificial light experiment. By taking in consideration this

51

phenomena that UV is 6x more intense than artificial light to degrade PET films other factors will be presented here only studied under UV light.

4.5.3 Effect of Distilled Water and Sea Water Conditions on Degradation of PET Films under UV light

Weight measurement of PET films irradiated by UV light was carried out in distilled water and sea water with different concentration of titania composite films shown in Fig.4.12. It indicates that both sea and distilled water conditions contribute appropriate photo-catalytic degradation with almost same weight loss except in higher titania composite films which showed lesser weight loss as compared to distilled water can be, due to salts accumulation. Maximum weight reduction of 26.8% was observed in distilled water of T-20 film while same film show 22.3% weight loss in saline conditions under UV irradiation exposure.

As our concern was to prepare PET-Titania composite films which can degrade in natural conditions. These results show a good compatibility with the hypothesis that PET can degrade in both fresh water as well saline water conditions without effecting the products ability for a suitable time period.
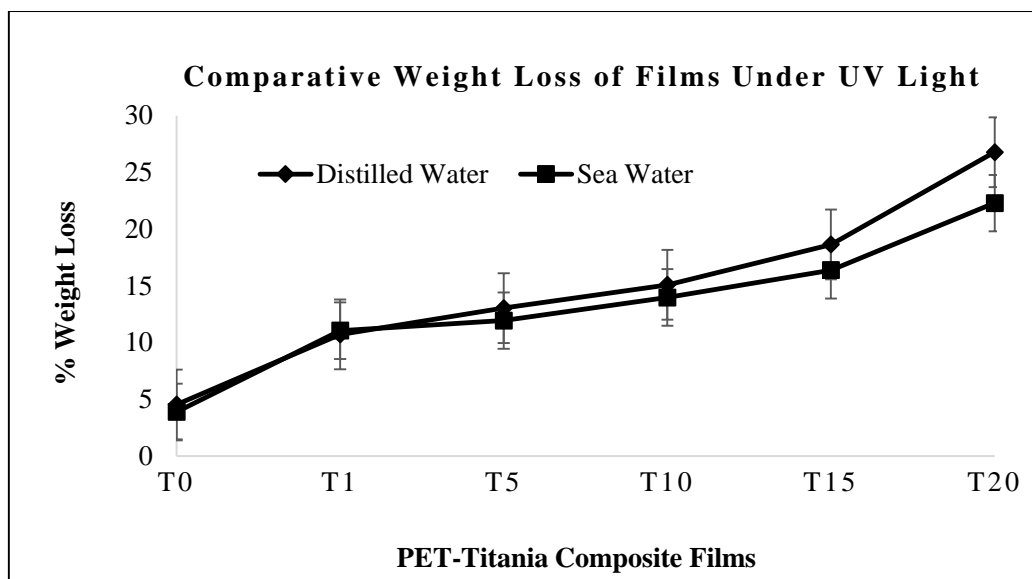
Figure 4.12: Comparative weight loss of PET Film in Sea and Distilled Water

4.5.4 Temperature and Mixing Effect on PET Films Degradation

PET films were degraded under UV light for 10 days under continue mixing (400 rpm) to keep steady internal temperature in both batch reactors with two different temperatures i.e., cold temperature as 4-7°C whereas warm as 37-40°C. Both temperature conditions show promising increase in photo-catalytic degradation results with continues mixing in sea water under UV light.

PET-Titania composite films (T-20, 5 replicates) were added in saline water after measuring initial weight and after applied conditions thin films start breakdown in smaller pieces and even powdered because of continue mixing. Final weight of films was measured after drying collected remains of films using filtration method to get larger parts while centrifuge method was used to get power.

Maximum of 28.43% of weight reduction was observed in high temperature verses 27.25% in cold temperature environment. Whereas, under UV light without controlled room

53

temperature and without mixing, weight loss of PET-Titania composite films (T-20) was 22.29%, which is much less than shown in both batch reactor experiments.

Table 4.5: Mixing and Temperature Effect on degradation of PET-Titania Composite Film

Samples	Wi (mg)	Wo (mg)	Weight Loss (%)
T-20 (Avg.)	-	-	22.29
T-20 (Low Temperature + Mixing)	22.6	16.5	27.25
T-20 (High Temperature + Mixing)	25.5	18.3	28.43

4.6 Fourier Transform Infrared (FTIR) Analysis of PET Films

Physical breakdown revealed in SEM analysis and weight loss data explained that PET films has been photo-catalytically degraded. But Infra-red Spectroscopy (FTIR) was used to explore photo-catalytic molecular breakdown of PET films by studying the nature of chemical bonds of PET through the characterization of the vibrational modes. It also facilitated to find chemical and morphological transformations of PET after photo-catalytic degradation. FTIR spectra of the pure PET films before and after artificial light irradiance exposed for 60 days and PET-Titania composite films after irradiation shown in the Figure 4.13.

The spectrum of the PET film i.e. Figure 4.13 (a) shows the characteristic absorption of long aromatic and aliphatic chain (C-H) in the region of $2915cm^{-1}$, $2857cm^{-1}$, ethylene glycol in $1463cm^{-1}$ and C-C bending in $729cm^{-1}$. Fig. 4.13 b), c), d), e), f) and g) display FTIR spectra of the PET-Titania composite films T-0, T-1, T-5, T-10, T-15 and T-20 respectively after 60 days irradiance.

The irradiated films showed similar pattern of FTIR spectra with overall diminution in intensities ($2915cm^{-1}$, $2857cm^{-1}$, $1463cm^{-1}$ and $729cm^{-1}$) and change in profile of these peaks as well changes in distinctive bands (addition of $1716cm^{-1}$, $1017cm^{-1}$) of virgin PET.

These changings show decrease in the concentration and/or the change in the chemical locality of the original bonds of pure PET because photo-catalytic degradation can modify chemical structure and this decrease in peaks intensity is constant till it becomes very small at concentration of 20% titania (T-20).

FTIR also shown evidence that PET-titania composite films are degraded as drastic change was shown in the number, intensity and shape of peaks in aromatic and aliphatic C-H region as Sammon and co-worker (2000) recognized this change caused in aliphatic chains by breakdown of polymer chain.

Interpretation of shift of peaks with different concentration of Titania can provide identification of species formed during degradation. After irradiation new absorption peaks for degraded PET films were also shown correspond to the carbonyl stretching in the region of $1716cm^{-1}$, CH_2 deformation band at $1463cm^{-1}$, the ethylene group wagging $1342cm^{-1}$ for the trans conformation, $O-CH_2$ stretching of ethylene glycol in PET at $980cm^{-1}$ and a small peak at $3610\ cm^{-1}$ was allocated to ^-OH stretching after irradiation (Djebara *et al*., 2012; Holland and Hay, 2002).

Appearance of new peaks corresponding to $C=O$ ($1716\ cm^{-1}$) suggest that photo-oxidation of the PET has started occurring in T-5 and T-10 films (Fig. 4.13 d and e). This oxidation leads to the formation of the ultimate product CO_2 of the PET degradation.
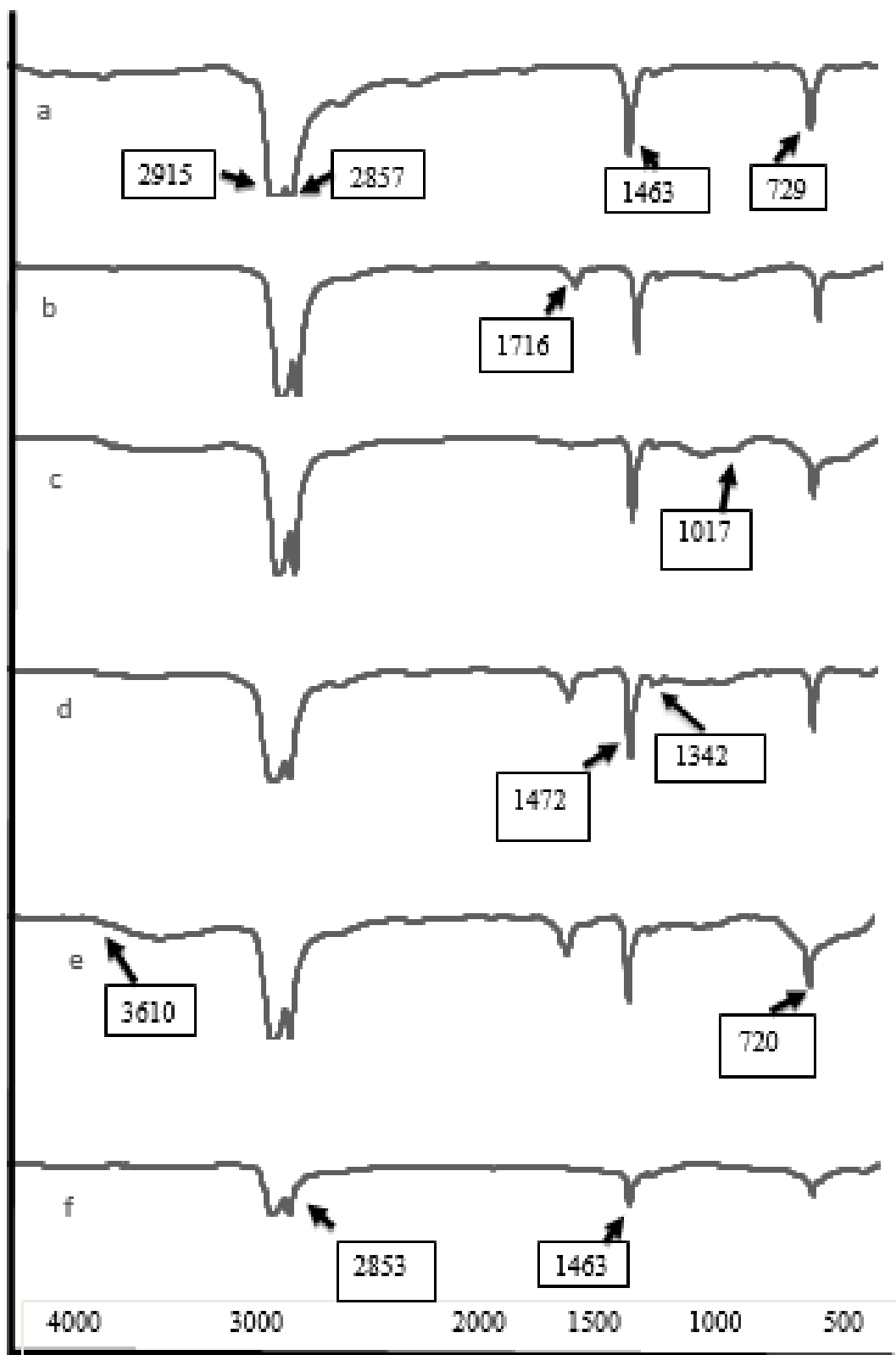
Figure 4.13: FTIR spectra of PET before and after Irradiation a) PET before Irradiation b) PET after Irradiation c) T-1 after Irradiation d) T-5 after Irradiation e) T-10 after Irradiation f) T-15 after Irradiation g) T-20 after Irradiation

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The following conclusions can be drawn from the work done in this study:

i.   Liquid Impregnation (LI) and calcination processes can produce good quality of nanoparticles (Anatase + Rutile) for polymer degradation.

ii.   Degradation of PET under both UV irradiation and artificial light are considerably enhanced with the increasing concentration of incorporated titania nanoparticles.

iii.   In general, PET-Titania composite films can easily degrade in natural light and sea water but required more time as compared to UV radiation still very less time as pure PET take to degrade in nature.

iv.   PET-Titania composite films have potential to degrade in both distilled and sea water conditions, able to degrade under natural conditions with wide range of temperature as well.

v.   The technique of incorporating titania nanoparticles into raw PET material, shows considerable potential for production of commercial PET products generally and PET bottles specifically that can help in antimicrobial for shorter time period and for longer time period polymer degradation when exposed to sunlight.

5.2 Recommendations for Future Work

In assessment of the results described in this study, some suggestions are given below for future investigation:

i. Only PET Titania composite film (T-20) was studied for temperature and mixing effect under saline conditions which can be further implemented for all titania concentrations to work out for optimum degradation results.

ii. Chemical changes due to salts accumulation on films can be further analyzed as it can help in degradation under longer time periods as we know salts help in breakdown of plastic into micro-plastics.

iii. The lab results may be further analyzed using field studies concerning long term exposure of PET composite films to solar radiation and can be extended to actual products.

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