1.1 Introduction

The increasing urbanization and industrialization to raise the living standard of human population has increased the environmental pollution many folds. It has resulted in huge generation of wastes simultaneously, which contaminated our natural resources such as soil, water and air. It led to the undesirable effects on the environment and human health. Various industries such as petro-chemical, carpet and textile industries create huge problems in the environment by disposing toxic waste, and generate oily sludge and wastewater (Vogt et al., 2016). Of these, wastes generated from the petro-chemical industries are of high significance due to their highly toxic and carcinogenic nature. The effective disposal of waste generated from petro-chemical industries during crude oil transportation, storage and refinery process is becoming a worldwide problem (Stasik et al., 2015). Improper disposal of oily sludge and wastewater lead to the contamination of water and soils, which further poses a serious threat to the groundwater (Vogt et al., 2016). Many of the constituents of such petro-chemical sludge are carcinogenic and potent immuno-toxicants. Similarly, waste generated from carpet and textile industries consists of organic compounds, which are carcinogenic, toxic and mutagenic in nature. A few constituents in these wastes are classified as unsafe and hazardous, which cannot be reutilised further in any manner.

Principally, the polycyclic aromatic hydrocarbons (PAHs) derived either from the direct sources or from secondary reactions of various chemical processes occurring in the natural environment, are of major concern today. They are carcinogenic, mutagenic and genotoxic to humans and other ecological receptors (Bahr et al., 2015; Shukla et al., 2014). Of the PAHs, Benzene, Toluene, Ethylbenzene, Xylene (collectively known BTEX) and phenolic compounds are posing serious threat to the environment, which are also classified as pollutants by USEPA having plethora of emitting sources (Mazzeo et al., 2011; Yeh et al., 2010). These compounds are commonly found in crude oil and its by-products (such as gasoline). They are the main components in surface and groundwater, which generally originate from leakage of petroleum storage tanks, spills at production wells, refineries, pipelines, and storage and distribution terminals (Deary et al., 2016; Folwell et al., 2016; Li et al., 2016; Mohamad Shahimin et al., 2016; Stasik et al., 2015). Further, accidents during oil transportation such as oil spillage, ship breakage and leakage of oil pipelines are the major causes of environmental pollution of land and water. Therefore, the remediation of these pollutants is highly required to eliminate the risk to the human life as well as to the environment (Hu et al., 2013; Megharaj et al., 2011; Vogt et al., 2016; Wang et al., 2016). Proper treatment of these organic pollutants is identified as the major challenge in the hazardous waste and environmental management (Mohamad Shahimin et al., 2016; Vogt et al., 2016).

Due to the excessive cost of waste management and water treatment, most of the textile industries in the developing nations (e.g. India) dispose wastewater and sludge in the agricultural fields, open dumps, fallow lands, and poorly managed sanitary landfills as well as along railway tracks. It pollutes the surface or sub-surface water, and causes public health hazards (Adar et al., 2016; Ahmad et al., 2016; Anjum et al., 2016; Bui et al., 2016; Cao et al., 2016). Contamination of soils from industrial sludge and wastewater has detrimental consequences on the ecosystems. It can make lands unsuitable for the agriculture and other value-added purposes (Ali et al., 2014; Feo and Gisi, 2014; Pandey et al., 2016). The carcinogenic petro-chemicals and other organic pollutants have become the serious concern among environmentalists and chemical engineers today (USEPA 1996). These pollutants causes many health ailments such as acute and chronic respiratory effects (Deary et al., 2016), neurological toxicity, lung cancer, fatigue, headaches, dizziness, nausea, lethargy, depression, as well as eye and throat irritation (Abdel-Shafy and Mansour, 2016; Fowles et al., 2016; Hu et al., 2016; Zhang & Fan, 2016). In this relation, BTEX group of contaminants hold crucial importance which constitute a significant percentage of petroleum products. It consists of volatile organic compounds (VOCs) such as benzene, ethylbenzene, toluene and three isomers of xylene. Occupational and non-occupational exposure to BTEX compounds and other hydrocarbons are extremely harmful to living organisms. For example, benzene is considered to be carcinogenic to human beings, which causes various disorders like leukaemia, lymphoma, chromosomal breakage, interference with their segregation, etc. (Bird et al., 2005). Most of these polycyclic aromatic hydrocarbons (PAHs) are highly lipidsoluble and readily absorbed in the gastrointestinal tract of mammals (Cerniglia, 1984). These may be accumulated in food chains and results in serious health problems and genetic deformations. These hydrocarbons also affect aquatic organisms adversely by reducing their chlorophyll content (Peng et al., 2015).



Fig. 1.1: An illustrated representation of various treatments methods available for degradation of organic pollutant (adapted from Shahidi et al., 2015).

Various organic and inorganic contents of these wastes have been well recognised as water and soil contaminants. Globally, various technologies are adopted for the treatment of the industrial wastewater; however, commercially and ecologically sustainable technique for its proper management is lacking. Moreover, limited space, more stringent waste disposal regulations and public consciousness have made the present techniques expensive and impractical. Therefore, there is an urgent need to develop sustainable waste management technologies for industries and municipalities (Ramteke & Gogate, 2015). In order to remove the damaging effect of organic pollutants on the environment, various new technologies for their degradation

have been discovered recently. Methods such as physical (Davarnejad et al., 2014; Hu et al., 2017; Mymrin et al., 2017; Siddique et al., 2016), chemical, biological (LeFevre et al., 2012; Li et al., 2016; Wang et al., 2015), and advance oxidation processes (AOPs) (Luo et al., 2016; Sun et al., 2016; Zhang et al., 2016) are being used to degrade these organic pollutants from industrial wastewater. Some of these methods are shown in Figure 1.1. Methods such as advanced oxidation, biofiltration, separation by membrane, absorption and adsorption have been evolved for the treatment of wastewater containing such pollutants. However, these have limited applications due to either being expensive or being associated with environmental consequences.

Several mechanical and chemical approaches, which are widely being used for urban wastewater treatment systems mainly by sewage treatment plants (STPs) have limitations. Due to high construction cost, operational and maintenance problems involved in STPs, their sustainability is questionable. Moreover, excess sewage sludge produced by these treatment plants is creating problem following increasingly stringent limitations on the discharge by several countries during the last few decades (Vigueros and Camperos, 2002). A number of studies conducted in this area suggest that none of these available conventional disposal methods are environment friendly. Even, many developing countries cannot afford the construction of STPs. Therefore, there is growing concern over installing some ecologically safe and economically viable small-scale on-site wastewater treatment.

In recent times, the most commonly used methods are microbial degradation and AOPs (Chen et al., 2016). Here, biodegradation and photocatalytic degradation are the most potent and widely applied methods for the degradation of petrochemical wastes. Biodegradation processes utilise microorganisms for the degradation of hazardous chemicals in soil, sediments, water or other contaminated materials (Wang et al., 2015). Microorganisms often metabolize the chemicals into CO₂ or CH₄, water and biomass (Megharaj et al., 2011; Mello et al., 2010; Wang et al., 2016). Alternatively, the contaminants may be enzymatically transformed to metabolites that are less toxic or innocuous. However, among AOPs, photocatalytic degradation and ultrasonication efficiently degrades the chemically stable and relatively less biodegradable organic pollutants (Verbruggen, 2015). In the present study, we are focusing on the comparative evaluation of photocatalytic and biodegradation of organic pollutants, particularly the petrochemical hydrocarbons as petrochemical industries have created serious concern for the environment (Mohamad Shahimin et al., 2016).

1.2 Treatment technologies for degradation of petrochemical wastes

Different treatment methods used for degrading petrochemical waste can be classified under the following three headings: physical, chemical and biological (Fig. 1). The choice of the best technology is based on waste chemistry, cost-effectiveness, space availability, reuse and discharge plans, durable operation and by-products. In the category of physical methods for the abatement of organic pollutant, adsorption and coagulation are the most commonly used processes (El-Naas et al., 2014). Dissolved organics can be easily adsorbed on activated carbon, organo-clay, copolymers, zeolites and other resins. Organic compounds and some heavy metals present in the petrochemical wastes get adsorbed on the porous surfaces of the activated carbon (Aivalioti et al., 2010; Bhatnagar and Anastopoulos, 2017; Uddin, 2017; Unuabonah and Taubert, 2014; Yang et al., 2016). Activated carbon is the most used adsorbent for the remediation of hydrocarbon (Anirudhan & Ramachandran, 2014; Hedbavna et al., 2016) and dye (Kurade et al., 2016) compounds. Other advance techniques involve the application of membrane technology (Li et al., 2006a; Rahman and Al-Malack, 2006). Recently, AOPs such as photocatalytic degradation, microwave assisted catalytic wet air oxidation (Sun et al., 2008), Fenton process, etc. have also gained popularity due to its various properties and efficiency for the degradation of pollutants. However, the problems include high maintenance cost, requirement of skilled manpower. Moreover, generation of toxic intermediates in these processes lead to a further increase in environmental contamination.

Besides these conventional physical and chemical methods, various biological methods such as activated sludge, trickling filters, sequencing batch reactors, chemostate reactors, biological aerated filters, bioremediation, bioaugmentation, etc. (Adelaja et al., 2015; Elreedy & Tawfik, 2015; Siddique et al., 2014) are also being used to degrade organic pollutants. Biological methods employ the diverse metabolic and enzymatic capabilities of microbes for detoxification or mineralization of pollutants (Siddique et al., 2015; Siddique et al., 2014; Yang et al., 2015; Yeruva et al., 2015). Bacteria can degrade a variety of hydrocarbons, including monoaromatic compounds, under aerobic and anaerobic conditions (Wiszniowski et al., 2011). These microbes utilize the carbon contained in the petrochemical waste for their metabolism, and bio-transform them into less toxic intermediates and by-products. Moreover, biological methods have low operating costs and they involve direct degradation of pollutants (Bajaj and Singh, 2015; Boonnorat et al., 2016; Megson et al., 2016; Tiwari et al., 2017).

Bioremediation is an integrated approach employing microbial community such as bacteria, fungi, actinomycetes and earthworms (Mazzeo et al., 2010). These processes have been found to be beneficial at small as well as large scale wastewater treatment by passing it through a batch/continuous reactor (Mello et al., 2010; Yeh et al., 2010; Kristensen et al., 2010). In addition, these processes are found to be sustainably used for conversion of toxic petro-chemical and textile wastes to the nontoxic end products (Luna et al., 2015). The biodegradation of xenobiotics in the microbial system is based on the action of the enzymes. Bioremediation encompasses the rhizo-remediation (plant and microbe), phyto-remediation (plants) (Chang et al., 2009; Gao et al., 2015; McCutcheon and Jørgensen, 2008; Sriprapat and Thiravetyan, 2016), and vermi-composting (worms and microbes) depending upon the microbial processes involved in the degradation of pollutants. Because bioremediation seems to be a promising alternative to conventional clean-up technologies, substantial research is increasing in this field rapidly. Also, bioremediation efficiency of indigenous microorganisms can be significantly enhanced by optimizing certain factors like adsorption, mass transfer and bioavailability (Sudip et al., 2002). However, more research is required for (1) the establishment of bioremediation technique at larger scale, and (2) the holistic analysis of environmental consequences of such products (Ray & Banerjee, 2015). Moreover, the biodegradation rate of one component in a mixture can be affected by the other components is also known. The by-products

produced during the degradation of one compound also can affect the degradation of another compound. Therefore, it is imperative to use an integrated bioremediation approach by using a consortium of microbes for simultaneous degradation of petrochemical waste containing many hydrocarbons. The recent developments also indicate that bioremediation approach may be a sustainable and economical for the management of petrochemical wastes and other organic pollutants (Nzila, 2013; Pimda & Bunnag, 2015).

Owing to the toxic, hydrophobic and multi-phased nature of the petrochemical wastes, its bioremediation is a complex phenomenon. Various studies on biodegradation of petro-chemical wastes have identified a number of physical, chemical and biological factors which affect the rate of biodegradation. To overcome all the involved limitations and effectively degrade all the hydrocarbons and related contaminants, there is a need to develop advanced bioremediation strategies. The development of hybrid pathways through genetic manipulation of microorganisms is also one of the most promising techniques, which would drastically improve the process of bioremediation. Therefore, various advanced oxidation processes (AOPs) are now evolving for the rapid and efficient degradation of petro-chemical wastes.

Among AOPs, heterogeneous photo-catalytic oxidation, which involves the acceleration of photoreaction in the presence of a semiconductor catalyst, has proved to be of utmost interest due to its efficiency in degrading recalcitrant organic compounds (Reddy et al., 2015; Fischer et al., 2014). Since 1970s, heterogeneous photocatalytic oxidation has been given considerable attention. Numerous studies

have been done regarding the application of heterogeneous photocatalytic oxidation processes with a view to decompose and mineralize recalcitrant organic compounds (Lan et al., 2013; Ravelli et al., 2010). Photocatalysts are the class of compounds which generate electron pair on coming in contact with or on absorption of light quanta. This causes chemical transformation of substrate that comes in contact with it (Kuen Jo and Tayade 2013). In this regard, semiconductor heterogeneous photocatalysis has enormous potential to treat organic contaminants in water and air (Jin et al., 2013). Among all heterogeneous photocatalysts, TiO₂ is the most widely used, as it can degrade a wide range of organic pollutants. Fujishima and Honda (1972) pioneered the concept of titania photocatalysis (also known as Honda-Fujishima effect) and showed the possibility of water splitting in a photoelectrochemical cell, containing an inert cathode and rutile titania anode. The applications of titania photo-electrolysis has since been greatly focused in environmental applications including water and wastewater treatment (Banerjee et al., 2015; Pindado Jiménez et al., 2015).

Photodegradation has emerged as one of the most recent and reliable technique for degradation of organic pollutant in wastewater (Zhou et al., 2015). Photocatalytic processes are a viable alternative for efficient degradation of monocyclic and polycyclic petrochemical wastes. However, many studies have suggested that the intermediates produced during photocatalytic degradation were much more toxic than the pollutants to various organisms in the environment. Researchers had studied the negative effects of nano-TiO₂ particles on plants which include inhibition of root growth in few plants (Barnes et al., 2013; Ghosh et al.,

2013; Goncalves and Girard, 2014; Leung et al., 2015). ZnO nanoparticles, bulk material and zinc salt are comparatively toxic, whereas CuO nanoparticles are more toxic than bulk material but lesser toxic than copper salt (Adam et al., 2015).

Various other studies showed that the amount of catalyst plays a vital role in the degradation of organic pollutants, mostly in aqueous phase. The amount of catalyst used in the degradation processes is directly proportional to the overall degradation rate of organic compounds (Akpan and Hameed, 2009; Diyauddeen et al., 2011; Jain and Srivastava, 2008). Effect of pH of the solution on photocatalytic degradation of organic pollutants and their adsorption on the catalyst surface has been extensively studied by various researchers (Akpan and Hameed, 2009; Alakahami et al., 2003; Mrowetz and Shelli, 2006; Wang and Ku, 2007). The effect of the concentration and nature of organic pollutants on the rate of photocatalytic degradation has been studied by various researchers. The organic compounds having high tendency to bind to the catalyst surface are much likely to be oxidized. The high concentration of pollutants in aqueous medium saturates the catalyst surface, which reduces photonic efficiency and consequently causes deactivation of photocatalysts. Photocatalysis reaction depends mainly on the radiation absorption by catalysts, which depends on the intensity of light. Generally, an increase in light intensity increases the rate of degradation of organic pollutants, which is attributed to an increased photon flux of electrons in the conduction band (Karunakaran and Senthilvelan, 2005; Qamar et al., 2006; Vohara and Tanaka, 2002). Reactor design and efficiency also plays a very critical role in the photodegradation of the organic pollutants. Various reactors used for the degradation processes by various studies are:

Banić et al., 2016; Boyjoo et al., 2013; Dzinun et al., 2016; Gao et al., 2011; Jayamohan et al., 2016; Jo & Tayade, 2016; Kumar & Bansal, 2013.

1.3 Background and bibliometric analysis of literature

In order to validate our study and establish a rationale behind the purpose of our study, we have carried out a bibliometric analysis on biodegradation and photocatalytic degradation of organic pollutants. Here, we addressed separately 'biodegradation' and 'photocatalytic degradation' and attempted to find out the interests of the research communities on both the subjects. We have considered a 25 years period from 1991 to 2016 and analyzed the original research and review articles published during that time. For the purpose of our study, we have exclusively considered research documents published in journals indexed or abstracted in 'Scopus' database. The rationale behind the selection of 'Scopus' over any other database such as 'Web of Science', is that Scopus has a much wider coverage as compared to other databases. We have carried out the study on 25th March. 2017 using different search queries as described in the following section. While formulating the search queries terms such as 'biodegradation', 'bioremediation', 'microbial degradation', 'photocatalystic degradation', 'heterogeneous photocatalysts' etc. are looked for in the 'title/abstract/keyword' of the papers in order to the locate the papers with specific focus on these areas.

1.3.1 Biodegradation of organic pollutants

The bibliometric analysis of biodegradation of organic pollutants was carried out using the search query '((TITLE-ABS-KEY ('Biodegradation' or 'Microbial degradation' or 'Bioremediation') AND TITLE-ABS-KEY ('organic pollutant' or 'petrochemical' or 'PAH' or 'BTEX' or 'MTBE' or 'Phenolic compound')) AND PUBYEAR > 1990 AND PUBYEAR < 2017). A total of 3889 research documents of various forms are reported in this search. We have further analyzed these 3889 documents with respect to the: 1) yearly distribution, 2) journals where these article got published, 3) research institute or university-wise distribution, 4) country-wise distribution, 5) number of documents in each category, and 6) subject-wise distribution.



Fig. 1.2: Yearly distributions of publication on biodegradation (Source: Scopus, 2016).

It has been observed that overall the number of publications has been on a rise during the last 25 years, from 1991 to 2016 baring some minute drop in one or two years in between. The first significant drop on the number of publications was observed in 2016. While the year 2015 produced 352 research documents on biodegradation or bioremediation of organic pollutants, 2016 observed 209 documents, a considerable 143 documents shorter than the level of the 2015 (Fig. 1.2). Whether this fall implied the gradual and relative disinterestedness of the research community on the topic can only be justified considering the number of publication is due to the different publication timelines or period of different journals which may vary from a few months to a few years. Considering the significance of the topic in the present global environmental scenario, it is unlikely that researches on the biodegradation and bioremediation of organic pollutants will dip down in the near future. Nevertheless, the focus may shift to some other potential areas of relevance.



Fig. 1.3: Top 10 institutions in the publication of biodegradation of petrochemical wastes.

There are a number of universities or research institutes who have made their presence felt in the research niche of biodegradation or bioremediation of organic pollutants by carrying out associated studies on diverse environmental pollution issues. Helmholtz Zentrum, for instance, has published 32 articles on the topic from 2000 to 2015, followed by Denmarks Tekniske Universitet with 19 papers (Fig. 1.3).

If we look at the country-wise distribution (Fig. 1.4), the contribution of China and United States is almost at par with each other. However, other countries are far behind as compared to both these countries. India, ranked sixth on the list, for instance, has produced about one third papers less than that of the second positioned United States. It implies that more research attentions are essential from the research communities of countries such as India which is laden with intense pollution crisis of almost all kinds, including severe threats from organic pollutants.



Fig. 1.4: The top 10 most productive countries for research on biodegradation.

Regarding the subject area, it has been observed that majority of the contributions come from the domain of environmental science with total 818 papers reported from the subject area (Table 1.1). Considering the rapid evolution of the subject of environmental science during the last decades, this research attention is justifiable.

Table 1.1: Subject area	a wise distribution	of publications in the	e field of biodegradation
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Subject	No. of Papers
Environmental Science	818
Immunology and Microbiology	220
Biochemistry, Genetics and Molecular Biology	206
Chemical Engineering	206
Chemistry	139
Medicine	128
Agricultural and Biological Sciences	119
Earth and Planetary Sciences	86
Engineering	61

1.3.2 Photocatalytic degradation of organic pollutants

The bibliometric analysis for photocatalytic degradation of organic pollutants was carried out using the search query ((TITLE-ABS-KEY ('photocatalytic degradation' or 'photodegradation' or 'heterogeneous photocatalysis' or 'catalytic degradation') AND TITLE-ABS-KEY ('organic pollutant' or 'petrochemical' or 'PAH' or 'BTEX' or 'benzene' or 'MTBE' or 'Phenolic compound')) AND PUBYEAR > 1990 AND PUBYEAR < 2017). A total of 983 documents were reported during the period from 1991 to 2016. It has been observed that the research focuses on biodegradation of organic pollutant is far more than that of photocatalytic degradation. While biodegradation reports 3889 research articles, photocatalytic degradation reports almost one fourth of that, at only 983 publications during the last 25 years on the topic. We have further analyzed these 983 documents with respect to the: 1) yearly distribution, 2) journals where these article got published, 3) research institute or university-wise distribution, 4) country-wise distribution, 5) number of documents in each category, and 6) subject-wise distribution.

On a positive note, it has been observed that there is a significant increase in the number of publications on photocatalytic degradation, especially during the last two years (Fig. 1.5). The year 2015 has observed a remarkable growth in publication from the 2014 level . Considering the depth of the organic pollution problem in the contemporary global scenario, such an increase in research interest is certainly encouraging.

Among the universities and research institutes, university of Porto records maximum number of publications of the topic of photocatalytic degradation of organic pollutants during the last 15 years with Fuzhou University stands a close second (Fig. 1.6).



Fig. 1.5: Yearly distribution of publications on biodegradation (Source: Scopus, 2016).



Fig. 1.6: Top 10 institutions in the publication of photodegradation of petrochemical waste.

Regarding the country-wise distribution, it has been observed that the research interest on photocatalytic degradation of organic pollutants is concentrated only on a single country, i.e. China. As compared to China, the other countries are lagging far behind. The third ranked United States. Such negligence on a global scale necessitates immediate attention from the international research community as photocatalytic degradation of organic pollutants has the potential to contribute significantly to avert the pollution load at a global scale.

Regarding the subject area, the domain of environmental science and chemistry are at par with each other with 241 and 202 papers published during the last 15 years period on photocatalytic degradation of organic pollutants as shown in table 1.2.



Fig. 1.7: Top ten most productive countries for research on photodegradation of petrochemical wastes.

photodegradation	
Subject Area	No. of Publications
Environmental Science	241
Chemistry	202
Chemical Engineering	184
Materials Science	102
Engineering	72
Physics and Astronomy	49
Energy	34
Medicine	33
Earth and Planetary Sciences	18
Biochemistry, Genetics and Molecular Biology	16

 Table 1.2: Subject area wise distribution of publications in the field of

 photodegradation

1.4 Comparative Studies of photo-catalytic and biodegradation processes

With majority of treatment techniques having major drawback of generation of another type of wastes, biodegradation and photocatalytic degradation appeared to be very promising techniques. Bioremediation is proved to be not only a cost-effective technique; it also leads to the complete mineralization of the organic pollutants and generates nontoxic end-products. It is undoubtedly a sustainable and economically feasible technique for the remediation of environmental pollutants. It has also proved to be a successful process in the laboratory and also in many cases, in the natural environment. Several *in-situ* and *ex-situ* bioremediation processes are operational at contaminated sites around the globe. However, microbial communities have also simply failed to perform as expected in the field in many cases. Therefore, it has not been easy to imitate laboratory results in the field. To overcome the drawbacks of bioremediation, photocatalysis is also one of the most promising techniques for the degradation of wide range of organic pollutants in liquid and gas forms. However, there are various drawbacks associated with photocatalytic degradation such as high energy consumption and capital cost associated with photodegradation process. Therefore, there is need of more research to make these processes more efficient.

Overall, there is a need to develop the hybrid methods involving biological and photocatalysis processes for efficient degradation of petrochemical wastes. It may be the most promising technology for the remediation of environmental pollutant in future. Therefore, research to devise and promote the hybrid processes (incorporating both bioremediations and photocatalytic degradation routes) is another unexplored areas of the degradation of organic pollutant.

Based on the above discussion, I have devised following objectives for my research work:

Biodegradation:

- (a) Collection of soil and water from the petroleum contaminated sites
- (b) Isolation of the microbes from the contaminated soil and water samples
- (c) Identification of the isolated strains using 16S rDNA gene sequence analysis

- (d) To optimize parameters responsible for the efficient degradation of pollutants
- (e) To design and fabricate sequence/batch bioreactor and evaluate their degradation efficiency
- (f) Degradation study

Photocatalytic degradation:

- (a) Synthesis and characterization of TiO₂/Activated carbon composites as photocatalyst for the degradation of organic pollutants
- (b) Investigation of efficiency of photodegradation in specifically designed and fabricated photochemical reactor
- (c) To study the environmental impact analysis of residual photo-catalyst.
