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Methods for Separation, Recycling and Reuse of Biodegradation Products

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Additional information is available at the end of the chapter

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1. Introduction

Thousands of chemicals and materials with varied properties and functionalities are manufactured and used for commercial and day-to-day applications, whose ultimate fate in the environment may not be known. During their manufacture and use, these substances are often discharged into the environment through different routes in air, water and land. Creation of tremendous quantities of solid waste of all kind and its effective disposal has posed innumerable problems that need technological breakthroughs. Many of these substances degrade slowly and exert toxic effects on plants and animals, thus causing large scale environmental degradation [1, 2]. Pollution by abandoned plastic articles is also a matter of great concern [3]. Industrial wastewaters associated with the manufacture of organic chemicals are voluminous and characteristically have concentrations ranging from a few ppm to a thousands of ppm. Biodegradation of such dissolved pollutants is an area of immense interest to various sectors. Emission of volatile organic compounds (VOCs) from various sources has detrimental effects on quality of air we breathe and on environmental phenomena. Biodegradation, either aerobic or anaerobic, can be an approach to cleave big molecules through a series of steps in to smaller molecules from a mosaic of chemicals and materials and some of them can be valorized as pollution abatement strategy and source of energy through biogas generation [2]. Biogas can be produced from nearly all kind of biomass, among which the primary agricultural sectors and various organic waste streams can be properly tapped as renewable source of energy. Untreated or poorly managed animal manure is a major source of air and water pollution. Nutrient leaching, mainly nitrogen and phosphorous, ammonia evaporation and pathogen contamination are some of the foremost threats [3]. A conservative estimate is provided by Steinfeld et al. [4] that the animal production sector is responsible for 18% of the overall green house gas emissions, measured in CO_2 equivalent and for 37% of the anthropogenic methane, which has 23 times the global warming potential of CO_2. Furthermore, 65% of anthropogenic nitrous oxide and 64% of anthropogenic

ammonia emission originate from the worldwide animal production sector. Biogas production from anaerobic digestion of animal manure and slurries can be harnessed to alleviate greenhouse gas emissions in particularly ammonia and methane [5].

Plastics are bane and benefactor simultaneously. Over 230 million tons of plastic are produced annually. Plastics are used in all walks of life and provide improved insulation, lighter packaging, are found in cars, aeroplanes, railways, phones, computers, medical devices, etc. but appropriate disposal is often not properly addressed. On one hand, plastic waste and disposal is a hotly debated issue globally whereas on the other, it can contribute to reduce the carbon footprint. Many leading European countries recover more than 80% of their used plastics, by adopting an integrated waste and resource management strategy to address each waste stream with the best options [6]. Plastic sorting and separation, recycling, depolymerisation, cracking, and production of fuel are some of the strategies used to abate plastic pollution. Development of biopolymers is pursued vigorously. Biodegradation of plastics by microorganisms and enzymes appears to be the most effective process. When plastics are used as substrates for microorganisms, evaluation of their biodegradability should not only be based on their chemical structure, but also on their physical properties such as melting point, glass transition temperature, crystallinity, storage modulus, etc. [7-11].

This chapter has covered the mechanisms of biodegradation, biodegradation of a variety of industrial chemicals, plastics and other biomass, advances in anaerobic digestion technologies and biogas generation, plastic processing, biopolymer synthesis and degradation. Synthesis of biopolymers is covered. The scope for treating municipal organic solid waste, manure and polymers to generate biogas as a renewable energy option, and also as a pollution abatement strategy is discussed including technological aspects. The synthesis of biohydrogen, bioethanol, biobutanol and other biotransformation leading to valuable chemicals, which also involve breaking down of larger molecules, plastics and biomaterials are not addressed [7,10]. Biorefinery is a concept which is akin to petrorefinery, wherein biomass is converted into useful platform chemicals through extraction, controlled pyrolysis, fermentation, enzyme and chemical catalysis [12].

2. Mechanisms of biodegradation

Cellulose, lignocellulose and lignin are major sources of plant biomass and are polymeric substances; therefore, their recycling is indispensable for the carbon cycle [13]. Each of these polymer is degraded by a variety of microorganisms which produce scores of enzymes that work in tandem. The diversity of cellulosic and lignocellulosic substrates has contributed to the difficulties found in enzymatic treatment. Fungi are the best-known microorganisms capable of degrading these three polymers. Because the substrates are insoluble, both bacterial and fungal degradation occur exo-cellularly, either in association with the outer cell envelope layer or extra-cellularly. Microorganisms have two types of extracellular enzymatic systems, namely, the hydrolytic system, which produces hydrolases and is responsible for cellulose and hemicellulose degradation; and a unique oxidative and extracellular ligninolytic system,

which depolymerizes lignin [13]. The man-made chemicals and materials are comprised of different entities and functional groups which need to be degraded effectively by microorganisms and no single microorganism is obviously capable of doing it [1,14].

Growth and co-metabolism are the two mechanisms of biodegradation. In the case of growth, organic substance is used as the sole source of carbon and energy, which leads to complete degradation (mineralization). Archaebacteria, prokaryotes and eukaryotes (like fungi, algae, yeasts, protozoa) play dominant role in mineralization [7]. On the contrary, co-metabolism encompasses the metabolism of an organic compound in the presence of a growth substrate which is used as the primary carbon and energy source. Thus, biodegradation processes and their rates differ greatly depending on the type of substrate and conditions such as temperature, pH, and aqueous phase solubility, but frequently the major final products of the degradation are carbon dioxide and methane [1,7,10].

## 2.1. Growth-associated degradation of aliphatic compounds

Growth-associated degradation produces CO_2, H_2O, and cell biomass. The cells act as the complex biocatalysts of degradation. Further, cell biomass may be mineralized after exhaustion of the degradable pollutants in a contaminated site. Bulk chemicals like aromatic hydrocarbons such as benzene, toluene, ethylbenzene, xylenes, and naphthalene are widely used as fuels, industrial solvents and feedstock for petrochemical industry. Phenols and chlorophenols are another class of chemicals, employed in a variety of industries. Since all micro-organisms make aromatic compounds such as aromatic amino acids, phenols, or quinines, in large amounts, many microorganisms have evolved catabolic pathways to degrade aromatic compounds. In general, man-made organic chemicals (xenobiotics) can be degraded by microorganisms, when the respective molecules are similar to natural compounds [7,10].

In general, benzene, condensed ring and related compounds are characterized by a higher thermodynamic stability than aliphatic compounds. Benzene oxidation begins with hydroxylation catalyzed by a dioxygenase leading to a diol (Scheme 1) which is then converted to catechol by a dehydrogenase.

Hydroxylation and dehydrogenation are also common in degradation routes of other aromatic hydrocarbons. The introduction of a substituent group onto the benzene ring renders alternative mechanisms possible to attack side chains or to oxidize the aromatic ring. Many aromatic substrates are degraded by a limited number of reactions such as hydroxylation, oxygenolytic ring cleavage, isomerization, and hydrolysis. The inducible nature of the enzymes and their substrate specificity enable bacteria such as *pseudomonads* and *rhodococci* with a high degradation activity, to acclimatize their metabolism to the effective utilization of substrate mixtures in polluted soils and also to grow at a high rate [10,15].

## 2.2. Co-metabolic degradation of organo-pollutants

Co-metabolism is a common phenomenon of microbial activities and the basis of biotransformation used in biotechnology to convert molecules in to useful modified forms. Microorganisms growing on a particular substrate also oxidize a second substrate. The co-substrate is not
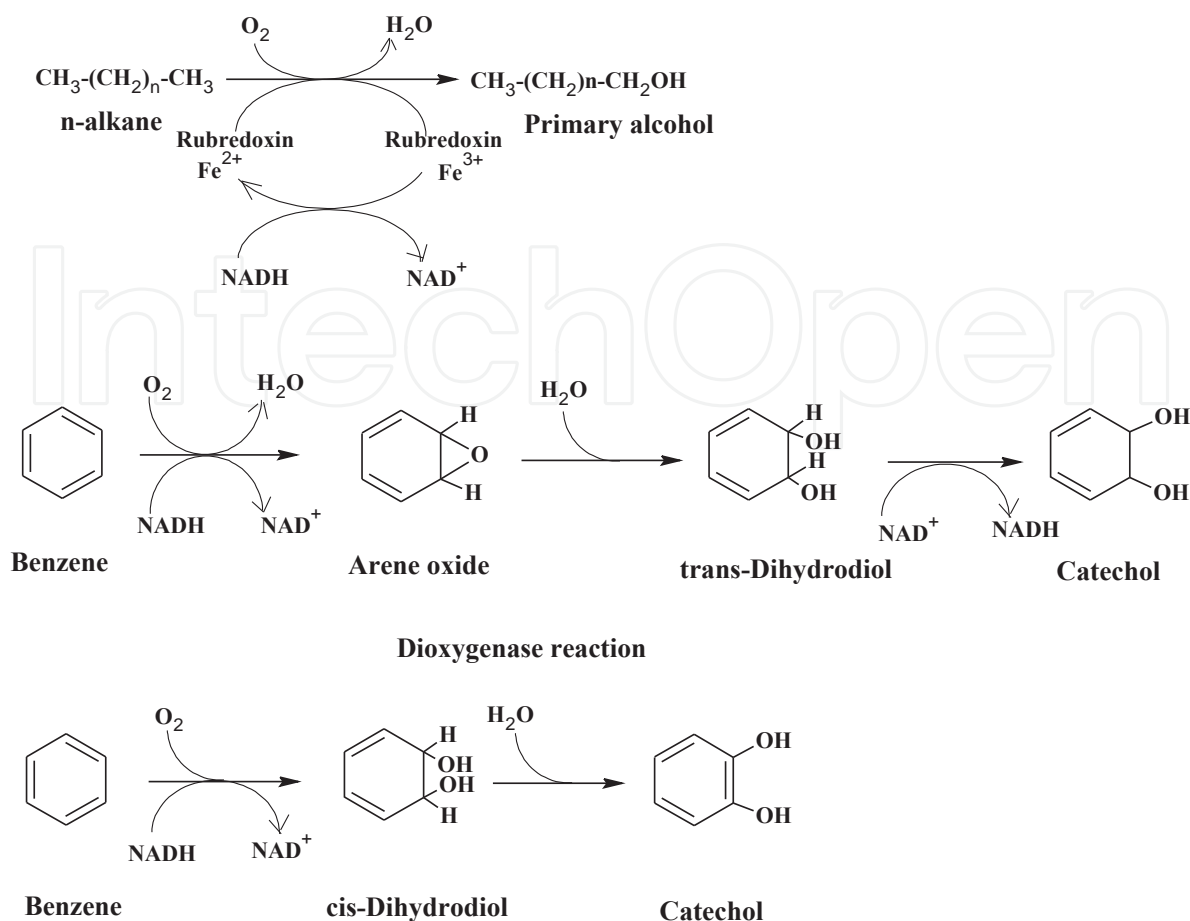
Scheme 1. Monooxygenase and dioxygenase reactions: In this mechanism, monooxygenase initially incorporates one O atom from O_2 into the xenobiotic substrate whereas the other is reduced to H_2O. On the contrary, dioxygenase incorporates both atoms into the substrate [15].

incorporated, but the product may be available as substrate for other organisms of a mixed culture. The rudiments of co-metabolic transformation are the enzymes of the growing cells and the synthesis of cofactors necessary for enzymatic reactions; for instance, of hydrogen donors (reducing equivalents, NADH) for oxygenases. Several aromatic substrates can be converted enzymatically to natural intermediates of degradation such as catechol and protecatechuate (Scheme 2) [15].

Co-metabolism of chloroaromatics is a general activity of bacteria in mixtures of industrial pollutants. The co-metabolic transformation of 2-chlorophenol leads to dead-end metabolites such as 3-chlorocatechol, which may be auto-oxidized or polymerized in soil to humic-like structures. Irreversible binding of dead end metabolites may fulfill the function of detoxification. The accumulation of dead-end products within microbes under selection pressure is the source for the evolution of new catabolic traits. Thus, recalcitrance of organic pollutants increases with increasing halogenation. Substitution of halogen as well as nitro and sulfo groups at the aromatic ring is accomplished by an increasing electrophilicity of the molecule. These compounds resist the electrophilic attack by oxygenases of aerobic bacteria. Compounds that persist under oxic condition are polychlorinated biphenyls (PCBs), chlorinated dioxins
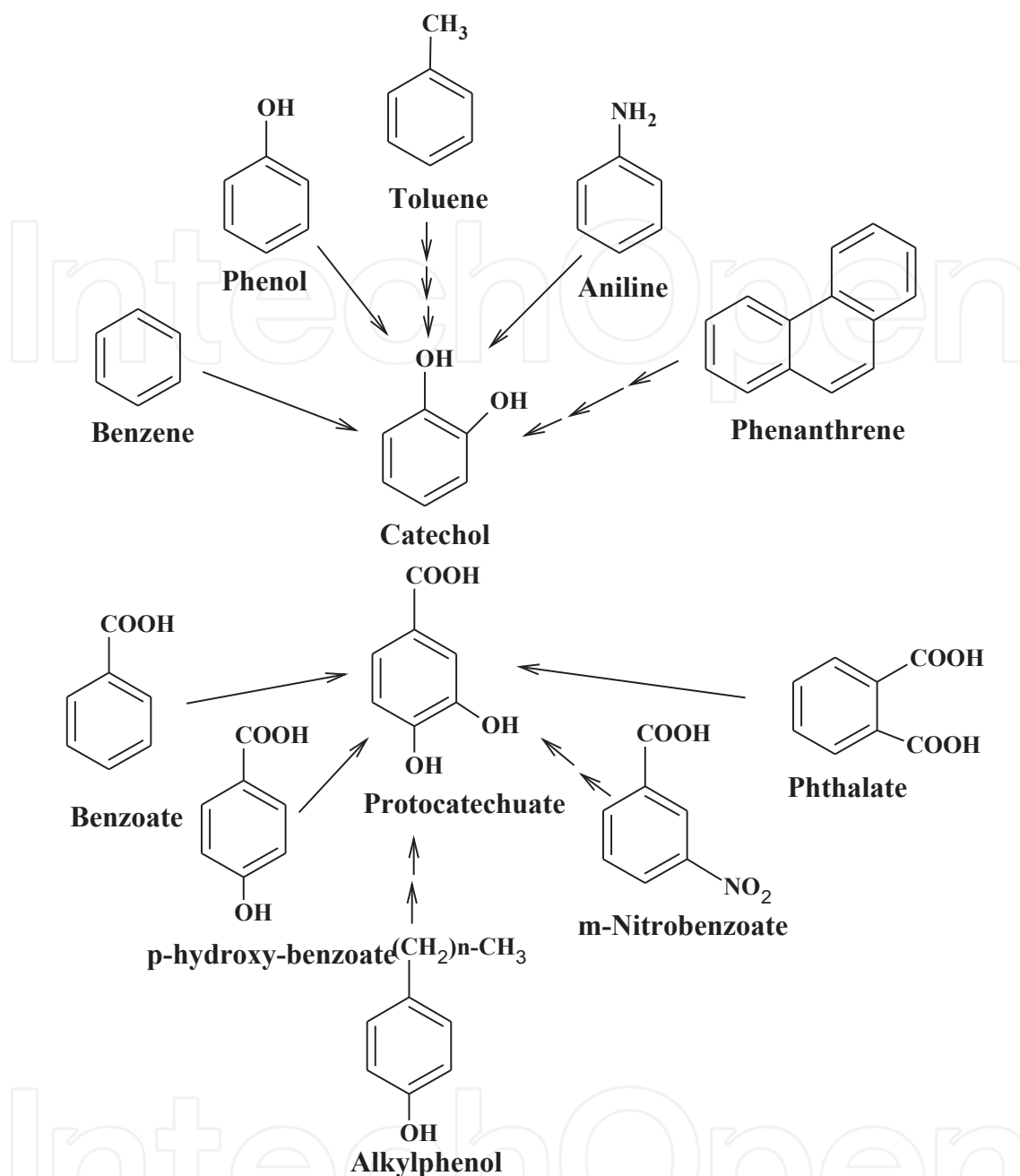
Scheme 2. Degradation of aromatic natural and xenobiotic compounds into two central intermediates, catechol and protocatechuate [15].

and some pesticides like DDT. To overcome the relatively high persistence of halogenated xenobiotics, reductive attack of anaerobic bacteria is of great value. Reductive dehalogenation achieved by anaerobic bacteria is either a gratuitous reaction or a new type of anaerobic respiration. The process reduces the degree of chlorination and, therefore, makes the product more accessible to mineralization by aerobic bacteria [7,15].

Reductive dehalogenation which is the first step of degradation of PCBs requires anaerobic conditions wherein organic substrates act as electron donors. PCBs accept electrons to allow

the anaerobic bacteria to transfer electrons to these compounds. Anaerobic bacteria capable of catalyzing reductive dehalogenation seem to be relatively omnipresent in nature. Most dechlorinating cultures are a mixed consortia. Anaerobic dechlorination is always incomplete and the products are di- and monochlorinated biphenyls. These products can be metabolized further by aerobic microorganisms [2,7,15].

The rates of biodegradability of particular substrate is mainly related to accessibility of the substrate for enzymes and can be enhanced by several means as reviewed by van Lier et al. [16] such as (a) mechanical methods: the disintegration and grinding of solid particles present in sludge: releases cell compounds and creates new surface where biodegradation take place, (b) ultrasonic disintegration, (c) chemical methods: the destruction of complex organic com-pounds by means of strong, mineral acids or alkalis, (d) thermal pretreatment: thermal hydrolysis is able to split and decompose a significant part of the sludge solid fraction into soluble and less complex molecules, (e) enzymatic and microbial pre-treatment: a very promising method for the future for some specific substrates (e.g. cellulose, lignin etc.),(f) stimulation of anaerobic micro-organisms: some organic compounds (e.g. amino acids, cofactors, cell content) act as a stimulating agent in bacteria growth and methane production. Most of the above methods occur at the pre-methanation step and result in a better supply of methanogenic bacteria by suitable substrates.

3. Aerobic biodegradation

Many microorganisms grow under aerobic conditions. The so-called cellular respiration process (CSP) begins with aerobes which employ oxygen to oxidize substrates such as sugars and fats to derive energy. Before the onset of CSP, glucose molecules are degraded into smaller molecules in the cytoplasm of the aerobes. The smaller molecules then enter a mitochondrion, where aerobic respiration takes place. Oxygen is used to break down small entities into water and carbon dioxide, accompanied by release of energy. Aerobic degradation does not produce foul gases, unlike anaerobic process. The aerobic process leads to a more complete digestion of solid waste reducing build-up by more than 50% in most cases [1, 2, 7]. The major enzymatic reactions of aerobic biodegradation are oxidations catalyzed by oxygenases and peroxidases. Oxygenases are oxido-reductases that incorporate oxygen into the substrate as given in Scheme 1. Degradative organisms need oxygen at two metabolic sites, namely, at the initial attack of the substrate and at the end of the respiratory chain. Higher fungi possess a unique oxidative system for the degradation of lignin based on extracellular ligninolytic peroxidases and laccases [13]. This enzymatic system is important for the co-metabolic degradation of persistent organic pollutants. The predominant bacteria of polluted soils belong to a spectrum of genera and species (Table 1) [15].

The most important classes of organic pollutants in the environment are mineral oil constitu-ents and halogenated petrochemicals, for the biodegradation of which the capacities of aerobic microorganisms are of great consequence. The most rapid and complete degradation of the majority of pollutants is brought about under aerobic conditions and these include petroleum

hydrocarbons, chlorinated aliphatics, benzene, toluene, phenol, naphthalene, fluorine, pyrene, chloroanilines, pentachlorophenol and dichlorobenzenes. Many cultures of bacteria grow on these chemicals and are capable of producing enzymes which degrade them into non-toxic species. [7,15].

Gram negative bacteria	Gram positive bacteria
Pseudomonas species	*Nocardia* species
Xanthomonas species	*Mycobacteria* species
Alcaligenes species	*Corynebacterium* species
Flavobacterium species	*Arthobacter* species
Cytophaga group	*Bacillus* species

Table 1. Predominant bacteria in soil samples polluted with aliphatic and aromatic hydrocarbons, polycyclic aromatic hydrocarbons, and chlorinated compounds [15]

There are several essential attributes of aerobic microorganisms degrading organic pollutants amongst which metalobic processes top the list. The chemicals must be accessible to the degrading organisms. For example, hydrocarbons are immiscible in water and their degradation requires the production of biosurfactants in order to have effective biodegradation [14]. The initial intracellular attack of organic pollutants is an oxidative process and therefore, the activation and incorporation of oxygen is the main enzymatic reaction catalyzed by oxygenases and peroxidases. Peripheral degradation pathways convert organic pollutants step by step into intermediates of the central intermediary metabolism, such as the tricarboxylic acid cycle. Biosynthesis of cell biomass from the central precursor metabolites (acetyl-CoA, succinate, pyruvate) is required [14,15]. Sugars needed for various biosyntheses and growth must be synthesized by gluconeogenesis. The predominant degraders of organo-pollutants in the oxic zone of contaminated areas are chemo-organotropic species that are able to use a large number of natural and xenobiotic compounds as carbon sources and electron donors for the generation of energy. Although many bacteria are able to metabolize organic pollutants, a single bacterium does not possess the enzymatic capability to degrade all or even most of the organic pollutants from a heterogeneous mixture originating from particular industries. Thus, mixed microbial communities have the most powerful biodegradative potential. The genetic information of more than one organism is necessary to develop a system which could be used on industrial scale to degrade the complex mixtures of organic compounds present in contaminated areas. The genetic potential and certain environmental factors such as temperature, pH, and available nitrogen and phosphorus sources govern the rate and the extent of degradation [14].

4. Anaerobic biodegradation

Among biological treatments, anaerobic digestion is frequently the most economical process, due to the high energy recovery linked to the process and its limited environmental impact.

Anaerobic biodegradation results when the anaerobic microbes are predominant over the aerobic microbes. Here oxygen does not serve as the final electron acceptor or reactant. Manganese and iron ions, and substances like sulfur, sulfate, nitrate, carbon dioxide, some organic intermediates and pollutants are reduced by electrons originating from oxidation of organic compounds [7]. The common example of anaerobic process is the biodegradable waste in landfill. Paper and other materials degrade more slowly over longer periods of time. Biogas, coming from anaerobic digestion, mainly consists of methane and can be collected efficiently and used for eco-friendly power generation as has been demonstrated on larger scale [3, 16]. Anaerobic digestion is widely used, as part of an integrated waste management system, to treat wastewater sludge and biodegradable waste because it provides volume and mass reduction of the input material. It reduces the emission of landfill gas into the atmosphere [17-20]. Anaerobic digestion is a renewable energy source because the process produces methane and CO_2-rich biogas suitable for energy production helping to replace fossil fuel requirement. Also, the nutrient-rich solids left after digestion can be used as fertilizer [16,21].

There are four major biological and chemical steps of anaerobic digestion: hydrolysis, acidogenesis, acetogenesis, and methanogenesis [17,18]. The mechanism commences with bacterial hydrolysis of the organic matter to break down insoluble organic polymers such as carbohydrates and make them available for other bacteria. Acetogenic bacteria convert the sugars and amino acids into carbon dioxide, hydrogen, ammonia, and organic acid. Methanogens then ultimately transform these products in to methane and carbon dioxide [19].

4.1. Advances in anaerobic digestion technologies

Thermophilic anaerobic digestion of manure [20] and assessment of biodegradability of macropollutants [21] have demonstrated the prowess of anaerobic digestion which is now a general method used to stabilize municipal wastewater treatment residuals [22,23]. The so-called phased or staged anaerobic digestion is a recent technology for digestion facilities which include four different configurations of reactors: staged mesophilic digestion, temperature-phased digestion, acid/gas phased digestion, and staged thermophilic digestion [24]. Phased or staged configurations are multiple reactor digestion systems. Phased anaerobic digestion is defined as a digestion system having two or more tanks, each with exclusive operating conditions that support unique biomass populations, which may be acid-forming, methane-forming, thermophilic, or mesophilic organism populations. Effective digestion is achieved by manipulating operational parameters such as solids retention time (SRT) and temperature. Temperature phased digestion system is found better than the other systems during each study phase by having higher volatile solids reduction (VSR), higher methane production, and lower residual biological activity [24,25].

On industrial scale, anaerobic digestion of solid waste is considered as a mature technology [16,26]. Around 60% of the plants are reported in Europe to operate at the mesophilic range (40% thermophilic) with continued increase in capacity over the years in most European countries. Yields from the biomethanization process are very much dependent on operating conditions and the kind of substrate used. Digestion of grey wastes or residual refuse after source separation, has caught attention of industry and some of the solutions considered are

landfilling or incineration [23]. However, anaerobic digestion is a better option since it gives number of advantages such as greater flexibility, the possibility of additional material recovery (up to 25%), and a more efficient and ecological energy recovery. In this case the low-calorific organic fraction is digested, the high-calorific fraction is treated thermally and the non-energy fractions can be recovered and reused. It is predicted that this residual refuse will be treated by anaerobic digestion [16, 23].

A very high growth potential is expected for the anaerobic digestion of organic fraction of municipal solid waste (OFMSW). Around 50% of MSW is landfilled, with a content of around 30% of organic fraction (without considering paper and cardboard). The growth potential for this technology is very important to reduce greenhouse gases emission as agreed at the Kyoto Summit [23]. Further, the consolidation of anaerobic digestion as a mainstream technology for the OFMSW should occur since the digested residue can be considered quite stable organic matter with a very slow turnover of several decades given adequate soil conditions. Thus, the natural imbalance in CO_2 can be adjusted by restoring or creating organic rich soil. The removal of CO_2 constitutes an extra benefit that would place anaerobic digestion as one of the most relevant technologies in this field. The degradation of chlorinated compounds need to be examined in greater depth, as anaerobic treatment offers high potential in this area [28].

Several novel reactors with high mass transfer rates, such as fluidized bed reactors, expanded granular sludge bed (EGSB) reactors [29-32], and membrane bioreactors [33] with different configurations have been used, in which hydraulic retention times (HRT) are uncoupled from the solids retention time (SRT) to make anaerobic technology economical alternative for conventional wastewater treatment systems. The upflow anaerobic sludge blanket (UASB) reactors [30] and/or related systems are mostly applied, wherein spontaneous formation of granular conglomerates of the anaerobic organisms occurs, leading to anaerobic sludge with an extremely low sludge volume index and optimal settling properties [21]. Besides, several large scale biogas plants have been built which combine waste from agriculture, industry and households and produce both biogas and a liquid fertiliser which is re-circulated back on agri-land. The combination of anaerobic digestion with other biological or physico-chemical processes has led to the development of optimised processes for the combined removal of organic matter, sulphur and nutrients. In conjunction with anaerobic digestion which removes mainly carbon, other processes are used to remove nitrogen and phosphorus (with oxic phase), which mainly use micro-organisms and also physico-chemical processes. For the treatment of municipal wastewater, the ANANOX process [34] takes advantage of sulphate reduction to sulphide to provide an electron donor for the denitrification process [35-37]. The integration of the nitrogen cycle in anaerobic digestion could be maximised with the application of the ANAMMOX process that makes use of particular micro-organisms that are able to oxidise ammonium to N_2 gas with nitrite as electron acceptor [38,39].

5. Biodegradation of industrial organic pollutants

Knowledge of fate of chemicals discharged in the environment, the life cycle analysis and the mechanisms by which they degrade are of great importance in designing biodegradation

systems since many of the industrial chemicals are toxic, recalcitrant and bioaccumulating in organisms [40-42].

5.1. Volatile Organic Compounds (VOCs)

There are two classes of VOCs that are responsible for a large number of land and groundwater contamination: (i) petroleum hydrocarbons (PHCs) such as gasoline, diesel, and jet fuel, and (ii) chlorinated hydrocarbon (CHC) solvents such as the dry cleaning agents such as tetra-chloroethylene, perchloroethylene (PCE) and the degreasing solvents such as trichloroethy-lene (TCE), 1,1,1-trichloroethane (TCA), and PCE.

PHCs biodegrade readily under aerobic medium, whereas CHCs characteristically biodegrade much more slowly and under anaerobic conditions [43]. Because PHC biodegradation is relatively rapid when oxygen is present, aerobic biodegradation can usually limit the concen-tration and subsurface migration of petroleum vapours in unsaturated soils. Further, CHC biodegradation can produce toxic moieties, such as dichloroethylene and vinyl chloride, while petroleum degradation usually produces carbon dioxide, water, and sometimes methane or other simple hydrocarbons. A second primary difference is density of pollutant. PHC liquids are lighter than water and immiscible. PHCs can float on the groundwater surface (water table), whereas chlorinated solvents being heavier than water sink through the groundwater column to the bottom of the aquifer. These major differences in biodegradability and density lead to very different subsurface behaviour that often reduces the potential for human exposure.

5.1.1. Petroleum Hydrocarbons (PHCs)

It is known that microorganisms capable of aerobically degrading PHCs are present in nearly all subsurface soil environments [44-49]. Effective aerobic biodegradation of PHCs hinges on the soil having adequate oxygen and water content to provide a habitat for sufficient popula-tions of active microorganisms. If oxygen is present, these organisms will generally consume available PHCs. Furthermore, aerobic biodegradation of petroleum compounds can occur relatively quickly, with degradation half lives as short as hours or days under some conditions [50]. Some petroleum compounds can also biodegrade under anaerobic conditions; however, above the water table, where oxygen is usually available in the soil zone, this process is insignificant and often much slower than aerobic biodegradation. Aerobic biodegradation consumes oxygen and generates carbon dioxide and water. This leads to a characteristic vertical concentration profile in the unsaturated zone in which oxygen concentrations decrease with depth and VOCs including PHCs and methane from anaerobic biodegradation and carbon dioxide concentrations increase with depth [51,52].

5.1.2. Chlorinated Hydrocarbon (CHC) Solvents

Chlorinated solvents such as tetrachloroethylene (TCE), 1,1,2,2-tetrachloroethane, carbon tetrachloride, and chloroform are released as waste products by spills, land-filling, and discharge to sewers during manufacture and their use as solvents in a variety of cleaning processes or as vehicles for solid slurries. TCE is a major pollutant of the industry. It is

biodegraded under anaerobic conditions through hydrogenolysis that sequentially produces isomers of 1,2-dichloroethylene (1,2-DCE), vinyl chloride (VC), and ethylene. Some labs have also reported ethane [53,54], methane [55], and carbon dioxide [56] as degradation products.

In addition to anaerobic degradation through reductive dechlorination (hydrogenolysis), TCE and other chlorinated VOCs can be susceptible to co-metabolic oxidation by aerobic microorganisms that have oxygenases with broad substrate specificity. Methanotrophs are microorganisms that primarily oxidize methane for energy and growth using methane monooxygenase (MMO) enzymes and are a group of aerobic bacteria transform TCE through co-metabolic oxidation [57-59]. In contrast to reductive dechlorination, where the degradation rate generally decreases as the degree of chlorination of the aliphatic hydrocarbon decreases, the less-chlorinated VOCs such as 1,2-DCE and VC are more straightforwardly and quickly degraded through aerobic oxidation reactions than the higher chlorinated compounds such as TCE [60]. Methane-oxidizing bacteria are known to convert TCE to its epoxide, which then breaks down immediately in water to form dichloroacetic acid, glyoxylic acid, or one-carbon compounds such as formate or CO. The two carbon acids accumulate in the water phase, while formate and CO are further oxidized by methanotrophic bacteria to CO_2. Hence, coupling of anaerobic and aerobic degradation processes has been recommended as the best possible bioremediation method for chlorinated VOCs such as TCE [60-62].

5.2. Quinoline

Quinoline occurs commonly in coal tar, oil shale, and petroleum, and is used as an intermediate and solvent in many industries [63,64]. Due to its toxicity and repulsive odor, quinoline-containing waste is detrimental to human health and environmental quality. The study of quinoline- degrading bacteria not only helps to reveal the metabolic mechanism of quinoline, but also benefits the bio-treatment of quinoline-containing wastewater. Although different genera of bacteria may produce different intermediates, almost all of them transform quinoline into 2-hydroxyquinoline in the first step [63, 65]. A quinoline-degrading bacteria strain, *Pseudomonas* sp. BW003, was isolated from the activated sludge in a coking wastewater treatment plant. *Pseudomonas* strains degrade quinoline via the 2-hydroxyquinoline and 2,8-hydroquinoline pathway, and then transform 2,8-hydroquinoline into 8-hydrocumarin, which is then transformed into 2,3-dihydroxyphenylpropionic acid, and finally to CO_2 and H_2O (Scheme 3) [66-69]. Quinoline-N is transformed into ammonia-N, as reported in few genera of bacteria. Thus, quinoline pollution can be eliminated by applying such degrading bacteria in the treatment with bio-augmentation [70-72].
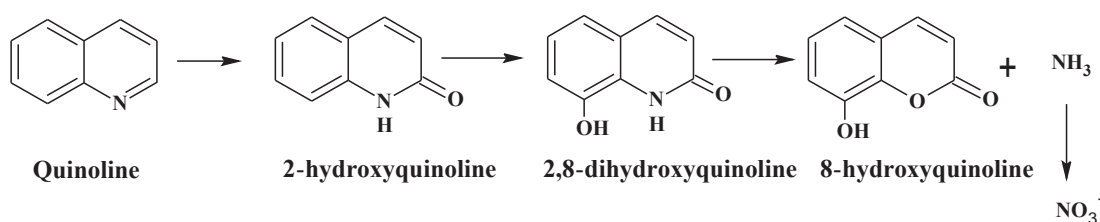
Scheme 3. Degradation products of quinoline [63]

5.3. Phenols

Phenols are harmful to organisms at low concentrations and classified as hazardous pollutants because of their potential to harm human health. They exist in different concentrations in wastewaters originated from coking, synthetic rubber, plastics, paper, oil, gasoline, etc. Biological treatment, activated carbon adsorption and solvent extraction are some of the most widely used methods for removing phenol and family compounds from wastewaters [73-76]. Biological treatment is economical, practical, promising and versatile approach for it leads to complete mineralization of phenol. Many aerobic bacteria are capable of using phenol as the sole source of carbon and energy [77]. In recent years, the strain of *Pseudomonas putida* has been the most widely used to degrade phenol. Under aerobic conditions, phenol may be converted by the bacterial biomass to CO_2; other intermediates such as benzoate, catechol, *cis*-cis-muconate, β-ketoadipate, succinate and acetate are formed during the biodegradation process [77, 78]. *p*-Nitrophenol (PNP) is one of the most widely used nitrophenolic compounds in industry and finds important applications in agriculture, polymers, pigment and pharmaceutical industries. However, PNP is highly toxic for both the environment and humans and its efficient removal from the environment is required. Hydroquinone (HQ), 4-nitrocatechol (4-NC) and 1,2,4-benzenetriol (1,2,4-BT) are the metabolic intermediates of the PNP biodegradation [80,81].

Chlorinated phenols are common and encountered even in relatively pristine environments [82,83]. These compounds are formed during the bleaching of pulp with chlorine [82-84]. As the pulp accounts only for about 40-45% of the original weight of the wood, these effluents are heavily loaded with organics [85]. Chlorophenols are also used as fungicides and may be formed from hydrolysis of chlorinated phenoxyacetic acid herbicides. Chlorophenols, part of the *adsorbable organic halides* (AOX), are present in bleaching effluents at concentrations ranging from 0.1 to 2.6 ppm [86]. Aqueous effluents from industrial operations such as polymeric resin production, oil refining and coking plants also contain chlorophenolic compounds. Pentachlorophenol (PCP) is the second most heavily used pesticide in the US. As compared to phenol, chlorophenolic compounds are more persistent in the environment. Toxicity and bioaccumulative potential of chlorophenols increases with the degree of chlorination and with chlorophenol lipophilicity. Haloaromatic compounds are degraded via the formation of halocatechols as intermediates which are subsequently cleaved by dioxygenases, by the mechanism delineated earlier. Dehalogenation then occurs by the elimination of the hydrogen halide, with subsequent double bond formation on the aliphatic intermediate [87]. In anaerobic environments, the biodegradation of chlorinated aromatics takes place through reductive dehalogenation leading to the formation of less toxic and more biodegradable compounds. Reductive dechlorination of 2,4-dichlorophenol is followed by carboxylation, ring fission and acetogenesis, and methanogenesis which finally led to the complete mineralization of 2,4-DCP, which is also biodegraded to 4-chlorophenol in anaerobic sediments. Similarly, biodegradation of PCP under anaerobic conditions occurs through reductive dechlorination [88].

5.4. Fluoro benzenes

Toluene degrading enzymes can transform many 3-fluoro-substituted benzenes to the corresponding 2,3-catechols with the concomitant release of inorganic fluoride. The substrates that induce 2,3-dioxygenase are 3-fluorotoluene, 3-fluorotrifluorotoluene, 3-flurohalobenzene,

3-fluoronisole, and 3-fluorobenzonitrile. While 3-fluorotoluene and 3-fluoronisole produce only deflorinated catechols, other substrates led to catechol products both with and without the toluene substituent [89].

5.5. Polycyclic Aromatic Hydrocarbons (PCAHs)

PCAHs are toxic, mutagenic and resist biodegradation [90]. Many strategies have been developed to treat them, including volatilization, photooxidation, chemical oxidation, bioaccumulation, and adsorption on soil particles [91]. Soil clean-up may be achieved using different remediation technologies, among which bioremediation is an effective and low-cost alternative that has garnered widespread use [92]. Two processes have been found to increase the activity of microorganisms during bioremediation: bio-stimulation and bio-augmentation. Bio-stimulation involves the addition of nutrients and/or a terminal electron acceptor to increase the meager activity of indigenous microbial populations. Bio-augmentation involves the addition of external microbial strains (indigenous or exogenous) which have the ability to degrade the desired toxic compounds [93]. The added specific PCAHs degrading strain, which has a competitive capacity to become dominant species with indigenous microbial strains or grow simultaneously with indigenous microbial strains, may greatly enhance the rate of PCAHs biodegradation [94,95]. The ability to degrade PCAHs depends on the complexity of their structure and the extent of enzymatic adaptation by bacteria. In general PCAHs with 2 or 3 aromatic rings are readily degraded, but those with 4 or more are usually recalcitrant and genotoxic. Such examples of PCAHs are acenaphthene, acenaphthylene, anthracene, naphthalene, fluorene, phenanthrene, chrysene, pyrene, etc. The major metabolites are 4-phenanthroic acid and 4-hydroxyperinapthenone. Cinnamic and phthalic acids are ring fission products [96].

Naphthalene is carcinogenic and persistent organic pollutant [97]. Bacteria such as *Pseudomonas putida*, *Rhodococcus opacus*, *Mycobacterium* sp., *Nocardia otitidiscaviarum*, and *Bacillus pumilus* are known to biodegrade naphthalene [98-102]. Some metabolites of naphthalene, such as salicylic acid, 1-naphthol and *o*-phthalic acid could be degraded and support cell growth (Scheme 4). Phenanthrene was used as a model compound for PCAH degradation which shows 1-hydroxy 2-naphthoic acid (1H2NA) as intermediate biodegradation product [103].

5.6. Plasticizers

Plasticizers are polymeric additives, used to impart flexibility to polymer materials. The biodegradation of some plasticizers can lead to the formation of metabolites with increased persistence and toxicity relative to the original compounds [104-106]. Use of plasticizers has grown considerably, both with respect to product variety and production volume [107]. Phthalates are the most widely used plasticizers. Presence of phthalates and their metabolites in rats, mice, human plasma and liver are related to adverse health effects such as endocrine disruption and peroxisome proliferation [108,109]. The high production volumes of phthalates and their incomplete biodegradation have led to the presence of these compounds and a number of toxic and stable metabolites in surface waters, groundwater, air, soil and tissue of living organisms [104, 110-113]. Such findings have led to stricter environmental regulations
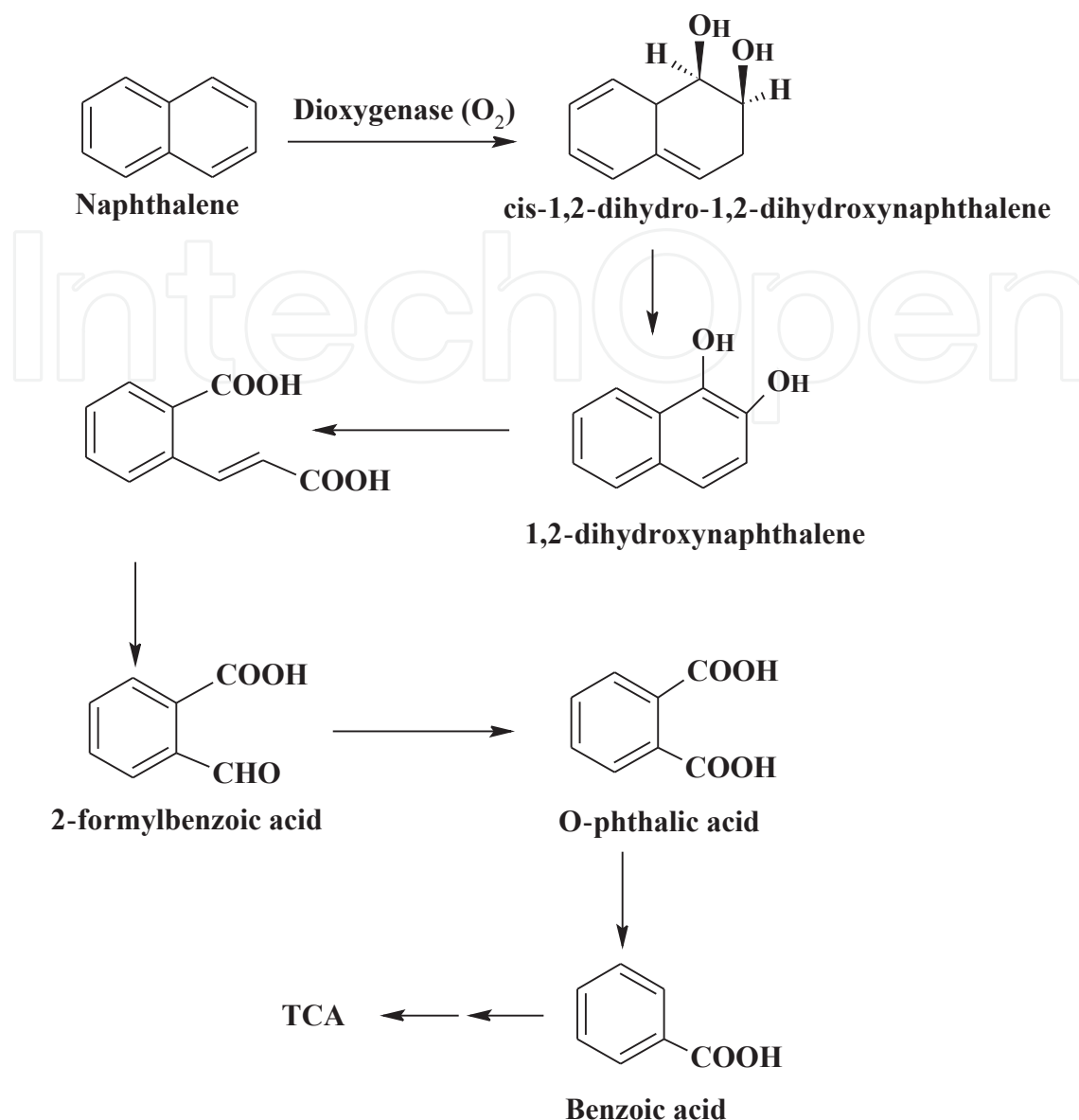
Scheme 4. Proposed pathway for the degradation of naphthalene [103]

and consequently have broadened the criteria used to evaluate plasticizers. Consequently, dibenzoates have been approved by the European Chemical Agency as alternatives to phthalates [114]. However, the degradation of dipropylene glycol dibenzoate (D(PG)DB) and diethylene glycol dibenzoate (D(EG)DB) by common soil microorganisms such as *Rhodotorula rubra* and *Rhodococcus rhodochrous* can lead to the formation and accumulation of monobenzoate metabolites [115,116] that exhibit high acute toxicity [115]. Other compounds including 1,5-pentanediol and 1,6- hexanediol dibenzoates were reported to produce less stable metabolites and have also been tested as potential alternatives to commercial dibenzoate plasticizers [116-118]. Scheme 5 shows the biodegradation products of dibenzoates by *R. Rhodochrous*, which include 2-[2-(benzoyloxy)propoxy] propanoic acid, 1,3-propanediol monobenzoate and 3-(benzoyloxy) propanoic acid [119].

5.7. Plastics

Over the years, plastics have brought economic, environmental and social advantages. Today's material world uses tremendous quantities of plastics of all hue and origins. However, their wide spread use has also increased plastic waste, which brings its own economic, environmental and social problems. The redesign of plastic products, whether individual polymer or product structure, could help alleviate some of the problems associated with plastic waste. Redesign could have an impact at all levels of the hierarchy established by the European Waste Framework Directive: prevention, re-use, recycle, recovery and disposal [120].
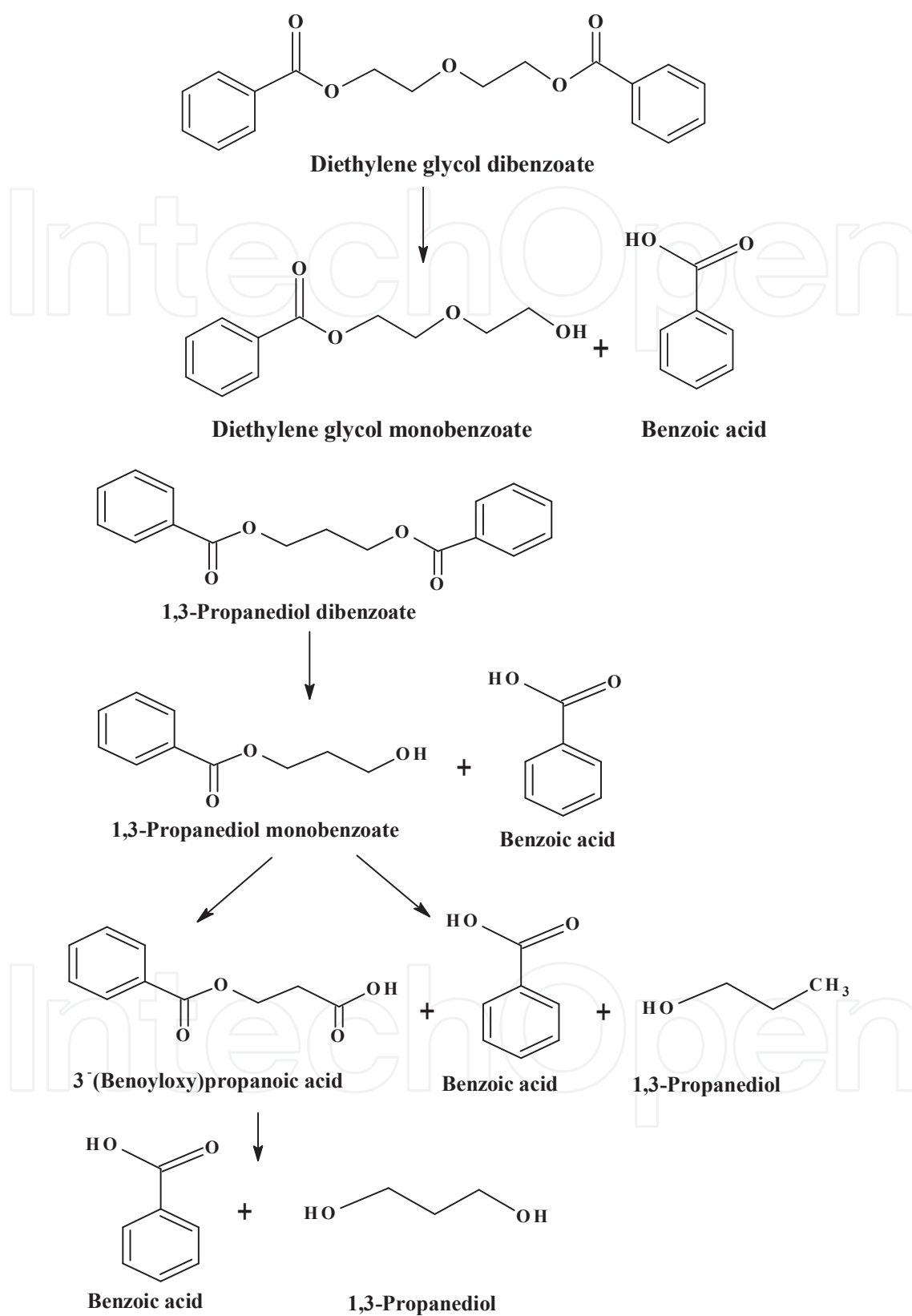
Polyethylene, polypropylene and polystyrene, and water-soluble polymers, such as polyacrylamide, polyvinyl alcohol and polyacrylic acid are bulk polymers used in a variety of industries and products. Some of the plastics are not biodegradable and deleterious to the environment due to their accumulation. Plastics can be disposed of by incineration or recycling, but incineration is very difficult, dangerous and expensive whereas recycling is a long process and not very efficient. Some plastics still cannot be recycled or incinerated due to pigments, coatings and other additives during manufacture of materials. Making biodegradable and ecofriendly plastics will avoid accumulation, recycling and incineration [121].

5.7.1. Polyvinyl alcohol

Polyvinyl alcohol (PVA) is water-soluble but also has thermoplasticity. In addition to its use as a water-soluble polymer, for instance, as a substituent for starch in industrial processes, it can also be molded in various shapes, such as containers and films. PVA can therefore be used to make water-soluble and biodegradable carriers, which may be useful in the manufacture of delivery systems for chemicals such as fertilizers, pesticides, and herbicides. Among the vinyl polymers produced industrially, PVA is the only one known to be mineralized by microorganisms [122]. Extensive use of PVA, in textile and paper industries generates considerable amount of contaminated wastewaters [121]. In aqueous solution, the biodegradation mechanism of PVA involves the random endocleavage of the polymer chains. The initial step is associated with the specific oxidation of methane-carbon bearing the hydroxyl group, as mediated by oxidase and dehydrogenase type enzymes, to give β-hydroxyketone as well as 1,3-diketone moieties. The latter groups are able to facilitate the carbon-carbon bond cleavage as promoted by specific β-diketone hydrolase, leading to the formation of carboxylic and methyl ketone end groups [123,124]. Most of the PVA-degrading microorganisms are aerobic bacteria belonging to *Pseudomonas*, *Alcaligenes*, and *Bacillus* genus. A very moderate PVA biodegradation was reported [125-128].

5.7.2. Polyhydroxyalkanoates

Polyhydroxyalkanoates (PHAs) are degraded to CO_2 and water in aerobic conditions and methane in anaerobic conditions by microbes found in soil, water and other various natural habitats. PHAs are the only proposed replacement polymers that are completely biodegradable [129]. The structures of these polymers have a very similar structure of the petroleum-derived thermoplastics [130].

Diethylene glycol dibenzoate

Diethylene glycol monobenzoate + **Benzoic acid**

1,3-Propanediol dibenzoate

1,3-Propanediol monobenzoate + **Benzoic acid**

3ˉ(Benoyloxy)propanoic acid + **Benzoic acid** + **1,3-Propanediol**

Benzoic acid + **1,3-Propanediol**

Scheme 5. Proposed biodegradation pathways of diethylene glycol dibenzoate and 1,3-propanediol dibenzoate [116]

PHAs also possess similar physical properties as plastics including the ability to be molded, made into films, and also into fibers. Efforts are underway to identify bacteria, which produce various kinds of PHAs [129] as well as the production of these polyesters or create certain kinds of PHAs by changing the kind of bacteria [130] and/or the substrates given to the bacteria and genetically enhancing bacteria [131].

6. Prospective of anaerobic digestion and biogas energy

The foregoing analysis shows that anaerobic digestion technologies have matured so far to treat several organic micro-pollutants, halogenated compounds, substituted aromatics, azo-linkages, nitro-aromatics and the like in industrial effluents and also for municipal effluents containing industrial loads. A very high growth potential is envisaged for the anaerobic digestion of organic fraction of municipal solid waste [27]. Novel reactor and control systems ought to be developed for different purposes depending on the source of pollutants or biomass. Anaerobic digestion of sewage sludge followed by recycling on agricultural land is currently the largest world-wide application of anaerobic processes. Treatment of sludge and slurries targeted at the production of safe end products can be tackled with niche anaerobic technologies [16]. It is predicted that major future process developments will come from the deployment of pre- and post treatment processes, including physical, chemical and biological processes, for the reclamation of the products from the wastewater treatment system. Wastewater treatment for reuse will be effective if anaerobic digestion is adopted for mineralizing organic matter. Hence, anaerobic digestion has the potential to play a major role in closing water, raw materials, and nutrient cycles in industrial processes [37]. Further development is required on the community on-site treatment of domestic sewage under a wide range of conditions, opting for the reuse of the treated water in agriculture and making use of the mineralized nutrients for fertilization purposes. An upstream integration of the anaerobic process with industrial primary production processes under extreme conditions of temperature, pH, salinity, toxic and recalcitrant compounds, and variable load is envisaged in future [39].

There is an emphasis worldwide on renewable energy system among which biogas produced from any biological feedstocks including primary agricultural sectors and from various organic waste streams will come in to prominence in near future [22]. It is estimated [3] that at least 25% of all bioenergy in the future can originate from biogas, produced from wet organic materials like animal manure, slurries from cattle and pig production units as well as from poultry, fish and fur, whole crop silages, wet food and feed wastes, etc. Anaerobic digestion of animal manure offers several environmental, agricultural and socio-economic benefits throughout such as improved fertilizer quality of manure, considerable reduction of odors and inactivation of pathogens and more importantly production of biogas production, as clean, renewable fuel, for multiple utilizations [16]. This biogas can be upgraded to natural gas to mix with the existing natural gas grid which will be cost effective. The potential development of biogas from manure co-digestion includes the use of new feedstock types such as by-products from food processing industries, bio-slurries from biofuels processing industries as

well as the biological degradation of toxic organic wastes from pharmaceutical industries, etc. [3,16,22]. This will also call for better reactor systems and careful process control to increase the biogas yield, which will be more attractive if coupled with less capital and operating costs. Integration of biogas production into the national energy grids will eventually be commercially viable since the biogas from anaerobic co-digestion of animal manure and suitable organic wastes would overcome the major environmental and veterinary problems of the animal production and organic waste disposal.

7. Plastic waste separation, reprocessing and recycle

In 2009, around 230 million tonnes of plastic was produced; ~25 % which was used in the European Union [131]. About 50 % plastic is used for single-use disposable applications, such as packaging, agricultural films and disposable consumer items [132]. Although plastics consume approximately 8 % world oil production: 4 % as raw material for plastics and 3-4 % as energy for manufacture [132], supplies are being depleted. Bioplastics make up only 0.1 to 0.2 % total plastics [115]. It is estimated that plastics reduce 600 to 1300 million tonnes of CO_2 through the replacement of less efficient materials, lighter and fuel efficient vehicles, housing sector, contribution to insulation, preservation of food, packaging, use in wind power rotors and solar panels [133]. However, plastic littering and pollution of land and sea have been matters of great concern which should be strategically and technologically solved. Plastics recovery, in addition to increased diversion from disposal, results in significant energy savings (~50-75 MBtu/ton of material recycled) compared with the production of virgin materials, which also leads to reductions in greenhouse gas emissions due to avoided fuel use. Limiting the plastics that enter landfills can lower the costs associated with waste disposal. It is believed that the recycled plastic will fetch as much as 70 % of the typical price for virgin plastics [136].

7.1. Waste reduction hierarchy

The motto of waste reduction by plastics is by following the principles of (i) prevention, (ii) reuse (iii) recycle, (iv) recovery, and (v) disposal [119].

i.   *Prevention* – Using minimum and as less types of plastic in the product by clever product redesign.

ii.   *Reuse* – Products could be designed for reuse by facilitating the dismantling of products and replacement of parts. This could involve standardizing parts across manufacturers [137].

iii.   *Recycle* – Some types of plastics are easier to recycle than others, for example polyethylene terephthalate (PET). By using fewer types and colors (or colorless) of plastics the recycling process becomes easier. The use of "intelligent" or smart polymers that undergo changes under certain conditions could also reduce disassembly time [138]. For example, a polymer that changes shape when subject to magnetic or electric fields could aid the disassembly of electronic goods.

iv.   Recovery – Energy can be recovered from plastics in waste-to-energy plants. By designing products to consider the possibility of energy recovery, plastic may have a greater end-of-life use.

v.   *Disposal* – Biodegradable plastics are less persistent in the environment than traditional plastics, but need specific and suitable end-of-life treatment.

7.2. Bioplastics

Since disposal is one of the important aspect, bioplastics are being favored. There are three main categories of bio-based plastics: (i) Natural polymers from renewable sources, such as cellulose, starch and plant-based proteins, (ii) Polymers synthesised from monomers derived from renewable resources. For example, polylactic acid (PLA) is produced by the fermentation of starch, corn or sugar, (iii) Polymers produced by microorganisms. For example, PHA (polyhydroxyalkanoate) is produced by bacteria through fermentation of sugar or lipids [139].

Biodegradable plastics are not by definition bio-based and bio-based plastics are not always biodegradable, although some fall into both categories, such as PHAs. The term *bioplastics* is often used to refer to both bio-based and biodegradable plastics. The main applications of bioplastics are disposable plastic bags, packaging and loose fill packaging (beads and chips), dishes and cutlery, electronic casings and car components. However, bioplastics cannot substitute all types of plastic; particularly certain types of food packaging that require gas permeability [135]. Development of novel biodegradable plastic is a solution for the plastic disposal problem since plastics are immiscible in water and are thermo-elastic polymeric materials. Biodegradability of plastics is governed by both their chemical and physical properties. Other factors affecting degradability are the forces associated with covalent bonds of polymer molecules, hydrogen bonds, van der Waals forces, coulombic forces, etc. Enzymatic degradation is an effective way. Lipase and esterase can hydrolyze fatty acid esters, triglycerides and aliphatic polyesters. These lipolytic enzymes have an important role in the degradation of natural aliphatic polyesters such as cutin, suberin and esteroid in the natural environment and animal digestive tract.

As stated earlier, biodegradable plastics decompose in the natural environment from the action of bacteria. Biodegradation of plastics can be achieved through the action of micro-bacteria and fungi in the environment to metabolize the molecular structure of plastic films to produce an inert humus-like material that is less harmful to the environment, along with water, carbon dioxide and/or methane. They may be composed of either bioplastics or petro-plastics. The use of bio-active compounds compounded with swelling agents ensures that, when combined with heat and moisture, they expand the plastic's molecular structure and allow the bio-active compounds to metabolize and neutralize the plastic [140]. Compostable plastics are biodegradable and meet certain criteria, such as rate of biodegradation and impact on the environment. Degradable plastics include biodegradable and compostable plastics, but also plastics that degrade by chemical and physical processes such as the action of sunlight. Purely biodegradable plastics are different from oxy-biodegradable plastics, which contain small

amounts of metal salts to speed up degradation. It has been suggested that this process be called "oxo-fragmentation" to avoid confusion [139,140].

It is possible to produce polymers biologically, e.g., PHA grown in genetically modified corn plant leaves, PLA (polylactic acid) produced by the fermentation of sugars extracted from plants, PHA produced by bacteria. Bioplastics could also help alleviate climate change by reducing the use of petroleum for the manufacture of traditional plastics. It is claimed that CO_2 emissions released at the end-of-life of bio-based plastics are offset by absorption of CO_2 during the growth of plants for their production [141].

7.3. Sorting plastic materials

The technical difficulties and high cost associated with separating plastics have limited recycling in the past. Consumer goods often contain as many as 20 different types of plastic as well as non-plastic materials such as wood, rubber, glass, and fibers. There is upsurge of new products and pigment types, which can pose a challenge to the recycling infrastructure. Consequently, the cost of producing virgin materials is often less than the cost of collecting and processing post-consumer plastics. Used plastic material will contain more than one base polymer, and resins with a variety of additives, including coloring agents and thus technologies for cleaning and separating the materials are an important part of most plastics recycling systems. A particular concern for recycled plastics is their use as food containers requiring stringent regulations to avoid contamination [140].

Separation of different types of polymers from each other is many times a desired part of plastics recycling processes which are classified as macrosorting, microsorting, or molecular sorting.

7.3.1. Macrosorting

Macrosorting involves the sorting of whole or nearly whole objects such as separation of PVC bottles or caps from PET bottles, separation of polyester carpet from nylon carpet, and sorting of automobile components by resin type. Various devices are now commercially available to separate plastics by resin type, which typically rely on differences in the absorption or transmission of certain wavelengths of electromagnetic radiation, or color or resin type. Particularly for recycling of appliances, carpet, and automobile plastics, several IR spectra based equipment are used [135].

7.3.2. Microsorting

Microsorting is a size-reduction process to reduce the plastic material in to small pieces which is then separated by resin type or color; for instance, separation of high-density polyethylene (HDPE) base cups from PET soft drink bottles using a sink-float tank. More modern separation processes, such as the use of hydrocyclones, also rely primarily on differences in the density of the materials for the separation. A number of other characteristics have also been used as the basis for microsorting systems, including differences in melting point and in triboelectric behavior. In many of these systems, proper control over the size of the plastic flakes is

important in being able to reliably separate the resins. Some systems rely on differences in the grinding behavior of the plastics combined with sieving or other size-based separation mechanisms for sorting. Sometimes cryogenic grinding is used to facilitate grinding and to generate size differences [135].

Three new separation technologies, developed by MBA Polymers, Argonne National Laboratory, and Recovery Plastics International (RPI), could break down these barriers and increase plastics recycling [138].

7.3.2.1. Automated separation

According to the process developed by MBA Polymers, plastic scraps from computers and other electronics are first ground into small pieces. Magnets and eddy-current separators then extract ferrous and non-ferrous metals. Paper and other lighter materials are removed with jets of air. Finally, a proprietary sorting, cleaning, and testing process involving various technologies, allows the separation of different types of plastics and compound them into pelletized products comparable to virgin plastics [138].

7.3.2.2. Froth flotation

Argonne National Laboratory (ANL) has developed a process to separate acrylonitrile-butadiene styrene (ABS) and high-impact polystyrene (HIPS) from recovered automobiles and appliances. The froth flotation process separates two or more equivalent-density plastics by modifying the effective density of the plastics. There is a careful control of the chemistry of the aqueous "froth" so that small gas bubbles adhere to the solid surface and facilitate the plastic to float to the top [135].

7.3.2.3. Skin flotation

Recovery Plastics International (RPI) has developed an automated process capable of recovering up to 80 % plastics found in automobile shredder residue (ASR). The process starts with the separation of light lint materials, followed by the removal of rocks and metals, granulation, washing, and, finally, automated skin flotation separation. This final step adds a skin of plasticizer to make the surface of the targeted plastic hydrophobic. Air bubbles then can attach to the plastic, allowing it to float above denser, uncoated pieces. It is estimated this new skin flotation technology could be used to treat about one-third of the estimated 7 million tons of ASR disposed off each year [141].

7.3.3. Molecular sorting

Molecular sorting deals with sorting of materials whose physical form has been completely disrupted, such as by dissolving the plastics in solvents using either a single solvent at several temperatures or mixed solvents, followed by reprecipitation. There is a need to control emissions and to recover the solvents, without any residual solvent in the recovered polymer to avoid leaching in stored material. There are at present no commercial systems using this approach. Some research effort has focused on facilitating plastics separation by incorporating

chemical tracers into plastics, particularly packaging materials, so that they can be more easily identified and separated.

It has become obvious that many of the difficulties of recycling plastics are related to difficulties in separating plastics from other wastes and in sorting plastics by resin type. Design of products can do a lot to either aggravate or minimize these difficulties [134,135]. The concept of green product embeds recycling at the design stage itself.

7.4. Plastic reprocessing and recycling

For plastics recycling to be effective, it is necessary to have (i) a system for collecting the targeted materials, (ii) a facility capable of processing the collected recyclables into a form which can be utilized to make a new product and, (iii) new products made in whole or part from the recycled material must be manufactured and sold.

Processing of recyclable plastics is necessary to transform the collected materials into raw materials for the manufacture of new products. Three general categories of processing can be identified: (1) physical recycling, (2) chemical recycling, and (3) thermal recycling, wherein the particulars of the processing are often specific to a given plastic or product.

7.4.1. Physical processes

Physical recycling, the most popular option, covers size and shape alteration, removing contaminants, blending in additives if desired, and similar approaches that change the appearance of the recycled material, but do not alter its basic chemical structure. Plastic containers, for example, are processed including grinding, air classification to remove light contaminants, washing, gravity-separation, screening, rinsing, drying, and often melting and pelletization, accompanied by addition of colorants, heat stabilizers, or other ingredients, depending on type of plastic [132].

7.4.2. Chemical reactions

Chemical recycling of plastics deals with chemical reactions using catalysis or solvents such as methanol, glycols or water leading to depolymerization or breaking polymers into monomers or useful chemicals, or fuels [134]. The products of the reaction then can be separated and reused to produce either the same or a related polymer. An example is the glycolysis process sometimes used to recycle polyethylene terephthalate (PET), in which the PET is broken down into monomers, crystallized, and repolymerized. Condensation polymers, such as PET, nylon, and polyurethane, typically much more amenable to chemical recycling than are addition polymers such as polyolefins, polystyrene, and polyvinyl chloride (PVC). Most commercial processes for depolymerization and repolymerization are restricted to a single polymer, which is usually PET, nylon 6, or polyurethane. Methanolysis is another common reaction using methanol [134].

7.4.3. Thermal cracking

Thermal cracking or recycling also involves cracking of the chemical structure of the polymer using heat in the absence of sufficient oxygen for combustion. At these elevated temperatures, the polymeric structure breaks down. Thermal recycling can be applied to all types of polymers. However, the typical yield is a complex mixture of products, even when the feedstock is a single polymer resin. If reasonably pure compounds can be recovered, products of thermal recycling can be used as feedstock for new materials. When the products are a complex mixture which is difficult to separate, they are most often used as fuel. There are relatively few commercial operations today which involve thermal recycling of plastics. Some European nations have such feedstock recycling facilities. Many plastic resin companies use fluidized bed cracking to produce a waxlike material from mixed plastic waste [134-136, 139]. The product, when mixed with naptha, can be used as a raw material in a cracker or refinery to produce feedstocks such as ethylene and propylene. In certain case, syn gas can be produced and used in Fisher-Tropsch synthesis to produce valuable chemicals.

In landfill, both synthetic and naturally occurring polymers do not get the necessary exposure to UV and microbes to degrade. The discarded plastics occupy space and none of the energy put into making them is being reclaimed. Reclaiming the energy stored in the polymers can be done through incineration, but this can cause environmental damage by release of toxic gases into the atmosphere. Therefore, recycling is a viable alternative in getting back some of this energy in the case of some polymers. With ever increasing petroleum prices, it would be financially viable to recycle polymers rather than produce them from raw materials [141].

8. Conclusions

The modern society needs thousands of chemicals and materials of all sorts which are produced annually and used in all sectors of economy. However, their fate in the environment is of great concern since some are toxic, recalcitrant and bioacumulating and hence their discharge into the environment must be regulated. Better understanding of the mechanism of biodegradation has a high ecological significance that depends on indigenous microorganisms to transform or mineralize the organic contaminants. Thus, biodegradation processes differ greatly depending on conditions, but frequently the main final products of the degradation are carbon dioxide and/or methane. Microorganisms have enzyme systems to degrade and utilize different hydrocarbons as a source of carbon and energy. Slow and partial biodegradation of chlorophenolic compounds under aerobic as well as anaerobic natural environment has been observed. Aerobic degradation takes place via formation of catechols while anaerobic degradation occurs via reductive dechlorination. Acclimatization of biomass to chlorophenols markedly enhances their ability to degrade such compounds, both by reducing the initial lag phase as well as by countering biomass inhibition. Aerobic processes as well as anaerobic processes partially remove chlorophenols. However, enhanced removal efficiency can be obtained by operating anaerobic and aerobic treatment processes in combination. Thus microbial degradation can be a key component for clean-up strategy of organopollutants and plastics.

Renewable energy system among which biogas produced from biological feedstocks will play a major role in energy sector. Anaerobic digestion of animal manure, slurries from cattle and pig production units as well as from poultry, fish and fur, whole crop silages, wet food and feed wastes, etc offers several environmental, agricultural and socio-economic benefits by improved fertilizer quality of manure, considerable reduction of odors, inactivation of pathogens and production of biogas production, as clean and renewable fuel. This biogas can be upgraded to natural gas to inject in to the existing natural gas grid which will be cost effective. Biogas from anaerobic co-digestion of animal manure and suitable organic wastes would overcome the major environmental and veterinary problems of the animal production and organic waste disposal.

The recycling of plastics is environmentally beneficial because plastics reduce millions of tonnes of CO_2 emissions through the replacement of less efficient materials, development of lighter and fuel efficient transport systems, housing material, energy saving insulation, food preservation and storage, energy efficient packaging, use in wind power rotors and solar panels. Processing of recyclable plastics is necessary to transform the collected materials into raw materials for the manufacture of new products. Bioplastics offer a very good solution to environmentally deleterious materials. Biodegradation of plastics can be achieved through the action of micro-bacteria and fungi.

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