A REVIEW ON BIODEGRADATION OF PLASTICS

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ABSTRACT

In modern era, the use of plastic product in different sector of industry is increasing day by day**.**Plastic waste management and recycling became a serious global issue as it affects living beings from all the ecosystems.Their disperse disposal in land andwater arouses threats for human, wildlife and aqua life. Researches have been carried out on plastic degradation to find solutionto overcome these environmental hazards. Biodegradation emerges as one of the promising solution to manage theplastic waste which could not be recycled. In biodegradation processmicroorganism and their enzymes are applied to degrade the syntheticand bio-based plastics. This review gives the current progresson biodegradation of various plastic polymers by microorganisms andenzymes to determine the extent of degradation**.**
Keywords :Plastics,Bacteria, Fungi, Actinomycetes, Enzymes,Biodegradation.

INTRODUCTION

The word "plastic" derived from the Greek word "Plastikos", that means which can be molded into different shapes. Plastics stated as the polymers which start moving on heating so can be casted into moulds. Generally, plastic materials are derived from petrochemicalsexcept biodegradable bioplastic. Plastics an indispensable part of modern world, are manmade synthetic polymer derived from natural fossil fuel(Scott, 1999). Plastic consists of chloride, oxygen, hydrogen, carbon, silicon and nitrogen. Polyethylene consists of 64% of total plastic and its general formula is CnH2n. From different hydrocarbons and petroleum derivatives high molecular weight organic polymers are obtained. These polymers are known as plastic(Dilara *etal.*, 2021)

Plastics are polymers derived from petrochemicals which are further synthetically made from monomers by some chemical processes to produce these long chain polymers (Shimao 2001). Plastics are light weight, low cost, highly durable and are of high strength. In our daily life the plastics are available in various forms such as nylon, polycarbonate, polyethyleneterephthalate, polyvinylidene chloride, Urea, formaldehyde, polyamides, polyethylene, polypropylene, polystyrene, polytetraflouro ethylene, polyurethane and polyvinyl chloride (Smith 1964.) Synthetic plastics, including polyethylene (PE), polystyrene (PS), polypropylene (PP), polyvinyl chloride (PVC), polyurethane (PUR), and polyethylene terephthalate (PET) have become fundamental to almost every aspect of our lives. The plastic pollution is threatening the environment because it has very slow degradation rate and high usage in regular activities.

The increase use of plastic is growing concern and major contributor to pollution across the globe. (Bakht*et al*., 2020)**,** Worldwide the annual production of non-degradable plastic ranges from 350 million to 400 million tons out of that yearly, 5 to 13 million tons of waste plastic are released into the ocean, which is negatively affecting the ecological environment (Jambeck*etal*,2015). It is predicted that up to 26 billion tons of plastic wastes will be produced by 2050, and more than half will be thrown away into landfills and finally enter ecospheres, such as oceans and lakes, leading to serious environmental pollution (Jambeck*et al*., 2015; Geyer *et al.,* 2017).

Polyethylene and polypropylene represent about 92% of the synthetic plastics produced, and they are used for production of plastic bags, disposable containers, bottles, packaging materials, etc. (Byuntae*et al*., 1991). An estimated more than 500 billion to 1 trillion plastic bags used globally disturb the ecosystem and ultimately result into serious environmental issues of recycling these materials from the environment (Andrews *et al*., 1992 ; Ishiaku*et al*., 2002). Poly(ethylene terephthalate) (PET) is used extensively worldwide in plastic products, and its accumulation in the environment has become a global concern.

Figure 1 : Plastic Pollution

Plasticclassification on the basis of thermal properties

On the basis of thermal properties plastics are divided into two classes, i.e.thermoplastics and thermosetting polymers. By the polymerization of small molecules, plastics can be synthesized.

Thermo- plastic

It is a type of plastic that can be molded for several times but on heating it cannot undergo any chemical change in its composition. Examples of thermo-plastics are polypropylene (PP), polyethylene(PE), polyvinylchloride (PVC),polystyrene(PS)and polytetrafluoroethylene (PTFE). These plastics are ranges from 20,000 to 500,000 amu (atomic mass unit) in molecular weight and are generally known as common plastics. Macromoleculesare arranged in linear manner in the form of chain in which atoms and molecules are attached end to end in carbon chains. By opening of double bond that is required to form linear macromolecules and the reaction is proceeded by free radical mechanism. This type of polymerization is known as addition polymerization and examples include are polypropylene and polyethylene.

Thermosetting plastic

Another type of plastic is the thermosetting plastic in which plastic once melt and casted into a certain shape, after solidification it cannot be melted and modified again. All chemical changes, irreversible, are not examples of thermosetting polymers(Ghosh*et al.*,2013). Polyurethanes and phenol–formaldehyde under favorable conditions are formed by step growth polymerization.At each step, H_2O and HCl are released as a by products and allowing the condensation of bi-functional molecules inter molecularly. In thermosetting plastic, monomersconvert themselves into an infusible mass by undergo small chemical changes on heating (Singh and Sharma, 2008).

MICROBIAL DEGRADATION OF PLASTICS

Microorganisms such as bacteria, fungi and actinomycetes degrades both natural and synthetic plastics [Gu*et al*., 2000]. Microbial degradation of plastics is caused by oxidation or hydrolysis using microbial enzymes that leads to chain cleavage of the large compound polymer into small molecular monomer by the metabolic process (Kumar *et al.*, 2013). The microbial species associated with the degrading materials were identified as bacteria, fungi, actinomycetes sp. and saccharomonospora genus (Swift *et al.,* 1989 and Chee*et al.,* 2010). The microorganism's growth is influenced by several factors including the availability of water, redox potential, temperature carbon and energy source [Sand 2003]. Microorganisms secrete both exoenzymes and endoenzymes that are attached to the surface of large molecular substrate and cleave in to smaller segments [Albinas*et al.,* 2003]. Microorganisms recognize polymers as a source of the organic compounds. Degrading enzymes are produced by several microorganisms [Gnanavel*et al.*,2012].

Table 1: Table showing different microbes and their plastic degrading efficiencies

Microorganisms	Types of plastics	Source of the microbes	Degradation Efficiency
Bacillus cereus	polyethylene	Dumpsite soil.	7.2-2.4%
Pseudomonas putida	Natural and synthetic polythylene	Sewage sludge dumpsite	46.2% and 29.1%
Micrococcusluteus	Plastic cup	Forest soil	38%
Aspergillusglaucus	Polythene and plastic	mangrove soil	20.80% and 7.26%
Pseudomonas sp	Polythene carry bags	Plastic dumping sites	12.5%

Bacteria

Microorganisms such as *Bacillus megaterium, Pseudomonas sp., Azotobactersp, Halomonas sp.,*etc are used to degrade plastics (Chee*et al.*, 2010) . In addition, *Bacillus brevis* , *Paenibacillusamyloticus*, *Bacillus pumilus*, *Bordetella*sp, *Pseudomonas aeruginosa* , *Shewanella*spare examples of bioplasticdegrading bacteria[Sekiguchi*et al.*,2010). In addition to these strains, a thermophilic bacterium, Bacillus brevis, with PLA-degrading properties has been isolated from soil. In past years polyethylene degrading bacteria has been reported such as, *Acinetobacterbaumannii*, *Arthrobacterspp*, , *Pseudomonas fluorescens*, , *Micrococcus luteus*, *Flavobacteriumspp*, *Delftiaacidovorans*, *RalstoniasppRhodococcuserythropolis*, *Pseudomonas aeruginosa* (Koutny*et al.*, 2009). The microbial species are associated with the degrading materials were identified as bacterial genus like (*Pseudomonas, Streptococcus, Staphylococcus, Micrococcus*, *Moraxella*(Swift G 1998).

*Ideonellasakaiensis*gramnegaive, and rod-shaped. It does not form spores.The bacterium grows at a pH range of 5.5 to 9.0 (optimally at 7 to 7.5) and a temperature of 15–42 °C (optimally at 30–37 °C). Colonies of *Ideonella.sakaiensis* are colorless, smooth, and circular. Its size varies from 0.6 to 0.8 μm in width and 1.2-1.5 μm in length. The bacterium was shown to grow on PET surfaces in a community with other *Ideonellasakaiensis* cells by adhering to the PET and other cells with thin appendages. These appendages may also function to secrete PET-degrading enzymes onto the PET surface.*Ideonellasakaiensis* , that is able to use PET as its major energy and carbon source. When grown on PET, this strain produces two enzymes capable of hydrolyzing PET and the reaction intermediate, mono (2-hydroxyethyl) terephthalic acid. Both enzymes are required to enzymatically convert PET efficiently into its two environmentally benign monomers, terephthalic acid and ethylene glycol.(Yoshida*et al.*, 2016)

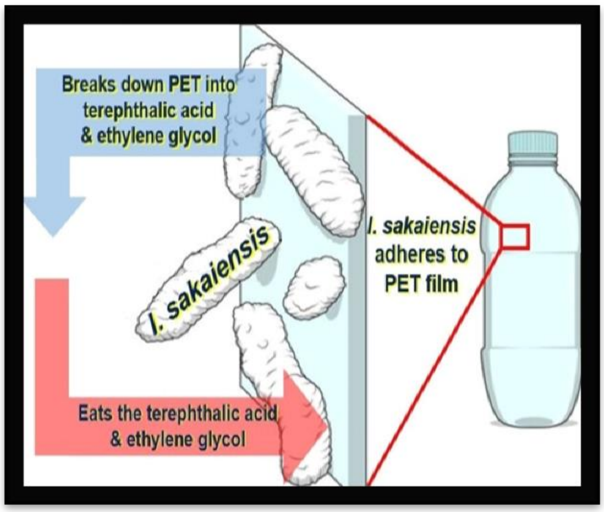

Figure 2 :*Ideonellasakaiensis*-can eat PET plastic

Fungi

The growth of many fungi can also cause small scale swelling and bursting, as the fungi penetrate the polymer solids. In recent years fungal strains have been reported for plastic degradation such as *Aspergillusversicolor*(Pramila*et al.*, 2011)*Aspergillusflavus* ,*Chaetomiumspp* , *Mucorcircinellodies* species etc. The polythene bags were degraded by some fungal species identified such as, *Aspergillusniger,* , *A. flavus, A. candidus and A. glaucus* were the predominant species. Sanchez et al., 2000 has reported that the PCL-degrading fungi, Aspergillussp is effective in biodegradation as plastics. Fungal degradation of the bioplastic have also been performed including *Paecilomyceslilacinus* , *Fusariummoniliforme* , *Aspergillusflavus* , *Thermoascusaurantiacus, Tritirachium album* , *Paecilomycesverrucosum*and Aspergillus sp. On the other hand, polylactic acid (PLA) is subjected to degradation by only two genera of fungi *(Penicilliumroqueforti and Tritirachiumalbum*) (Mogilnitskiiet al., 1987) reported that *Aspergillusniger* had the ability to degrade PVC. PHB and polyesters are degraded by many fungal genera such as Acremonium, *Cladosporium, Debaryomyces, Emericellopsis, Eupenicillium, Fusarium, Mucor, Paecilomyces, Penicillium, Rhodosporidium, and Verticillium. Similarly, PCL is degraded by Aspergillus, Aureobasidium, Chaetomium, Cryptococcus, Fusarium, Rhizopus, Penicillium,* and Thermoascus. PEA is degraded by *Aspergillus, Aureobasidium, Penicillium, Pullularia. Fungus like Alternariasolani, Spicaria sp.,*

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Aspergillusterreus, Aspergillus fumigates, Aspergillusflavus were isolated from soil where plastic have been dumped.

Actinomycetes

PLA-degrading actinomycete can degrade PLA, PCL and PBS such as actinomycetes. Several actinomycetesincluding *Amycolatopsis sp.,Saccharothrix, Kibdelosporangiumaridum,Actinomadurakeratinilytica* (Sukkhum et al., 2011) *Amycolatopsisthailandensis, Streptomyces bangladeshensis, Streptomyces thermoviolaceus subsp. Thermoviolaceus*were reported as bioplastic degraders. *Cryptococcus sp.* and*Pseudozymaantarctica* were reported to be bioplastic-degradings yeasts.

Table 2 :Microorganisms involved in biodegradation of plastics(Grover et al., 2015, Bhardwaj et al., 2012).

Type of plastic	Microorganisms involved in biodegradation
Polyurethane	*Cladosporium sp., Fusariumsolani , Pseudomonas sp,Curvulariasp*
Polyethylene	*Bacillus brevis, Bacillus. circulans, Bacillusamyloliquefaciens, B.acilluscirculans, Bacillus. thuringiensis, fluorescens, Pseudomonas. aeruginosa, Staphylococcus xylosus, S. cohnii, Aspergillusflavus, Aspergillus. niger*
Polyesters	*Aspergillusniger, Aspergillus. flavus,*
Polyvinyl chloride	*Aspergillusniger, Pseudomonas putida*
Poly(3-hydroxybutyrate)	*Pseudomonas sp, Aspergillusfumigatus, Alcaligenesfaecalis, Penicillium*
Polycaprolactone	*Aspergillusflavus, Clostridium botulinum, Fusariumsolani, Bacillus brevis*
Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)	*Streptomyces sp., Clostridium acetobutylicum, C. botulinum*

Enzymes Involved in Plastics Biodegradation

Many microbes produce various kinds of important enzymes in plastic biodegradation. Enzymes such as laccase, lignin peroxidase, manganese peroxidase, lipase, esterase, and amylase are potential catalysts of plastic constituent polymers degradation (Matsumura2005 and Ganesh P *et al.*,2017). Lignin peroxidase, manganese peroxidase, and laccase are the three main lignolytic enzymes (Hofrichter*et al.*, 2001). Lignolytic enzymes are including phenol oxidase or laccase, heme peroxidase consisting of lignin peroxidase, manganese peroxidase, and versatile peroxidase (Dashtban*et al.*, 2010). There are two reactions involved in the polymer biodegradation process, hydrolysis and oxidation. Hydrolysis is the breaking down of polymers catalyzed by hydrolases enzymes, while oxidation is a biodegradation process catalyzed by various oxidoreductase enzymes. Hydrolase enzymes catalyze the hydrolyzing reactions of esters, carbonates, amides, and glycosidic bonds of various hydrolyzed polymers to produce monomers. Meanwhile, oxidoreductase enzymes catalyze oxidizing and reducing reactions of ethylene, carbonate, amide, urethane, and others. The polymers hydrolysis process usually includes a reaction involving three amino acid residues including aspartate, histidine, and serine. Aspartate will interact with the histidine ring to form hydrogen bonds. The histidine ring will interact with serine. Histidine conducts the deprotonating process with serine to form a nucleophilicalkoxide (-O), a group attacking the ester bonds . Then, water attacks the acyl-enzyme complex to form a carboxyl-end and free enzyme that will be further processed by microorganisms (Lucas*et al.*,2008). Bacillus sp. is one of the hydrolases producing bacteria. It produces lipase, CMCase, xylanase, chitinase, and protease that are important in the degradation of plastic polymers (Dang*et al.*, 2018).

Factors Affecting Biodegradation

Biodegradation is influenced by several factors including the chemical structure of the polymers, the phase structure (amorphous or crystalline) of plastic polymers, molecular weight, miscibility of the polymer's constituent. Moreover, the presence of hydrolyzed and oxidized compounds also affect the biodegradation process carried out by microorganisms. Other factors that also affect the rate of the biodegradation process are hydrophobicity or hydrophilicity compatibility between the microorganism surface and the plastic film surface, the polymeric bonds, and the level of plastic surface roughness. Environmental factors also affect the biodegradation process, including temperature and humidity (Bikiaris 2013). Nutrition also has important roles in the biodegradation (Mukherjee, S. and S. Chatterjee. 2014).

Mechanism involved in biodegradation of plastic

A plastics waste processing effective method is needed to balance the increasing uses of plastics every year (Pratomo*et al.,* 2011). Biodegradation is an effective, profitable, and economically valuable plastics waste processing method. The ability of many microorganisms to break down plastic polymers is an advantage that can be used in dealing with problems arising from the increasing accumulation of plastics waste every day. Some microorganisms produce various kinds of enzymes, both intracellular and extracellular, catalyze plastic polymers degradation into safe smaller fragments. The utilization of microbial cells directly to degrade plastic C-C bonds is considered more effective (Wei and Zimmermann 2017). Biodegradation is a specific enzymatic process. The plastic waste biodegradation process occurs through several stages, including biodeterioration, depolymerization, and assimilation. Biodeterioration is a cooperation between several microbes and abiotic factors that breaks down polymers into smaller ones. This process will be continued with depolymerization. Biodeterioration is a process of changing or modifying plastic polymers carried out by some microorganisms on the plastic surface. The changes include chemical, physical, and mechanical changes (Helbling*et al.*, 2006). This process will be accelerated by biofilms formed by microorganisms on the plastic surface. A biofilm is a form of living things community. Microbes attach themselves and colonize the surface of an object to form biofilms assisted by an extracellular compound produced by them. In the form of biofilms, microbial cells attach one to another in a polymer matrix containing polysaccharides and proteins . Extracellular polymeric substances (EPS) produced by microorganisms help them to break down the plastic surface (Bonhomme*et al.*,2003). EPS consists of polysaccharides, proteins, and nucleic acids (33). EPS penetrates the plastic surface porescausing enlargement of the pores. It is enhanced microbes, bacteria, to damage plastic polymers, to form holes, and to encourage the physical deterioration of plastic polymers (Sharma *et al.*,017). Also, the formation of biofilms on plastic surfaces encourages the formation of various kinds of acid compounds changing the pH of plastic polymers leads to chemical plastic deterioration causing changes of the polymer microstructures. These acids are including nitrous acid, nitric acid or sulfuric acid, citric, fumaric, gluconic, glutaric, glyoxylic, oxalic, and oxaloacetic. The plastic surface damages associated with metabolites and extracellular enzymes released by bacteria (Rosario LLD 2017) Depolymerization of the plastic constituents is carried out by depolymerase enzymes. Depolymerization occurs in which microbes secrete catalytic compounds in the form of enzymes and free radicals to form biofilms helping them to break the polymer chains progressively . The results of this reaction can be in the form of oligomers, dimers, and monomers that are simpler than polymers. They will be further processed according to the presence of oxygen molecules in metabolism. Aerobic degradation of those components will produce microbial biomass, CO2, and H2O. While anaerobic degradation will change those components into microbial biomass, CO2, H2O, and CH4 or H2S (Tiwari*et al.*,2018). Extracellular and intracellular depolymerase enzymes secreted by microbes have important roles in plastic waste degradation. During the degradation process, the released enzymes will break down complex polymers into smaller and simpler chains. These decomposed small molecules will be easily dissolved in water then absorbed through microbial semipermeable cell membranes to be used as carbon and energy sources. Assimilation occurs in microbial cytoplasms in which the metabolic process occurs to produce energy, biomass, food reserves, primary and secondary metabolites . After degraded into smaller ones, plastic fragments such as monomers will enter the cells. These components enter the microbial cell metabolism system to undergo a subsequent degradation process to form energy and biomass for microorganisms. Even though monomers have formed, sometimes they do not fully assimilated. They will be released outside of the cells and will be used by other microorganisms that have a suitable assimilation pathway for those monomers . The next process of biodegradation is mineralization. Mineralization is the final metabolic process of plastic waste toxic compounds. This process changes those hazardous compounds into more environmentally safe compounds(Alshehrei2017). Mineralization is a process of converting biodegradable materials or biomass into gases, water, salt, minerals, and other residues. The formed gases include carbon dioxide, methane, and nitrogen components. The mineralization process will be ended when all biodegradable compounds have been consumed by microorganisms and all carbons are converted to carbon dioxide(Kyrikou J and Briassoulis D. 2007)

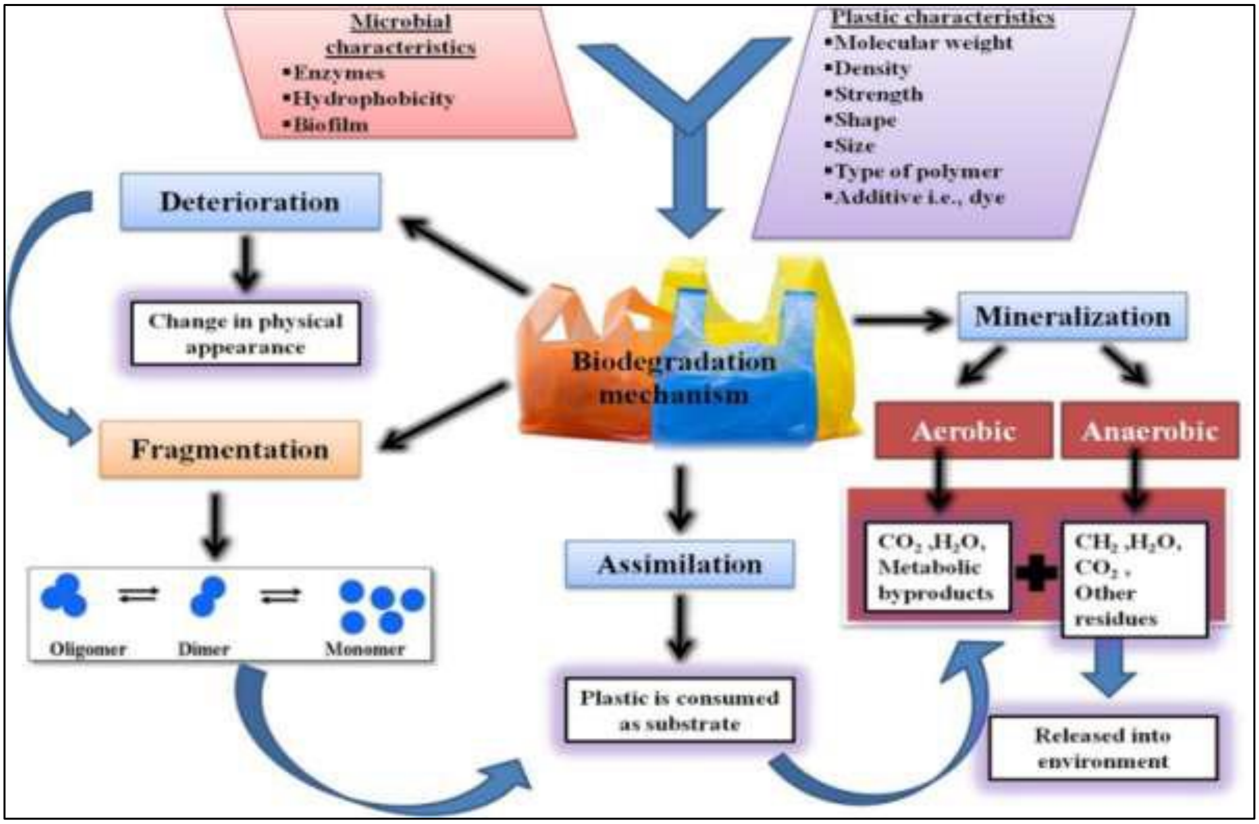

Figure 3: Mechanism of biodegradation of plastic (Shweta et al., 2020).

Disposal of plastic

The current methods for disposing of plastic wastes mainly include landfilling, incineration, and mechanical and chemical recycling (Peng*et al*., 2018). However, the accumulated plastic wastes have occupied a great amount of land. Incineration of plastic wastes can reduce the demand of landfills and recover heat energy, but we also need to reduce the environmental effects of secondary pollutants generated from the incinerating process, such as dioxins, carbon monoxide, nitrogen oxides, and so on. Although mechanical recycling has become the primary recycling method and is applied for reusing thermoplastic wastes, the properties of most recycled materials are significantly compromised after a number of processing cycles, and the resulting commercial values are thus limited. As an alternative, chemical recycling can recover the monomers and other chemicals from plastic wastes, but its success relies on the affordability of processes and the efficiency of catalysts (Rahimi and García, 2017). Nowadays, it is reported that only 9 and 12% of global plastic wastes is recycled and incinerated, while up to 79% is discarded into landfills or the natural environment, indicating that there is a great need for exploring innovative recycling methods to dispose of plastic wastes (Garcia and Robertson, 2017; Geyer *et al*., 2017).

Disadvantages of plastic

Many animals die of waste plastics either by being caught in the waste plastic traps or by swallowing the waste plastic debris to exert ruinous effects on the ecosystem (Usha*et al.*,2011).

Some of the plastic products cause human health problems because they mimic human hormone. Vinyl chloride is classified by the International Agency for the Research on Cancer (IARC) as carcinogenic to humans (Rudel Ruthann*et al.*,2007). It has also shown to be a mammary carcinogen in animals. PVC is used in numerous consumer products, including adhesives, detergents, lubricating oils, solvents, automotive plastics, plastic clothing, personal care products (such as soap, shampoo, deodorants, fragrances, hair spray, nail polish) as well as toys and building materials. Styrene is classified by IARC as possibly carcinogenic to humans and is shown to cause mammary gland tumors in animal studies. It also acts as an endocrine disrupter (Gray *et al.*,2009). BPA has been linked with premature birth, intrauterine growth retardation, preeclampsia and still birth (Benachour and Aris 2009). It has also been noted that prolonged exposure to BPA shows a significant effect on the sex hormones (progesterone) in females (Hao*et al.*, 2011)Burning plastics usually produce some noxious gases like furans and dioxins which are dangerous greenhouse gases and play an important role in ozone layer depletion. In fact, dioxins cause serious problems in the human endocrine hormone activity, thus becoming a major concern for the human health (Pilz*et al.*,2010). Dioxins also cause very serious soil pollution, causing a great concern for scientific community worldwide.

CONCLUSION

Plastics become compulsory materials in our everyday life, as a result plastic wastes are increasing gradually withthe increased use of plastic products. The synthetic nature, durability and stability of plastic makes it difficult to degrade naturally, thus long persistency in ecosystem creates harmful effect on environment. Different aerobic and anaerobic microorganisms present in the soil and water have minimal capability to degrade synthetic plastic partially. In the natural environment, different kinds of microorganisms play an important role in various steps involved in the degradation of plastics. The plastic materials have high-molecular-weight and have hydrophobic surfaces, making them difficult for the microorganisms to form stable biofilms and degrade them into small molecular oligomers. Various plastic-degrading methods are available, but the cheapest, eco-friendly, acceptable method is degradation using microbes.

The microbe releases the extracellular enzymes to degrade the plastic with the complex enzymatic reaction, but further investigation still needed to be carried out. Utilization of molecular techniques to detect specific groups of microorganisms involved in the degradation process will allow a better understanding of the organization of the microbial community involved in the attack of materials. Microorganisms could be genetically engineered so that they can produce upgraded metabolic enzymes to degrade plastic. It is necessary to focus the further researches on more suitable additives, microorganisms and better technique to complete biodegradation in landfill.

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