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Review

Recent advances in the bio-remediation of persistent organic pollutants and its effect on environment

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ABSTRACT

This paper presents a comprehensive review of the current state of research activities on the application of biodegradation/bioremediation for removing persistent organic pollutants (POPs) such as pesticides, PCBs, PAHs and PPCPs from wastewater. Several potential enzymes have been reported from various microorganisms, which breakdown the complex compounds through biodegradation, biostimulation or bioaugmentation process. Various microorganisms, harbouring numerous plasmids and catabolic genes, acclimatize to these environmentally unfavourable conditions by gene duplication, mutational drift, hypermutation, and recombination. Genetic aspects of some major POP catabolic genes such as biphenyl dioxygenase (bph), hydroxylation, phosphotriesterases and oxygenase etc. assist in degradation organic pollutants. However with the advent of technological advancements in genetic engineering is being considered the possibility for the role of genetically modified organisms, metagenomics and metabolomics is being considered to develop low cost, effective and reliable method for detection, determination and removal of ultra-trace concentration of POPs. In addition, development in microbial fuel cell, nano-materials, biofilms and constructed wetlands augments the biodegradation process. Therefore, this review highlights the effect of POPs on the environment, health hazards, microbial degradation and its mechanism along with brief study of advanced oxidation process for wastewater treatment.

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1. Introduction

Due to industrialization and urbanization, it very difficult for the modern society to imagine their life without utilization of chemicals. Many industries like pulp and paper industry, leather industry, pharmaceutical industry etc. contribute to our modern standard of living. However, increase in consumption of chemicals have led to increase in pollution in the environment. Pollution, in terms of chemicals, refers to the harmful effects caused by the chemicals (Harrison, 2001). Sources of pollution can be categorised as Natural and Anthropogenic. Natural sources include volcanic activity, vegetation fires etc. and anthropogenic sources include extensive use of chemical substances, pesticides, organic pollutants and heavy metals. Out of the above mentioned anthropogenic sources, toxicological phenomenon caused by POPs is highly damaging. (Gaur et al., 2014).

Organochlorine pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs), poly chlorinated biphenyls (PCB), dioxins and dibenzofurans are the chief pollutants that bring about the persistent organic pollutant contamination (Érseková et al., 2014). These compounds remain intact in the environment exceptionally for a long period of time as they are non-biodegradable (resist to photolytic, chemical and biological degradation) in nature. In addition, these compounds are of great concern because of long range transport, persistence nature and bioaccumulation propensity, Once they enter into the food chain they get accumulated in the fatty tissue of human body and poses a risk to cause adverse effects to the environment and human health (Kallenborn et al., 2012; Venkatesan and Halden, 2014).

Conventional treatment methods like incineration, solvent extraction, and gas phase chemical reduction, alkali metal reduction, land filling and stabilization/solidification are used for the eradication of POPs from soil and sediments. Nonetheless, the major drawback of being expensive is because of the fact that they need sophisticated infrastructure and well experienced man power to handle the instruments correctly. In addition, these methods might not completely remove the toxic organic compounds (Perelo, 2010).

Biodegradation is an eco-friendly and sustainable process that can remove the organic pollutants more effectively and efficiently from soil and water by employing microorganisms (Megharaj et al., 2011). The aim of biodegradation process is to clean up the environment without disturbing the normal biological processes associated with it. According to Joutey and Bahafid, biodegradation is a process that reduced the complex chemical compounds into simpler ones by living microbial organisms (Gadd, 2010; Joutey et al., 2013). As compared to the conventional methods, biodegradation technology is extremely preferred as it provides improved results through the application of cost effective and economic inputs. Thus, biodegradation can be considered owing to their highly economical, eco-friendly and more prominent way out to the problem arising due to the organic pollutants.

2. Persistent organic pollutants

POPs are carbon based organic chemicals that occurs either in vapour phase or as adsorbed on atmospheric particles. These compounds are less soluble in water but highly soluble in lipids and these properties allow POPs to accumulate in fatty tissue. However, these pollutants can disperse to long distances in the atmosphere, where POPs have never been used, before deposition and therefore produce adverse effect on both environment and human health (Farrington and Takada, 2014). To overcome the problems that arose due to POPs world scientific, technical and political energy came forward to implement The Aarhus protocol and Stockholm Treaty on POPs. On 24th June 1998 in Aarhus (Denmark) the protocol on POPs was adopted by Executive Body for the Convention on Long-range Transboundary Air Pollution (CLRTAP). To control the POPs in future it was a great step towards global agreement that focus on international air pollution controls for the area comes under United Economic Commission for Europe (UNECE). The CLRTAP has been completed by eight protocols and five out of eight have been already entered into force after receiving 16 ratifications while three of them still requires further ratification before being enforced. The basic aim of this protocol was to eliminate any discharge, emission and losses of POPs (Fiedler and Borja-Aburto, 2003).

The leader of Stockholm Treaty agreement was United Nations Environment Programme (UNEP) with major input from non-governmental organization, trade unions and private companies (Pollutants, 2011). This treaty has been able to address “a global public health treaty” which aims to protect human health and ban all the chemicals that are hazardous to environment. In May 2001 delegates from different countries signed the agreement and after four years this treaty came into force. Pesticides, industrial chemicals and by-products covered by the treaty and chemicals were classified on the basis of their toxicity. Except DDT all the compounds comes under Annexure A, which aims is to completely eliminate these toxic pollutants. The first aim of this agreement was immediately stop the production and remove the use of PCBs. DDT comes under Annexure B which aims to restrict the use of DDT and its use is allowed until any effective alternative is unavailable for the cure of malaria. Any unintentionally produced pollutant comes under Annexure C (Porta and Zumeta, 2002). Table 1 shows the 12 dirty dozen according to Stockholm treaty that were listed in three categories.

2.1. *Sources of POPs*

The two possible natural sources of dioxins and dibenzofurans are volcanic activities and vegetation fires. As mentioned above, POPs are stable in all components of the environment and through the number of industrial sources such as power stations, incinerating plants and heating stations they enter the atmosphere (Dong et al., 2016). In addition, POPs can enter into the atmosphere from household furnaces, use of agricultural sprays, transport and evaporation from soil, water surfaces or landfills. Incinerations, diverse combustions, chemical facilities, putrefaction and waste containing PCBs and bushfires are the sources of unintentionally produced organic pollutants. Apart from these sources, unintentionally POPs can be found in many areas and halting from different activities such as demolition of building, use of obsolete oil, evaporation, animal carcass incinerator, repairing and maintenance of equipment's and recycling operations, medical waste, organichlorine pesticide storage etc (El-Shahawi et al., 2010; Santillo et al., 2000).

Wastewater from plants producing or using POPs, alongside overflows from fields and roads and from atmospheric depositions is the primary source of addition of substances, oil, fats, liquid fuels, soil, ash and sediment into the water system. Oceans and seas become their chief repositories where they accumulate from sources like river sediments, atmospheric deposition, disposing waste and by accident. On the beds of seas, oceans and large lakes sediments, these organic pollutants are stored and after a time they again re-enter the atmosphere (Bouwman, 2003).

According to the study in Poland, lot of sources of POPs over the past 10 years have been stopped because of changes in economic structure of the country. Additionally, lots of new wastewater treatment plants have been built during this period. Another major reason observed for lowering POPs prevalence in waters and sediments is the ecological politics of government and local authorities. In addition, no extensive investigations of dioxin related environmental contamination, particularly the presence of these compounds in human tissues and milk of breastfeeding mothers, have ever been performed. All publicly accessible records are random or based totally on unreliable estimates (Szyrwińska and Lulek, 2007). According to the data provided to the Central Statistical Office by the Institute for Environmental Protection, the dioxin and furan emissions in 1998 are estimated at 290.353 g TEQ. According to the study in Poland, the main sources of dioxin emissions in Poland are road transport (0.918%), fossil fuel powder boiler (169.41%), industrial combustion (4.49%), energy production (11.77%), production of chemicals and goods (68.94%) and waste incineration (34.80%) (El-Shahawi et al., 2010).

The Ministry of Environment has recently undertaken great endeavours in providing a foundation for estimating the actual emission of dioxins and furans. 118 geological samples have been taken from different regions of Poland including urban areas and areas which are potentially free from dioxin contamination. Their analysis will allow the determining of the so-called background dioxin level. The experiment was done on a group of 462 women from Warsaw and other localities. The increased level of persistent organic pollutants was primarily found in older women, aged 30 and above, and those who gave birth to more than four children (El-Shahawi et al., 2010; KORUNI, 2001).

2.2. *Classification of POPs*

In general POPs can be divided into two main categories: 1. Intentionally POPs and 2. Unintentionally POPs (Fig. 1). In the former category, the wanted products are produced by chemical reactions and are known as organochlorine compounds (OCs) as it includes chlorine atom in the reaction. These compounds shows high lipophilicity and neurotoxicity. On the basis of their use these can be further divided into two types: organochlorine pesticides and industrial chemicals (El-Shahawi et al., 2010).

The organochlorine pesticides (DDT, Mirex, Endrin, Dieldrin, Heptachlor, Chlordane, Aldrin and Hexachlorobenzene) are the compounds which are used to kill pesticides. These pesticides can be chemical or biological substances, which comes into three major classes: insecticides, fungicides and herbicides (Chopra et al., 2011). Apart from these classes, the pesticides also come under synthetic group that includes rodenticides, molluscicides and acaricides. Industrial chemicals constitute the important class of specific wastes i.e. polychlorinated biphenyls (PCBs) that were first discovered as a pollutant in 1966. Later, it was found in water, sediments, birds and

Table 1
Chemicals listed in annexes of Stockholm convection.

ANNEX	POPS	Exemptions	
		Production	Use
Annexure A: Substances for elimination of production and use	Aldrin	None	Local insecticide
	Chlordane	By registrar parties	Insecticide, termiticide and as an additive in plywood adhesives
	Dieldrine	None	Agriculture operations
	Endrin	None	None
	Heptachlor	None	Termiticide, for organic treatment and in underground cable boxes
	HCB	By registrar parties	Chemical intermediate and a solvent for pesticides
	Mirex	By registrar parties	Termiticide
	PCB	None	According to part II of annex A
	Toxaphene	None	None
Annexure B: Substances scheduled for restrictions on use	DDT	Production and use as an intermediate in the production of dicofol and other compounds	
Annexure C: Substances for which emission s must be reduced	PCBs Dioxins/Furans HCB	None	None

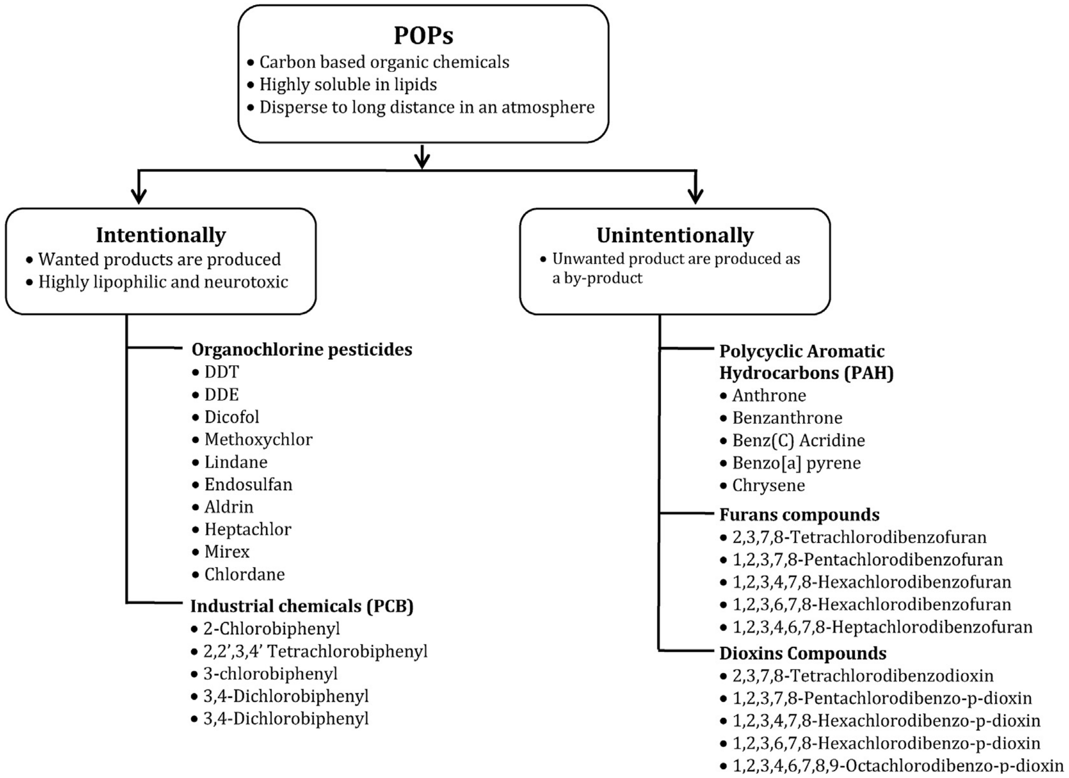

Fig. 1. Classification of persistent organic pollutants.

fish tissue throughout the biosphere (Selendy, 2011). Moreover, in spite of having their agricultural applications, these pollutants are now much less used because of their harmful impact on environment.

Since middle of the last century, pesticides have been widely used throughout the world. Nearly 1000 active components have been employed and from that thousands are currently being formulated into different commercial products. Insecticides, fungicides and herbicides are the commercially available products having very different physicochemical properties, polarity, volatility and persistence. Pesticides can be used for different purposes (Tieyu et al., 2005). In agriculture, about 80% of the pesticides are used and by the means of volatilization, runoff, infiltration, transport along the food chain etc. they are relocated in the environment. Because of the toxic effects on the environment and its ecosystem, the application of the OCPs have been forbidden for a considerable period in many countries. Insecticides, molluscicides are the chemicals which are used for the control of snails and slugs (invertebrates) while for the control of microscopic roundworms nematicides are used. However, vertebrates such as rodents, birds and fishes are controlled by rodenticides, avicides and pesticides respectively. Herbicides, fungicides, bactericides, algaecides and slimicides are used to kill plants, fungi, bacteria, algae, and slime causing organisms respectively. In mid-90s around 900 million kg of insecticides was used in U.S in non-agricultural applications (forestry, landscaping, gardening, home peat control and food distribution) while around 365 million kg of pesticides per year was used in agricultural purposes. Therefore, a large amount of pesticides in water enters either directly through pest control or indirectly through drainage of agricultural lands (El-Shahawi et al., 2010).

Yamamoto et al. in 2007 studied the usage of pesticides in various counties such as Japan, China, United States, Australia and Canada. They found that dichlorvos, carbofuran, chlorpyrifos, dimethoate (insecticides), mancozeb, carbendazim, thiophanate-methyl, chlorthalonil (fungicides), glyphosate, 2,4-D, paraquat, acetochlor (herbicides) were frequently used as a pesticides in many countries. While china mainly used carbendazim, thiophanate-methyl, acetochlor and dichlorvos and in various food items, dithiocarbamates are used frequently in various countries (Yamamoto et al., 2007).

In unintentionally POPs the unwanted products are produced as a by-product of chlorine compounds during combustion or burning. This category of compounds includes polycyclic aromatic hydrocarbons (PAHs), dioxins and furans. PAHs are formed by the fusion of two or more benzene ring containing only carbon and hydrogen in linear, angular or cluster arrangements These are also produced during the incomplete combustion at high temperatures (500-800 °C) or subjection of organic material to low temperatures between 100 and 300 °C for long period of time by the subsequent recombination of organic molecules. The Environmental Protection Agency (EPA, US) generated a list of most hazardous 16 PAHs as they are considered as human carcinogen. Therefore, lot of attention have been focused on their distribution and possibility of human exposure to them. PAHs can be produced naturally by oil seeps, forest and rangeland fires, exudates from trees and through anthropogenic activities like burning of fossil fuels, municipal soil waste incineration and petroleum spills and discharge. In addition, cooking as well as agricultural fires may also release PAHs and their distribution in the sediments can give information if they are pyrogenic or petrogenic (Ladygina and Rineau, 2013).

Dioxins and furans are abbreviated name of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzo-furans (PCDFs) respectively. From the past 10 years they have been of concern because of their toxic properties in human, animals, birds etc. Especially since the 1930s, from which there had been a steady increase in environmental level coinciding with the large scale use and production of chlorinated chemicals and man-made activities and sources are the greater contributor to the environmental pollution of PCDDs and PCDFs. Chemical process, combustion process and secondary sources are three main categories of man-made sources of PCDDs and PCDFs. For example, in Hong Kong the main sources of PCDDs and PCDFs are coal combustion, chemical waste incineration plant, municipal waste incinerator, cement manufacture, crematoria and landfill gas combustion (El-Shahawi et al., 2010). These are also produced during the production of herbicides, bleaching of wood pulp and when products of some industries are burned. Congeners of dioxin and furans are considered to be highly toxic if chlorine substitution is at 2,3,7 and 8 position while in PCBs congeners with chlorine substitution at 3,3′,4,4′,5 or 5′ position and no or only one 2- or 2′- substitution are able to exhibit dioxin like toxicity. (Garrett et al., 2010). Table 2 shows the classification of POPs, its half-life, uses partition coefficient and log K_{ow}.

Apart from the mentioned organic pollutants, there are many other organic pollutants which are produced by industries intentionally or unintentionally and are listed in Table 3. The Organophosphorus pesticides (OPs) are cholinesterase inhibiting chemicals which are characterised into four groups depending upon their molecular structure: phosphates, phosphorothioates, phosphorodithioates, and phosphorothiolates. OPs can be absorbed via skin, cornea, respiratory epithelium and gut either through ingestion of contaminated food or vapours as these compounds are liquid at room temperature. It affects many organs upon exposure like skeletal muscles, nervous system, gastro intestinal tract, secretary glands and respiratory system. The most sensitive target as compared to the other OPs induced toxicity is nervous system (Pehkonen and Zhang, 2002; Rahimi and Abdollahi, 2007).

High exposure of OPs induced toxicity may cause fatal consequences like weakness, glandular secretion, fasciculation, acute pancreatitis, convulsion, and respiratory failure. The major mechanism of OPs persuaded toxicity is the stimulation of oxidative stress. It is a phenomenon in which the imbalance occurs between the ratio of pro-oxidant and anti-oxidant (Gaur et al., 2014; Rahimi and Abdollahi, 2007).

2.3. Effect of climate change and fate of POPs in environment

The ubiquitous nature of POPs allows it to cause adverse effects on the surroundings due to their diverse properties such as semi volatile character ($P_{V=}10^{-4}$-10^{-11} atm at 25 °C), their capability to associate with atmospheric particles and dispersion between two phases of atmosphere. Although the organic pollutants biochemical equivalence and geochemical cycles are general components of the earth's crust, onset of the industrial rebellion has led to a rise in the level of usage of these organic contaminants because of which their concentration in the earth's crust has exponentially increased. (Loibner et al.).

Scientists are taking interest in studying the fate and behaviour of the POPs, mainly when local release have resulted in distributed pollutants far from source region (Paul et al., 2012). Surface characteristics such as soil, water, vegetation etc. and physicochemical properties of the compounds are the factors on which transport distance and the number of air –surface exchange episodes depends. Therefore, depending on the vapour pressure organic pollutant deposition takes place. For instance, organic pollutants having high vapour pressure are transported far away from the source while having low vapour pressure will be preferably deposited in the area closer to the emission source. Moreover, there are other factors and mechanisms (capability of the environmental compartment to accumulate or degrade POPs, kinetics of the air-surface exchange and the general atmospheric patterns) also which effect the dispersal of POPs in the environment.

Recently, climate change has attracted some interest because of its potential to alter the environmental distribution and biological effects of chemical toxins. Directly or indirectly environmental factors like wind speed, precipitation, temperature and solar radiation have influence on the environmental transport and fate of POPs. Obviously those factors will be altered by the climate change, usually it is acknowledged that climate change can affect every step along the fate, transport and distribution pathways of semi-volatile organic chemicals, including PAHs and POPs (Gusev et al., 2012). The global distribution of the POPs in the environment is severely affected by the temperature, which is the key meteorological parameter (Cai et al., 2014). The POPs degradation rates in the environment according to the results of multi-compartment

Table 2
POPs listed by the Stockholm Convention.

Persistent organic pollutants			Molecular weight	Half-life (yrs)	Partition Coefficient	Log K_{ow}	Uses/sources	References
Intentionally POPs	OCPs	Aldrin	364.9	>5	5.17–7.4	6.50	Soil pests control	(Arienzo et al., 2013; Kasza et al., 2016; Ladygina and Rineau, 2013; Rani et al., 2017; Starek-Świechowicz et al., 2017; Varma and Varma, 2005)
		Dieldrin	380.9	5	3.692–6.2	5.40	Soil pest control	
		Heptachlor	373.3	Up to 2	4.40–5.5	6.10	Kill termites and insects	
		Mirex		Up to 10	N/A	6.89	Control fire ants and other ants	
		DDT	354.5	10–15	4.89–6.914	6.91	Control malaria and typhus	
		Endrin	380.9	Up to 12	3.209–5.339	5.20	Insect and rodent control	
		Chlordane	409.8	1	6.00	6.16	Agricultural insecticide and fungicide	
		HCB	284.8	2.7–22.9	3.03–6.42	5.73	Wood preservative and fungicide	
	Industrial chemicals	PCBs	–	10 days-1.5yr	4.3–8.26	3.76–8.26	In electrical industry, additives in paints and carbon less copy paper	(Hawker and Connell, 1988)
Unintentionally POPs	PAHs (Toxaphene)		411.77	100 days-12yrs	3.23–5.50	3.7–8	Formed during manufacture of certain pesticides, paper bleaching and waste incineration	(Brooks, 2017)
	Dioxins		84.07	10–22	4.75–8.20	6.4		(Hauptman et al., 2016)
	Furans		68.07	10–22	5.44–8.0	1.3		(Ramamoorthy and Ramamoorthy, 1997)

Table 3
Physicochemical properties of organic pollutants other than Stockholm Convention.

Persistent organic pollutants			Half-life (yrs.)	LD_{50} in rat (oral) (mg/kg)	Log K_{ow}	Uses/sources	References
Intentionally POPs	OCPs	DDT	10–15	113–130	6.91	Acaricide, Insecticide	(Jayaraj et al., 2016)
		DDD	1	4000	6.2	Pesticide	(Jayaraj et al., 2016)
		DDE	8	800–1240	6.51	Kill termites and insects	(Jayaraj et al., 2016)
		Dicofol	2–4 months	684–1495	4.3	Acaricide	(Jayaraj et al., 2016)
		Methoxychlor	8–10 days	5000–6000	5.08	Pesticides	(Jayaraj et al., 2016)
		Lindane	1–2	88–270	3.61–3.72	Soil and seed treatment	(Jayaraj et al., 2016)
		Endosulfan	35–150 days	18–220	3.8	Insecticide, Pesticide and Acaricide	(Jayaraj et al., 2016; Leadprathom et al., 2009)
		Isodrin	46	8.8	6.5	Insecticide	(Howard, 2017; Jayaraj et al., 2016)
		Isobenzan	2–7	4.8	4.51	Insecticide	(Jayaraj et al., 2016; Sullivan and Krieger, 2001)
		Chloropropylate	–	5000	4.7	Arcaricide	(Jayaraj et al., 2016)
		1,4-dichlorobenzene	25–31 days	1516–2138	3.4	Pesticides and disinfectants	(Garny, 2008; Jayaraj et al., 2016)
		Benzene hexachloride	7–8	10,000	–	Insecticide Rodenticide Arcaricide	(Jayaraj et al., 2016)
		Pentachlorophenol	–	27–211	5.12	Herbicide Pesticide	(Jayaraj et al., 2016)
	Industrial chemicals (PCBs)	2-Chlorobiphenyl	80 days	4470	4.46	In electrical industry, additives in paints and carbon less copy paper	(Hawker and Connell, 1988; Tang, 2016)
		2,2′,3,4′Tetrachlorobiphenyl	2.6–4.8	794–1269	5.69		
Unintentionally POPs	PAHs	Anthrone	65–480 days	–	3.7	Formed during manufacture of certain pesticides, paper bleaching and waste incineration	
		Benzanthrone	840–6116 days	–	4.3		
		Benz(C) Acridine	–	–	4.8		
		Benzo [a]pyrene	14–16 month	250	6		
		Chrysene	371 days	>320	5.7		
	Dioxins		10–22	0.022–0.045	6.4		(Hauptman et al., 2016)
	Furans		10–22	5.2	1.3		(Ramamoorthy and Ramamoorthy, 1997)

chemistry-transport models are expected to increase by the factor of two to three for increment of every 10 °C. Hence, the environmental behaviours of POPs are probably influenced by global warming. Global warming augments the volatilization from primary and secondary sources and also influences their partitioning between sediments, water, soil and atmosphere. The POPs depositions onto soil can be raised by increase in rainfall. Moreover, the regular storm flows may increase the mobilization of chemicals in the soil compartment and by land runoffs they can be transported to the aquatic organisms. It has been established that the probabilities of flooding will increase according to the climate change predictions. Flood events will make re-suspension of sediments easier. It further implies that the transfer of contaminants contained in the polluted sediments will be transferred to the surrounding waters more easily (Perrie et al., 2012; Teran et al., 2012; Wu et al., 2015a; b).

Even with very less knowledge about the effect of climate change on the POP, it has been suggested the increase in temperature should initiate faster degradation of these chemicals in the aquatic ecosystem, result of which a reduction of the dietary exposure to POPs (Nadal et al., 2015). Nevertheless, the pollutants can be transported to higher altitude areas because of the increase in temperature where wet deposition will lead to increased POP dietary intake in the exposed northern and indigenous communities. POPs do not show any immediate health impacts. The health impacts are usually a result of chronic, cumulative and long-term exposure to one or more of these substances with major exposure being non atmospheric. Therefore, usually POPs do not cause respiratory health effects. Whereas, ingestion and bioaccumulation of these substances are the routes of concern. Furthermore, though toxic effects of POPs are explained at multiple endpoints, they are not clear when assessing POPs mixtures (Hung et al., 2013; Sonne et al., 2014).

Recently, result of one of the most meaningful studies on the climate change effects over the fate and transport of PCDD/Fs was reported (Chi et al., 2013). Especially, extreme weather conditions (winter monsoon, southeast biomass burning, and tropical cyclone -typhoon-) were studied in Taiwan. The quantity of PCDD/Fs absorbed into air total suspended particles was found to have increased during the winter monsoon period. Hence, it was found that the monsoon transported air pollutants and dust along with cold air over long distances, from mainland China to Taiwan. The authors demonstrated how typhoons events effect the long term remobilization of PCDD/Fs and also supported the theory that remobilization of previously deposited pollutants is possible by such events. As a consequence, higher wind speeds during the climate change will alter the release of primary and secondary PCDD/Fs. Airborne transportation will increase towards downwind locations (e.g., Taiwan) from the main emission areas of the Asian continent due to stronger air circulation. Possibility of Increased frequency and intensity of extreme weather events will result in increased release and a higher risk of remobilization of PCDD/Fs from soils, sediments, and other reservoirs of PCDD/Fs.

Kong et al. (2013a, 2013b) reported that the dominating factor of the variance of modelled absolute fate of POPs is uncertainty in chemical properties and not the uncertainty associated with the climate change. These findings were reported when evaluation of the influence of input data to multimedia models was done, on the modelled fate of 6 PCB congeners under various climate and emission scenarios. When comparing the present conditions with the estimated for the period of 2080–2099, the long term average environmental concentrations of PCBs were forecasted to change in a factor of 2 Kong et al. (2013a, 2013b). The same group of researchers in another investigation (Kong et al., 2014), calculated the steady-state concentrations of hypothetical perfectly persistent chemicals in the Baltic Sea water column under two alternative climate change scenarios (IPCC A2 and B2), being compared to results for a baseline climate scenario. It was highlighted by the application of the POPCYCLING-Baltic multimedia chemical fate model that temperature is the most influential individual climate parameter, more significant than precipitation, wind speed and particulate organic carbon.

Atmosphere plays a major role in transport and fate of POPs and also the interaction of POPs with environmental compartments. Studies revealed that the distribution of POPs in northern hemisphere requires days to weeks while in ocean currents it requires years and decades. Meteorological conditions, POP's physical and chemical properties, removal processes and physical depositional mechanisms are some properties on which the transports of POPS in atmosphere depends. It is a two-step process by which chemicals are transferred from land to atmosphere: 1) phase transition from liquid or solid state to vapours. 2) Turbulent mixing for subsequent dispersion (Toose et al., 2004).

Analysis of the levels of DDTs and HCHs (Cheng et al., 2014), to assess time trends and recycling was done using lake sediment cores form five critical regions in the Tibetan Plateau. Most likely due to the retreat of glaciers as a response to climate warming, an increase in both of these chemicals was found. Because of the climate warming, in the past 30 years with the largest retreat since mid-1980s, glaciers have shrunk by more than 6606 km^2. Due the melting of these glaciers and snow due to the climate warming, stored contaminants are released which were accumulated during the years of high transportation of these pollutants in this region. As a consequence of this, more deposit of DDTs is expected in the lake sediments as the glaciers water discharges into the lakes. In particular, the closed-basin lakes whose main source of water is from melting of the glaciers, became e more important monitor of global warming in terms of temporal trends of OCPs.

As soon as the organic contaminants comes in contact with soil surface, various phenomena's occur which includes leaching of contaminants into groundwater, photodecomposition or/and volatilization, uptake of contaminants by roots and physical and chemical interaction of organic contaminants to the soil components (Fig. 2) (Loffredo and Senesi, 2006). The main component of soil is humic substance which help in the adsorption of organic pollutants in the soil through specific physical and chemical binding mechanism. These properties/mechanism include size, shape, molecular structure, hydrogen and covalent bonding, ionic strength, redox potential, dipole-dipole and Van Der Waals forces (Loffredo and Senesi, 2006). Recently Hansen and co-workers used the Danish Eulerian Hemispheric Model to investigate how likely climate change will affect the atmospheric transport of 13 POPs to the Artic and their environmental fate within the Arctic. They found that at the end of the 2090s the total mass of all compounds were predicted to be up to 55% lower across the Northern Hemisphere than in the 1990s under the applied climate and emission scenarios. In addition, depending on the congener and the applied initial environmental concentrations the change in mass of the PCBs were predicted to range from 38% lower to 17% higher, whereas the mass of hexachlorocyclohexane (HCHs) was predicted to be up to 38% higher within the Arctic. They concluded that in future warmer climate, the pollutants with no or a short emission history will be more rapidly transported to and build up in the arctic environment (Hansen et al., 2015). Later, Khairy et al. did

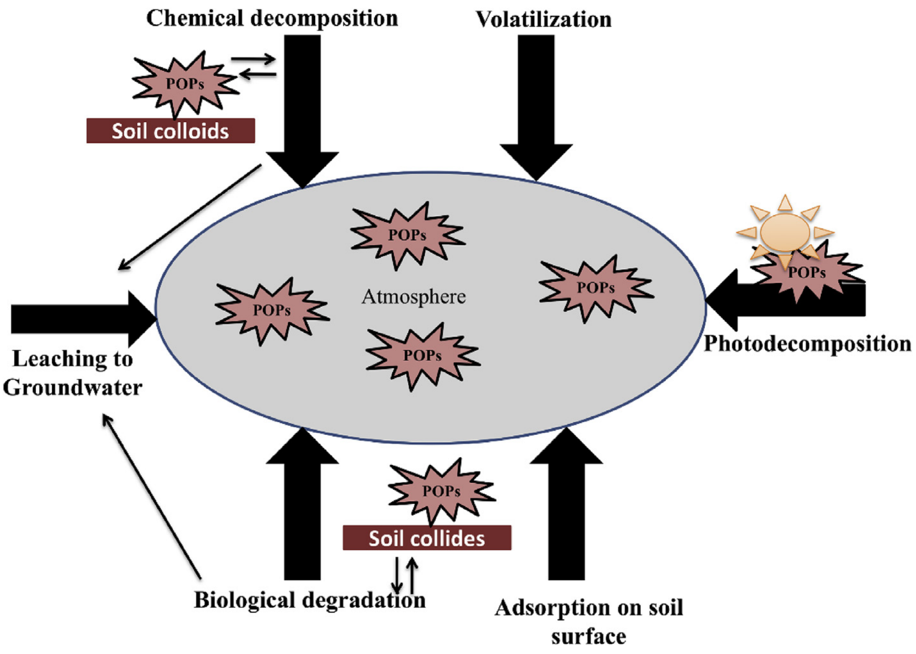

Fig. 2. Fate of POPs in environment.

some studies on the chemical fate of POPs in the atmosphere and snow along the Western Antarctic Peninsula. They have collected air and snow samples during austral spring and analysed for OCPs, PCBs and polybrominated diphenyl ethers (PBDEs). The main idea of this was to assess the relative importance of long range transport versus local primary or secondary emissions. They found that HCB (4.22 pg/m^3), PCBs (11.6 pg/m^3), cis-chlordane (2.43 pg/m^3), heptachlor (5.64 pg/m^3) and PBDEs (4.22 pg/m^3) were the most abundant contaminants. In addition, they have concluded that PBDEs seems to have originated from local source and PCBs, PBDEs and DDTs were observed in highest concentration in the glacier's snow sample (Khairy et al., 2016). South Korea and the Arctic are the only two areas where the climate change impact on the fate of PAHs have been studied. The impact of the climate change on the transport and fate of PAHs within and across environmental media in South Korea was quantitatively assessed by (Cai et al., 2014). For the period from 2009 to 2049, simulations were conducted under the A1B scenario, being compared with a non-climate change scenario. Changes within a factor of 2 for the average concentration of PAHs in air, soil and water was estimated similar to the recent investigations on other POPs. While in soil, degradation rate will play a leading role in the change of PAH levels, whereas in water, runoff and degradation would be the ley process. (Friedman et al., 2014) investigated the effects of PAH emissions for the period 2000–2050 and the climate change on the atmospheric transport of three PAHs (phenanthrene, pyrene, and benzo [a]pyrene). The GEOS-Chem model, combined to meteorology from a general circulation model, was used. The impacts to Northern hemisphere mid-latitudes and the Arctic was the main focus of the study. A minor 2050 “climate penalty” for volatile PAHs, and “climate benefit” for particle-bound PAHs, was estimated. The suggested critical factors for the increase or decrease of environmental PAHs in air were the deposition and surface-to-air fluxes of the 3 analysed PAHs.

In soil and water, the mobility is administered by their half-life, aqueous solubility and sorption or retardation factors such as K_d, K_{oc}, K_{ow}. When hydrophobic organic compounds such as PAH comes in contact with soil, through hydrogen bond and Vander Waal forces some of its portions are rapidly sorbed by the soil components while the remaining gets slowly sorbed. Similarly, when the organic contaminants are desorbed, it follows the same pathway i.e. the desorption proceeds it first rapidly (weak surface chemical interaction) and then slowly (strongly bound) and further very slowly (covalently or physically trapped) (Lohmann et al., 2007). In a similar manner to soil, the organic pollutant from natural (forest fires, volcanic activities) and anthropogenic source (pesticides, hydrocarbons, industrial waste) contaminates the surface and ground water too. Ogbeide et al. examined the relationship between geosorbent properties and field based partition coefficient for pesticides in surface water and sediments of agricultural catchments at Owan, Ogbesse and Illushi communities of Edo State, Nigeria. The results of field-derived pesticides partition coefficients ($K_d < 100$ and $\log K_{oc} < 3$) indicated that pesticides species were largely mobile and by adsorption process, they are less likely to be retained in sediments. In addition, the log K_{ow} values of OCs (DDT, dieldrin and heptachlor epoxide) signify substantial bioaccumulation risk to humans and biota across sites (Ogbeide et al., 2018).

There are different pathways through which POPs are transported in the atmosphere: single hop pathway and multi hop pathway or grasshopper effect. Both the pathways are temperature dependent, wherein in the former one the pollutant never returns to the atmosphere after deposition while in the latter one the deposited pollutant re-enters into the environment for further transport via subsequent multiple atmospheric hops. The organic pollutants are exchanged through volatilization between air and terrestrial surfaces under high temperature which results in the deposition and re-emission of POPs before reaching the final destination (Fig. 3) (Smaranda and Gavrilescu, 2008).

2.4. Health hazards

“Silent spring”, a book written by Rachel Carson discusses about the detrimental effects of pesticides and after the publication, this book spurred a nationwide ban on DDT for agriculture use (Hill, 2013). POPs are one or more cyclic ring structures which can be either aromatic or aliphatic in nature. These cyclic ring structures lack polar functional group and have variable amount of halogen usually chlorine. According to The Aarhus protocol and The Stockholm Convention, DDT, polychlorinated biphenyls, dioxins and furans shows toxicity upon exposure (Harmens et al., 2013). Table 4 shows the occupational exposure limits and lethal dose of POPs according to occupational safety and health administration (OSHA), National Institute of Occupational Safety and Health (NIOSH) and The American Conference of Governmental Industrial Hygienist (ACGIH).

The mechanism of POPs induced toxicity in vertebrates is not clear but several studies showed that the most of the organic pollutants binds to the Aryl Hydrocarbon Receptor (AhR) and induce harmful effects by forming reactive oxygen species (ROS) and finally lead to cell death (Selvakumar et al., 2013; Zhao et al., 2012) (Fig. 4). Chiefly, human expose to these organic pollutants occurs from industries and toxic waste sites. The non-biodegradable nature of these organic pollutants and its prolonged persistence in the environment makes it hazardous to life forms on earth (Augusto, 2012).

3. Microbial degradation

Biodegradation is an evolving technology that comprises the application of selected living microorganisms to degrade, metabolise/immobilise any unwanted substances such as pesticides, organic pollutants and hydrocarbons from soil and water, to improve its quality (Singh and Ward, 2004).

Though every microorganism has the ability to eradicate

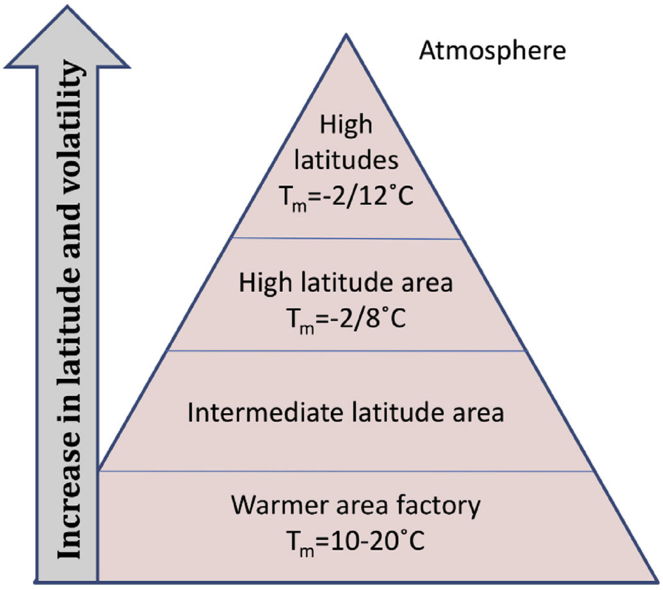

Fig. 3. Mechanism of multi-hop pathway.

Table 4
Occupational exposure limits, lethal dose (LD_{50}) and health hazards of POPs.

POPs	Exposure limit (mg/m^3)			LD_{50} (mg/Kg)	Health hazards	Microbes degrading the pollutants	Mechanism of degradation	References
	OSHA PEL TWA (Skin)	NIOSH REL TWA (Ca)	ACGIH TLV TWA					
Aldrin	0.25	0.15	0.25	83	Carcinogenic, malaise, dizziness, nausea	*Arthrobacter, Bacillus*, *Burkholderia* sp., *Cupriavidus* sp., *Pseudomonas*	Dioxygenation	(Ritter et al., 1995) (Edwards, 1965; Hagley, 1965; Morillo and Villaverde, 2017)
Dieldrin	0.25	0.15	0.25	70	Liver and biliary cancer	*Burkholderia* sp., *Cupriavidus* sp., *Pseudonocardia* sp., *Mucor racemosus*	Dioxygenation	(Morillo and Villaverde, 2017; Ritter et al., 1995)
Chlordane	0.5	–	–	29-40 (oral), 428 (dermal)	Carcinogenic	*Oscillatoria* sp., *Chromatium* sp. *Streptomyces* sp. A2, A5, A6, and A13, *Streptomyces coelicolor* A3, and *Streptomyces* sp. M7	Reductive dechlorination	(Ritter et al., 1995) (Holsapple et al., 1991; Morillo and Villaverde, 2017)
Heptachlor	0.5	–	–	90	Cancer, mutation, stillbirth, birth defects and liver disease	*Phlebia tremellosa*, *Phlebia brevispora*, *Phlebia acanthocystis*	Reductive dechlorination	(Ritter et al., 1995) (Li et al., 2011; Morillo and Villaverde, 2017; Pohanish, 2011)
DDT	1	0.5	1	500	Liver cancer and immune system suppression	*Aerobacter*, *Agrobacterium*, *Alcaligenes*, *Bacillus*, *Clostridium*, *Dehalospirilum multivorans*, *Hydrogenomonas Klebsiella*, *Pseudoxanthomonas jiangsuensis*, *Staphylococcus*, *Stenotrophomonas*, *Streptomyces*, *Xanthomonas*, *Xerocomus chrysenteron*	Reductive dechlorination	(Turusov et al., 2002) (Ritter et al., 1995) (Marion et al., 2011) (Morillo and Villaverde, 2017; Skinner et al., 2013)
Endrin	0.1	–	–	171	Carcinogenic	*Arthrobacter*, *Bacillus*, *Burkholderia* sp., *Cupriavidus* sp., *Pseudomonas*	Dioxygenation	(Dikshith, 2010; Ritter et al., 1995)
HCB	–	–	.002	<5-40	Photosensitive skin lesions, hirsutism hyper-pigmentations,, porphyrinuria and debilitation	*Sphingomonas quisquiliarum*, *Sphingobium lucknowense*, *Eupenicillium baarnense*, *Eupenicillium crustaceum*	Oxidative dechronination	(Gocmen et al., 1989; Ritter et al., 1995) (Gocmen et al., 1986; Morillo and Villaverde, 2017)
PCBs	0.5	1	–	–	Dermal & ocular lesions, irregular menstrual cycle, lowered immune response	*Pseudomonas pseudoalcaligenes* KF707, *Alcaligenes xylosoxidans*, *Pseudomonas stutzeri*, *Ochrobactrum anthropic*, *Pseudomonas veronii*, *Rhodococcus* spp., *Pseudomonas* spp., *Pseudoxanthomonas* spp., *Agromyces* spp., and *Brevibacillus* spp	Reductive dechlorination	(Borja et al., 2005; Gioia et al., 2014) (Mackova et al., 2010; Morillo and Villaverde, 2017)
PAHs	0.2	0.1	1	–	Carcinogenic,, liver and kidney problems chromosome aberrations	*Pseudomonas putida* NCIB 9816, *P. putida* G7, ND6 and BS202, *Pseudomonas* sp.C18, *Ralstoni* Sp.U2, *Cunninghamella elegans, Pleurotus ostreatus, Phanerochaete chrysosporium*	Dioxygenation, P450 monooxygenation, ligninolytic enzymes	(Baek et al., 1991; Boström et al., 2002; Morillo and Villaverde, 2017)
Mirex	–	–	–	600 −740	Acute toxicity, termiticide possible cancer	*Bacillus sphaericus*, *Streptomyces albus*	Reductive dechlorination	(Jayaraj et al., 2016; Morillo and Villaverde, 2017; Ritter et al., 1995)

TWA: time weighted average, REL: recommended exposure limit, PEL: permissible exposure limit and TLV: thresh hold limit value.

pollutants, only few particular or engineered microorganisms are used broadly to eradicate pollutants efficiently such as *Bacillus, Corynebacterium, Staphylococcus, Streptococcus, Shigella, Alcaligenes, Acinetobacter, Escherichia, Klebsiella and Enterobacter* and among them *Bacillus* sp. have been extensively employed in remediation of organic pollutants (Haritash and Kaushik, 2009). Bioremediation technology, applied in perspective to persistent organic pollutant removal takes into consideration the following techniques (Fig. 5):

- Introduction of aeration system (**Bioventing**): It is a process of aerating soil/water to stimulate in situ biodegradation of organic contaminants and promote bioremediation (Hinchee and Leeson, 1996; Hyman and Dupont, 2001).
- Introduction of nutritive media (**Biostimulation**): It involves the modification of contaminated media to provide the nutrition to soil microbiota by adjusting pH, addition of limiting nutrient to improve C: N: P ratio (Singh et al., 2011).
- Introduction of microbial strain under controlled condition (**Bioaugmentation**): It is a process of addition of microbial community (bacteria and fungi) and any biocatalyst (gene and enzyme) to degrade organic/inorganic pollutants (Stroo et al., 2012).

Compared to other traditional technologies (incineration, solvent extraction, and gas phase chemical reduction, alkali metal reduction, landfilling), bioremediation is an economical and eco-friendly process that utilise microorganisms for the removal of organic pollutants from the soil and water. The degradation process could be done under either aerobic (requires molecular oxygen such as mono- and dioxygenase which not only act as a terminal electron acceptor but also as a co-substrate) or anaerobic (requires presence of electron withdrawing group for initial reductive attack) conditions with the help of microorganisms. They either alter the functional groups or degrade the basic structure of the compound leading to the formation of carbon dioxide, water and inorganic salts. In addition, degradation of highly chlorinated compounds are done in anaerobic condition as they are difficult to degrade in aerobic condition (Kot-Wasik et al., 2004; Mehboob, 2010).

The method is not only composed of single strain but also employs diverse, synergistic or antagonist communities in soil or

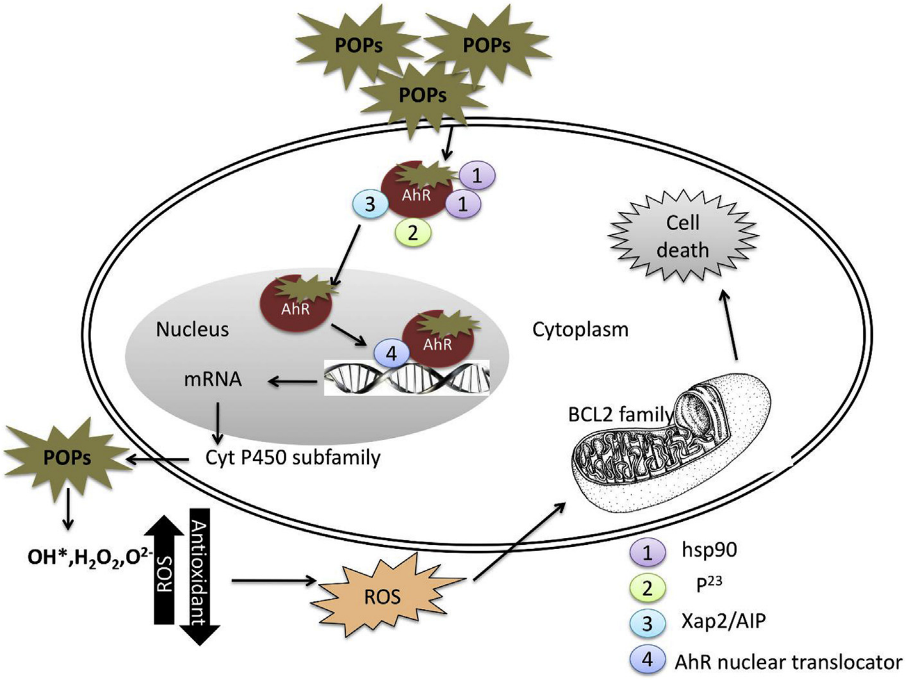

Fig. 4. Mechanism of AhR and ROS induced apoptosis by the influence of POPs.

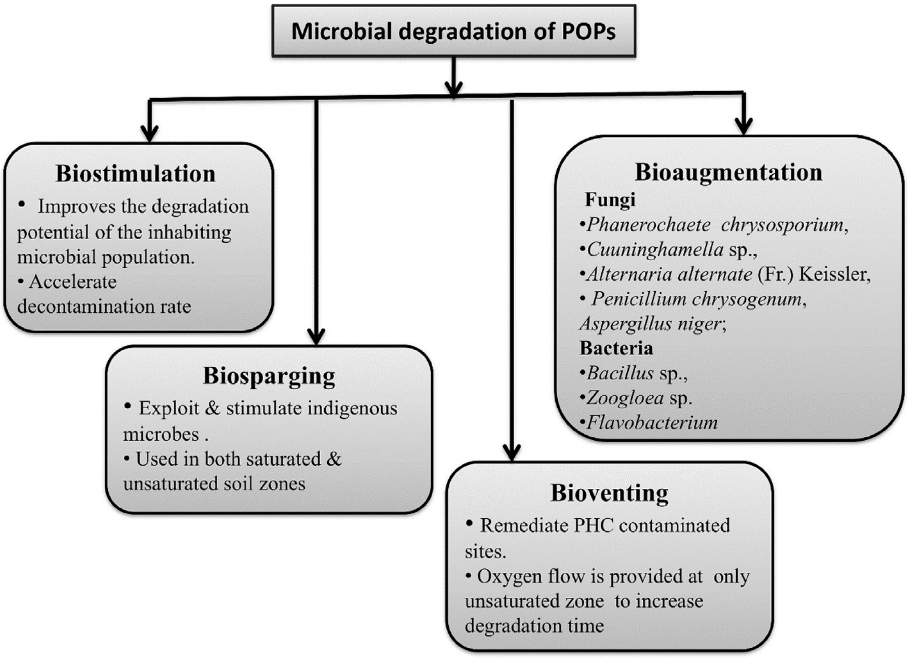

Fig. 5. Degradation techniques of persistent organic pollutants.

aquatic environment. Metabolic cooperation is a process that occurs within a well-coordinated microbial community and biodegradation involves transferring the substrates and products. In this context Table 5 showed the highlights of classification of various bio-remediation techniques, their advantages and limitations. Among microbial community, bacteria, algae and fungi have the ability to bio-transform the persistent organic pollutants, rendering it nontoxic Fungi and bacteria are known to produce different enzymes which acts on a broad array of organic contaminants and help in the degradation of organic pollutants.

3.1. Bacterial degradation

These are the class of microorganisms which involves in the degradation of organic pollutants from the polluted sites and play a vital role in sustainable development of environment and geochemical cycle. Several studies have been done on the degradation of environmental contaminants by different bacteria

Table 5
Various bioremediation methods, their advantages and limitations.

S.No	Bioremediation technique		Pollutants degradation	Advantages	Limitations	References
1	Ex-situ	Biopile	• **Total petroleum hydrocarbon** (TPH) reduction (90.7%). High TPH reduction- due to synergistic interaction between bio-augmentation and bio-stimulation. • **PAH** reduction- 71%	• Limit volatilization of low molecular weight pollutants • Effectively remediate pollutants in extreme environmental conditions such as in very cold regions • Shortens the remediation time by increasing the microbial activities and contaminant availability • Easily scaled up the system up to pilot scale to achieve similar performance obtained during lab studies • Effective in degrading or removing semi and non-volatile organic compounds	• Effective only in removing biodegradable pollutants • If there is a concern about leaching from the pile, biopiles may requires the placement of a bottom liner under the cell • Large area of land will be needed with large quantity of contaminated soil • Drying of soil undergoing bioremediation due to excessive heating, which results in inhibition of microbial activity and promotes volatilization rather than biodegradation • May release unpleasant odors and requires the use of soil conditioner to mitigate	(Abraham et al., 2014; Ali et al., 2016; Asif et al., 2018; Azubuike et al., 2016; Dias et al., 2015; Liang et al., 2014; Morillo and Villaverde, 2017; Shahsavari et al., 2017; Whelan et al., 2015; Zangi-Kotler et al., 2015)
		Windrows	• PAH removal • Eldrin and Endosulfan • DDT and HCH removal	• Speed up the rate bioremediation process, which can be accomplished through assimilation, biotransformation and mineralization • Showed higher rate of hydrocarbon removal depending on the soil type as compared to biopiles	• Due to periodic turning associated with it, windrows may not be the best option to remediate soil polluted with toxic volatiles	
		Bioreactor	• Carbofuran • Benzene, toluene, ethylbenzene and xylene • Total petroleum and PAHs • Naphthalene • Dicofol • Endosulfan, chlorpyrifos, monocrotophos • Ibuprofen, atrazine, benzophenone, diclofenac, ketoprofen, gemfibrozil	• Excellent control of bioprocess parameters such as temperature, pH, agitation speed, aeration rate, substrate and inoculum concentration • Ability to control and manipulate process parameters • Controlled bioaugmentation, nutrient addition, increased pollutant bioavailability and mass transfer can effectively established in bioreactor	• Cost-ineffective, requires more manpower, capital and safety measures in transportation if the volume of soil or other pollutant is too large • Process will be less effective if any parameter or variable of the bioreactor is not properly controlled/maintained at optimum value • Pollutants respond differently to different bioreactor	
		Land Farming	• PAH removal (diesel) • Hexachlorocyclohexane (HCH) • Alachlor, atrazine, metolachlor, and trifluralin	• Requires less equipment for operation and cost effective • Relatively easy to design, construct and maintain • Compiles with government regulations and can be used in any climate and location • Construction of suitable land-farm system – reduces the leaching of pollutants into neighbouring area	• Requires large operating space • Reduction in microbial activities due to unfavourable environmental conditions • Additional cost due to excavation • Reduced efficacy in inorganic pollutant removal • Not suitable for treating soil polluted with toxic volatiles especially in hot climate region. • These limitations makes it time consuming and less efficient	
2	In-situ	Natural attenuation	• Chlorinated solvents • PAHs • Dyes	• Does not requires any excavation thus no extra cost required for this • Used to treat chlorinated solvents, dyes, heavy metals and hydrocarbons	• Soil porosity strongly influence its application to any polluted site	(Azubuike et al., 2016; Gaur et al., 2014; Morillo and Villaverde, 2017; Smith et al., 2015)
		Enhanced Bioslurping	–	• Used to remediate volatile and semi-volatile organic compounds • Designed for free products recovery such as light non-aqueous phase liquid (LNAPLs), hence remediate	• Excessive soil moisture limits air permeability and decrease oxygen transfer rate which reduces microbial activities • Technique is not suitable for remediating soil with low permeability	

Table 5 (*continued*)

S.No	Bioremediation technique	Pollutants degradation	Advantages	Limitations	References
			capillary, unsaturated and saturated zone • This system uses "slurp" that extends into the free product layers and draw up free products and soil gases • Saves cost due to less amount of groundwater resulting from the operation thus minimizes storage, treatment and disposal cost	• Vacuum establishment on a deep high permeable site and water table fluctuation leads to create saturated soil lenses that are difficult to aerate	
	Bioventing	• Toluene contaminated site • Phenanthrene • Chlorinated compounds	• Indigenous microbes activity is increased by controlled stimulation of airflow by delivering oxygen to vadose zone • Addition of nutrients and moisture to achieve microbial transformation of contaminants to harmless state • Popular technique among all other in-situ in restoring sites polluted with light petroleum products • Low air injection increases biodegradation • Number of air injection point helps uniform air distribution and increases bioremediation • Can be used for anaerobic bioremediation especially in treating vadose zone polluted with chlorinated compounds (recalcitrant under aerobic condition)	• High airflow rate does not bring about increase in biodegradation rate not make effective transformation of pollutants • Technique is not suitable for remediating soil with low permeability • Time consuming • Higher air flow rate leads to transfer of volatile organic compounds to the soil vapour phase, which requires off-gas treatment before releasing into the environment	
	Biosparging	• Benzene, toluene, ethylbenzene and xylene (BTEX)-> 70%	• Air is injected at the saturated zone, which causes the upward movement of volatile organic compounds to the unsaturated zone to stimulate biodegradation • Biosparging promotes biodegradation on high airflow rate • Widely used to treat aquifers polluted with petroleum products especially kerosene and diesel	• Major limitation is predicting the direction of airflow	
	Phytoremediation	• DDE • Aldicarb • PCP • DDT • Endosulfan • Cypermethrin • Lindane • HCHs	• Metals can be recovered after remediation which are accumulated in plants • It is an aesthetically pleasing, efficient and eco-friendly process • Economical method, requires low installation and maintenance cost • Not only clean polluted soil but also prevent soil erosion and metal leaching	• Longer remediation time, pollutant concentration, toxicity and bioavailability to plant, plant slow growth and depth of plant roots • Possibility of transferring of accumulated toxic pollutants along with food chain • Plants cannot use organic compounds as a source of carbon and energy because of lack of catabolic enzymes • Plant microbe interaction might not always be optimal for phytoremediation therefore human interventions are required to enhance pollutant removal	
3	Vermiremediation (use of earthworms for remediation)	• DDT • DDE • PCP • Atrazine	• Earthworm gut can greatly modify the structure of soil, destroy and form organomineral complexes	• Need well defined condition to survive such as enough food, adequate climate condition, soil water content	

(*continued on next page*)

Table 5 (*continued*)

S.No	Bioremediation technique	Pollutants degradation	Advantages	Limitations	References
			• Earthworm activity- increases water soluble carbon and carbohydrate concentration- used by microbial community- increases POP degradation rate	• Cost might be too high to remediate large contaminated area	

exclusively on hydrocarbons and these bacteria are known as hydrocarbon degrading bacteria.

Benzene ring after glucosyl residue is widespread in nature and its persistence and thermal stability in the environment contributes to its increases as a pollutant. Out of two types of aforementioned conditions, the biodegradation in anoxic environment is carried out by either strict anaerobes or facultative microorganisms. In addition, these microorganisms uses nitrate (denitrifying organisms), sulphate (sulphate reducers), Fe (III) (ferric-iron reducer), CO_2 (methanogens), or other electron acceptors (chlorate, Mn, etc.) depending upon their electron – acceptor availability and competition of electron donating ability in different microorganisms (Diaz, 2004).

The concentration of sulphate in seawater is high as a result of its involvement as major electron acceptor in marine environment for anaerobic degradation. In terms of energy, sulphate reducer and methanogenic conditions generates less energy as compared to nitrate and Fe (III). Fermentative strains favours the complete degradation process only when associated methanogens or sulphate-reducing bacteria rapidly use the metabolic end products (Muyzer and Stams, 2008). These products are produced during breakdown of aromatic compounds by fermenter and due to this reason the fermentive strains are likely to be limited to syntrophic existence. Acetyl- CoA is produced as an intermediate metabolite during anaerobic degradation of aromatic compounds by the use of photosynthetic bacteria in the presence of light. Reductive dechlorination is a type of bioremediation reaction in which bacteria removes chlorine from contamination (Carmona et al., 2009).

Successful removal of hydrocarbons, pesticides, dioxins and furans by the addition of bacteria has been reported earlier for many compounds, including PAH, PCB, DDT etc. Wanwasan et al. did their study on PAH degrading bacteria, isolated from mangrove sediments and they found that out of all these bacteria strains *Novosphingobium* sp. PCY, *Microbacterium* sp. BPW, *Ralstonia* sp. BPH, *Alcaligenes* sp. SSK1B, and *Achromobacter* sp. SSK4, PCY has a versatility to degrade various PAHs (Wongwongsee et al., 2013). Recently a study has been done on degradation of pesticides by bacterial consortium (*Acinetobacter* sp, *Pseudomonas putida*, *Bacillus* sp, *Pseudomonas aeruginosa*, *Citrobacter freundii*, *Stenotrophomonas* sp, *Flavobacterium* sp, *Proteus vulgaris*, *Pseudomonas* sp, *Acinetobacter* sp, *Klebsiella* sp and *Proteus* sp) isolated from contaminated sites. The result of this study showed that the consortia was able to degrade pesticides successfully (Pino and Peñuela, 2011). Kong et al. carried out studies on degradation of organochlorine pesticides by bacterial strain *Alcaligenes faecalis* JBW4. They found that the strain JBW4 has greater potential for the degradation of endosulfan residue Kong et al. (2013a, 2013b). In another study, *Streptomyces* strains were also used for the degradation of chlordane and 56% reduction of ϒ-chlordane was observed (Cuozzo et al., 2012).

3.2. Fungal degradation

Fungi are ubiquitous organism which plays a vital role in all ecosystems. These are microscopic eukaryotic organism which has the capability to grow on various substrates and are competent of continuing their function almost for an indefinite period of time. These are the diverse group of organisms which includes yeast, molds, and filamentous fungi which has the capability to remediate waste from various industrial wastewaters.

Mycodegradation is a process through which fungi degrades or deteriorates a wide variety of chemicals or compounds. Fungi are known to have an efficient degradation capability as it has been documented in various situation where they destroy different types of materials like wood, textile, plastic, leather and paper materials. PAH, is degraded by *Irpex lacteus* and *Pleurotus ostreatus* from contaminated industrial soil. It was found that the white-rot fungal cultures are capable of not only degrading PAH but also remove the different PAHs (Bhatt et al., 2002). Fungi are also assists in the degradation of pesticides, dyes, hydrocarbons, polychlorinated biphenyls, chlorinated and phenolic compounds by the use of different enzymes produced by them such as laccases, manganese peroxidase (MnP) and lignin peroxidises (LiP) (Bhattacharya et al., 2012).

Fungi also have the ability to modify the soil permeability, ion exchange capability and detoxify contaminated soil. As they are slow growing, they require substrate for co-metabolism. Several white-rot fungi such as *Phanerochaete chrysosporium*, *Pleurotus ostreatus*, *Trametes versicolor*, *Irpex lacteus* and *Lentinula edodes* has the ability to degrade various toxic compounds by using numerous oxidative and reductive mechanisms.

Many fungi (*Mucor alternans*, *Fusarium oxysporum*, *Tricoderma viride* and *Phanerochaete chrysosporium*) are known for a long time to have capability to degrade DDT. Fungi uses lignin peroxidises for the mineralization of DDT and in some fungal strains the rate of mineralization is depend upon the carbon source. The rate and extent of mineralization of DDT is lesser as compared to its analogues such as dicofol and methoxychlor.

Tricoderma harzianum degrades endosulfan and is catalyses oxidation to endosulfan sulphate followed by hydrolysis to endosulfan diol. To enhance the metabolism process nicotinamide adenine dinucleotide phosphate (NADPH) is added. The endosulfan metabolism involves two pathways: hydrolytic and oxidative. The endosulfan can be oxidised to sulfur containing endosulfan or non sulfur containing endosulfan. The hydrolysed endosulfan produces the endosulfan diol and after its oxidation endosulfan hyroxyether is produced which then finally form endosulfan lactone and endosulfan dialdehyde. The sulfur containing endosulfan (endosulfan sulphate) can be inhibited by cytochrome P450 and it enhances the hydrolysis process.

Recently studies have been conducted on mycoremediation of PAH contaminated oil based drill cuttings by using white rot fungi. The results showed that the fungi are suitable in biotreating PAH contaminated oil based drill cuttings (Okparanma et al., 2013). In another study, the capability of *Pleurotus ostreatus* in the utilization of benzo-(α) pyrene by the production of ligninolytic enzyme was also studied. The study revealed that the selected strain is capable of degrading of benzo-(α) pyrene with certain alteration in the process and it could serve as a better option in remediation of PAH (Bhattacharya et al., 2012).

It is well known that white rot fungi are able to degrade PAHs from soils and sediments. To increase the extent of degradation, mycelia of several species have been used. *Phanerochaete chrysosporium* is known to be best strain that oxidize pyrene, anthracene, fluorine and benzo [a]pyrene into quinines by LiP and MnP. Several reports have shown that PAHS oxidation mechanism by lignolytic fungi is similar to non-phenolic lignin degradation (Cerniglia, 1997; Peng et al., 2008). A relationship between ionization potential (IP) and specific activity of MnP and LiP has been found and it was concluded that IP and Oxidation rate are inversely proportional to each other. The IP of LiP and MnP are 7.55eV and 8.2ev respectively.

3.3. Algal degradation

In ecosystem, many microalgae and protozoa are present which are involved in various activities but only few of them are reported in the degradation of hydrocarbons, pesticides and PCBs (Jain and Bajpai, 2012). Some microorganisms utilise the non-chlorinated aliphatic and aromatic hydrocarbons as a carbon source in their metabolic pathway. Due to the hydrophobic nature of these hydrocarbons, they pass very slowly to the active site of the microorganisms. Algae that are capable of degrading petroleum hydrocarbons into their less toxic form, functions with the help of certain enzymes produced by them (Chekroun et al., 2014). Studies has been done on *Scenedesmus obliquus* GH2, which was used to construct an artificial microalgae-bacterial consortium for degradation of crude oil and it was found that both the aliphatic and aromatic hydrocarbons were efficiently degraded by artificial consortium (Tang et al., 2010).

Similarly, many algal species like *Rhodococcus genus*, *Caepidium antarticum*, *Desmarestia* sp., *Focus* sp. and *Ascophyllum nodosum* are found to be effective in efficient degradation of hydrocarbons (Chekroun et al., 2014). Not only hydrocarbons, but also, pesticides are degraded by many algae. Recent investigation has been done which showed that the *Scenedesmus obliquus* and *Scenedesmus quadricauda* were capable of removing dimethomorph, pyrimethanil and isoproturon from their medium (Dosnon-Olette et al., 2010).

Degradation of xenobiotics in algae or photosynthetic organism occurs in three phases (Fig. 6). In phase I the addition of reactive functional groups like oxidations, reductions, or hydrolysis occurs. These groups are catalysed by membrane bound protein MFO i.e. Cyt P450 and Cyt b5, which transforms the lipophilic xenobiotics into water soluble compounds and NADPH cytochrome P450 reductase. The phase I is further divided into various steps: 1) Binding of substrate to the prosthetic heme ferric iron group of the enzyme. 2) Reduction of iron by flavoprotein P450 reductase. 3) The release of product by the formation of substrate radical after the addition of second electron by Cyt b5. Subsequently the peroxides are formed and O—O bond gets cleaved.

In Phase II, **to** facilitate the excretion, the large and polar groups such as GSH and glucuronic acid (GA) are covalently added to xenobiotics. Several xenobiotics are metabolises by an integrative process involving previous exploits of the phase I enzymes while others posse the essential functional groups like —COOH, —OH or —NH_2 by conjugative phase II enzymes such as GST and UDP-glucoronyl transferases (UDPGTs) in direct metabolism. In phase III, the xenobiotics gets compartmentalised in cell wall fraction or in vacuole (Torres et al., 2008).

4. Mechanism of degradation

4.1. Pesticides

The process of biodegradation of organic pollutants depends upon accessibility, bioavailability and metabolic potential of microorganisms to detoxify or transform the pollutants. Hydrolysis, oxidation, addition of oxygen to double bond, oxidation of amino group to nitro group, dehalogenation, reduction of nitro group to amino group, replacement of sulfur to oxygen, ring cleavage and addition of hydroxyl group to benzene ring are the several enzyme

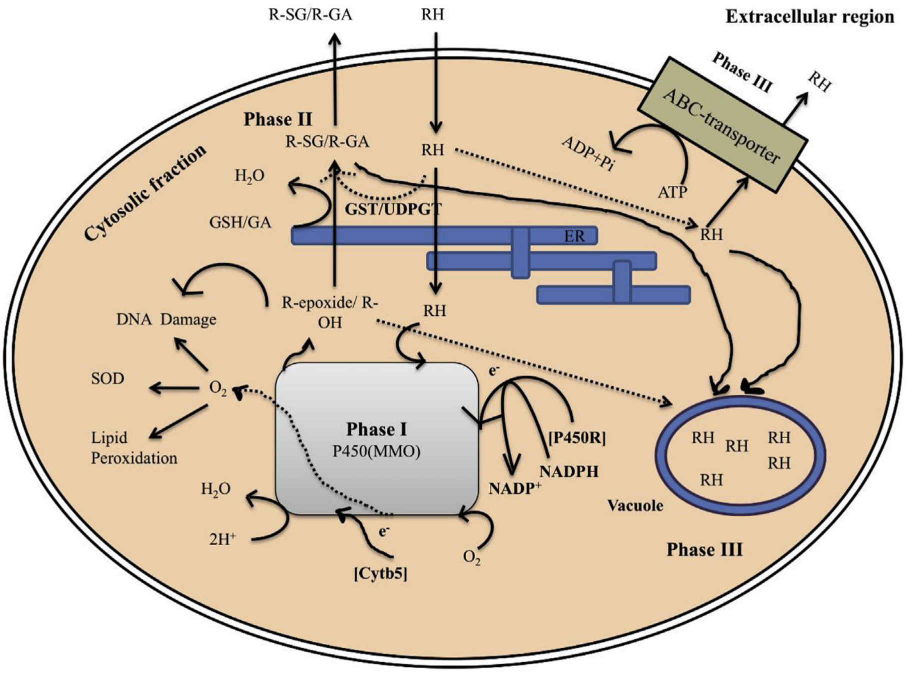

Fig. 6. Metabolism of xenobiotics in photosynthetic organisms. By pass reactions are represented by dot lines. ER: Endoplasmic reticulum.

catalysed metabolic reactions which occur during degradation (Ortiz-Hernández et al., 2013).

Enzymes involved in the degradation of pesticides are divided into two systems: First metabolism stage (hydrolases, estrases and mixed function oxidases) and Second metabolism stage (glutathione S-transferases). Pesticide metabolism is a three phase process: Phase I metabolism, Phase II metabolism and Phase III metabolism. Some extracellular or intracellular enzymes like Hydrolytic enzymes, peroxidises, oxygenases etc are the enzymes that are produced by the fungi or bacteria during pesticide metabolism. The more water soluble and less toxic product is produced in phase I metabolism by the transformation of parent compounds through oxidation, reduction and hydrolysis. In phase II, the pesticides or pesticide metabolites are conjugated with sugar or amino acids to increase the solubility in water and reduce toxicity as compared to the parent compound. While in the final phase, phase II metabolites are converted into secondary conjugates, which are also non-toxic (Ortiz-Hernández et al., 2013).

Hydrolases, are the broad group of enzymes which operates in the absence of redox cofactor that are involved in the degradation of pesticides containing ester, amide, carbon-halide or phosphate linkage (Mirsal, 2008). Similarly different hydrolysing enzymes are also present which helps in the degradation of pesticides.

Phosphotriesterases (PTEs) are homo-dimeric protein having molecular weight of 36Kda (monomeric) which detoxify and hydrolyze pesticides that contains organophosphates. The microorganism that produces PTEs has the *opd* (organophosphate-degrading) gene which decreases the ability of OPs to inactivate acetyl cholinesterase (AchE). The proposed mechanism of PTEs activity is as follow: The water molecule is activated by the removal of proton from it with the help of enzyme active site and the inverted configuration product is obtained by attacking activated water to the phosphorus present at the centre of pesticide. In addition, with the participation of zinc atom, the active site is also polarized by the oxygen atom (Jaiswal et al., 2017; Verma et al., 2014).

Estrases are the class of hydrolases that are highly variable and has been identified as most important in the metabolism of organic pollutants. There are different types of estrases but two amongst them are important and these are Estrases A and Estrases B. The easterases A contains the Cys residue and the organophosphate interacts with the –SH functional group and are easily hydrolysed by water while the Esterases B contains the Ser residue, known as Carboxiestrases, which hydrolyses the endogenous compounds, organic pollutants with ester, amide, thioester, phosphate esters and acid anhydrides in mammals. In addition, the organophosphate interacts with the Ser-OH bond forming a P=O bond which is then hydrolysed by water (Zhang and Qiao, 2002).

Mixed function oxidases (MFO) enzyme system comprises of two membrane proteins: Cytochrome P450 and NADPH-cytochrome P450 reductase. MFO requires NADPH and O_2 for its activity as one molecule is reduced to water while the other is incorporated into the substrate. The cytochrome P450 family is large and well characterised group of monooxygenase enzyme as it uses molecular oxygen for hydrolyses and oxidation of substrate. In addition, to the remediation of pesticides, P450 requires a non-covalently bound cofactor to recycle their redox centre. MFO is also found in endoplasmic reticulum and mitochondria of insects and helps in the growth, development, reproduction etc (Zacharia, 2011). Glutathione-S-transferase (GST) is a system in transferases which catalyses the conjugation of glutathione (GSH) to an electrophilic site on the introducing xenobiotics. It plays a vital role in the detoxification of pollutants. Glycine, cysteine and glutamic acid form the glutathione (Prione et al., 2016). Oxidoreductases are another group of enzymes that uses molecular oxygen as an electron acceptor and catalyse the oxidation/reduction reaction. .

4.2. Polychlorinated biphenyls

Biphenyl (Bph)- utilizing bacteria are ubiquitous in nature. Till date, several gram-positive and gram-negative PCBs degrading bacteria have been isolated. For the degradation of PCBs and other organic pollutants including dioxins and chlorinated ethanes, biphenyls dioxygenase can be used. Biphenyl-utilizing bacteria uses biphenyl-catabolic enzyme for the degradation of PCBs into chlorobenzoic acid through an oxidative route (Abramowicz, 1990; Unterman, 1996).

The Bph gene produces different types of dioxygenase such as BphA, BphB, BphC and BphD which are involved in the catabolic degradation of biphenyl. A Resike-type, three component enzymes known as Biphenyl dioxygenase is composed of an electron transfer chain and terminal dioxygenase. The electron transfer chain involves the transfer of electron from NADH to the terminal dioxygenase and consist of ferredoxin and ferredoxin reductase. While the terminal dioxygenase consist of large and small subunit and these subunits are connected as $\alpha_3\beta_3$ heterohexamer and primarily large subunit is involved in substrate recognition (Furukawa et al., 2004).

In *Pseudomonas pseudoalcaligenes* KF707 the degradation of biphenyl occurs in two pathways (Fig. 7): Upper pathway and lower pathway. In biphenyl metabolism the upper pathway enzymes are encoded by Bph gene clusters where the subunits of terminal dioxygenase are encoded as *bphA1* (large subunit) and *bphA2* (small subunit). In addition the *bphA3* and *bphA4* encodes ferredoxin and ferredoxin reductase respectively (Ohtsubo et al., 2000). 2,3-dihydro-2,3-diol are obtained by the activation of molecular oxygen by terminal dioxygenase which introduce molecular oxygen into biphenyl molecule at 2,3 position, followed by the dehydrogenation of 2,3-dihydro-2,3-diol to 2,3-dihydroxybiphenyl by dihydrodiol dehydrogenase (BphB). 2-hydroxy-6-oxo-6-phenylhexa-2,4-dienoic acid (HOPD) is produced by the cleavage of 2,3-dihydroxylated ring between carbon atoms 1 and 2 by the 2,3-dihydroxybiphenyl dioxgenase (BphC) as it does not involve any external reductant (Gibson et al., 1993).

Studies on biodegradation of PCBs by *Sinorhizobium meliloti*, which is a rhizobial strain was done. It was found that the *S. meliloti* plays a vital role in degradation of PCBs in both liquid and soil culture. Moreover, it may also increases the biphenyl degrading bacteria count and HOPDA was produced as a biotransformation product of 2,4,4′-TCB by *S. meliloti* (Tu et al., 2011). Recently another work was conducted on four bacterial strains isolated from PCB contaminated sites and the expression of PCB degrading enzymes was also studied. The four bacterial isolated strains were *Alcaligenes xylosoxidans*, *Pseudomonas stutzeri*, *Ochrobactrum anthropi* and *Pseudomonas veronii*. Among the four bacterial strains *Alcaligenes xylosoxidans* was found to be most promising for degradation of PCB (Murínová et al., 2014). Several studies have been done and are going on in isolation and identification of PCBs degrading bacteria's. Several bacterial species such as *Rhodococcus* spp., *Pseudomonas* spp., *Pseudoxanthomonas* spp., *Agromyces* spp., and *Brevibacillus* spp. have also been found which displayed the greater biodegrading capability (Nabavi et al., 2013; Shuai et al., 2010).

4.3. Polycyclic aromatic hydrocarbons (PAH)

According to the clean-up standards it is essential to eliminate PAH during remediation of contaminated soil. Dioxygenase, ligninolytic enzymes and cytochrome P450 monooxygenases are involved in the degradation of PAHs. Naphthalene, phenanthrene and anthracene are the low molecular weight PAHs that are

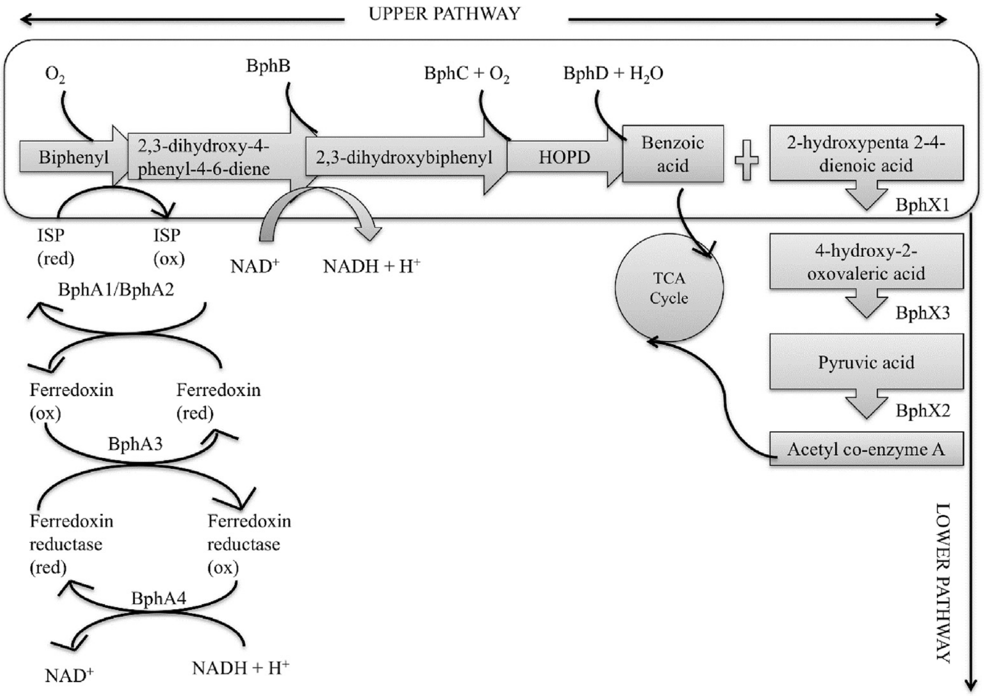

Fig. 7. Degradation pathway of biphenyl in *P. pseudoalcaligenes* KF707. ISP, iron-sulfur protein.

degraded by bacteria in soil. Several filamentous fungi, basidomycetes, white-rot fungi are found to be capable of utilizing PAHs (naphthalene, phenanthrene, pyrene, catechol etc.) more efficiently as compared to bacteria. The two main mechanisms through which PAH are degraded by fungi are Cytochrome P450 system and ligninolytic enzymes (Peng et al., 2008; Simarro et al., 2013). Apart from aerobic degradation PAHs can be degraded by anaerobic process by the formation of reducing product. Fig. 8 shows the different pathways in the metabolism of PAHs by different enzymes.

4.3.1. Dioxygenase

Molecular oxygen is required for the initiation of enzymatic attack of PAH ring in the bioremediation mechanism. Initially, the vicinal *cis*-dihydrodiols are produced in the aerobic bacterial system by the oxidation of arenes in the presence of dioxygenase. Protocatechuates and catechols are produced by the cleavage of dihydroxylated intermediates through any of the pathway, either an *orhto*-cleavage or a meta-cleavage pathway by intradiol or extradiol ring cleavage dioxygenases. The two products formed are then further converted into tricarboxylic acid (TCA) cycle

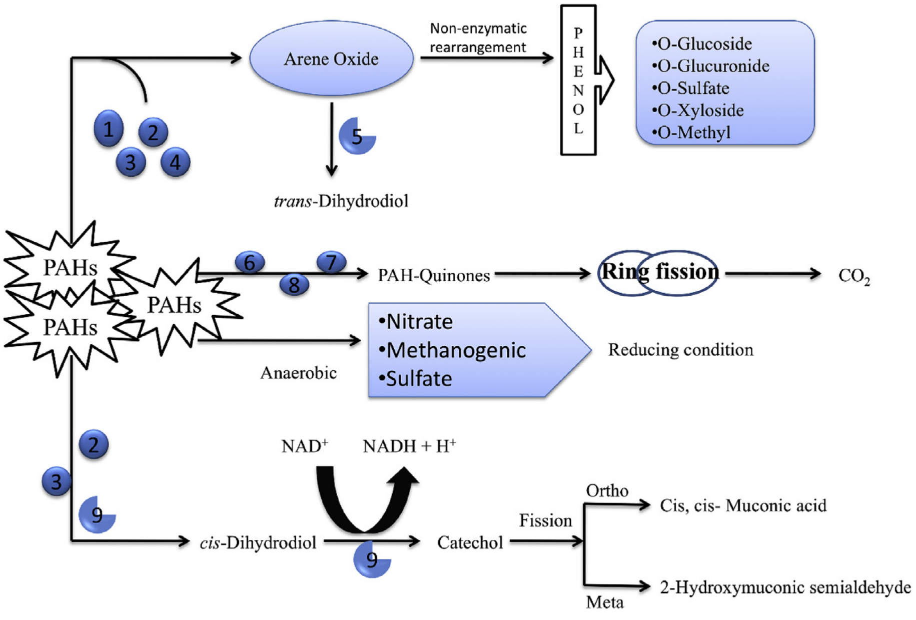

Fig. 8. Proposed pathway of microbial catabolism of PAHs. 1. Fungi 2. Bacteria 3. Oxygen 4. Cyt P450 monooxygenase 5. Epoxide hydrolase 6. White rot fungi 7. Hydrogen peroxide 8. Ligninolytic enzymes 9. Dioxygenase.

intermediates. The bi- and tri-cyclic PAH substrates are oxidised by bacterial naphthalene dioxygenase system which is a multicomponent enzyme which includes an NADH oxidoreductase, a ferredoxin and an oxygenase component (contains active site). Unlike Biphenyl dioxygenase, naphthalene dioxygenase system (NDO) contains catalytic portion composed of large (α) and small (β) subunits in $\alpha_3\beta_3$ configuration. The large subunit (α) of catalytic portion contains the Rieske [2Fe–2S] centre and mononuclear non-heme iron. Naphthalene degrading bacteria is ubiquitously present and the enzyme which is responsible for its degradation has been purified and characterised from different bacterial strains. The *nal* (convert naphthalene to salicylate and encodes the upper pathway enzymes) and *sal* (convert salicylate to pyruvate and acetyl coenzyme A and encodes lower pathway enzymes) are the two operons of the naphthalene catabolic gene (*nah*) of NAH7. These operons are tightly linked genetically to each other and to their common regulatory gene terms nahR. The transacting positive regulator which is encoding by nahR gene belongs to the LysR family of transcriptional regulator that are broadly distributed in bacteria.

ndo genes from *Pseudomonas putida* NCIB 9816, *nah* genes from *P. putida* G7, ND6 and BS202, *dox* genes from *Pseudomonas* sp. C18 have been reported before, which encodes the upper pathway enzymes. *nag* gene is the naphthalene dioxygenase gene which is present in *Ralstoni Sp.* U2 that contains all the genes equivalent to *nah* gene of *Pseudomonas* strains. The difference in the *nah* and *nag* gene is of the two extra genes that are inserted between ferredoxin and ferredoxin reductase gene in nag gene (Yang et al., 1994).

Heme-thiolate is the protein, associated with the endoplasmic reticulum membrane of fungi and cytochrome P450 monooxygenases are its superfamily. P450 monoxygenase catalyse the introduction of oxygen into a wide array of compounds to achieve its biological function such as detoxification and steroidogenesis. The metabolism pathway for PAH of fungi and mammals are similar as both secretes the same enzymes. Cytochrome P450 monooxygenase/epoxide hydrolase is the chief pathway in the primary oxidation of PAHs and trans-dihydrodiols are formed by the catalysis of reaction. Some non-ligninolytic fungi such as *Cunninghamella elegans* show similar metabolic steps as liginolytic fungi (*Pleurotus ostreatus*). Fluoranthene is metabolized into fluoranthene trans-2,3-dihydrodiol, 8- and 9-hydroxyfluoranthene trans-2,3-dihydrodiol by *C. elegans* while pyrene is metabolized into pyrene trans- 4,5-dihydrodiol by *P. ostreatus* (Peng et al., 2008).

Numerous PAHs and phenols are conjugated with sulphate, glucoronic acid or glucose and all can be oxidised by cytochrome P450. Studies have been done on *Phanerochaete chrysosporium* that has the capability to produce P450 monooxygenase. The two genes pc-1(CYP63A1) and pc-2 (CYP63A2) of P450 monooxygenase were regulated under nutrient rice and limited medium to check its response against environmental pollutants like PAHs, DDT and lignin derivatives. The results showed that these two genes showed positive response against the mentioned pollutants (Doddapaneni and Yadav, 2004). In another similar study benzo(α) pyrene was degraded by white rot fungus *Phanerochaete chrysosporium* using P450 monooxygenase in both ligninolytic and non-ligninolytic phase. In non-ligninolytic phase the P450 –hydroxylated metabolites were formed along with the up regulation in pc-2 (CYP63A2) and pah4 (CYP5136A3) while in ligninolytic phase the degradation rate gets higher (91.6%) (Bhattacharya et al., 2013).

4.4. Lignin degradation

The lignin catabolism enzyme of fungi are more likely to be appear than bacteria to make the initial attack on PAHs in soil because of the benefit of being capable to diffuse to the immobile PAHs. As the nutrients in the medium get depleted the ligninolytic peroxidises gets produced in secondary metabolic process. Degradation of PAHs by *Irpex lacteus* has been studied and it was found that this strain is proficient in PAHs degradation. Along with effective degradation this strain also produces mainly MnP and showed higher activity in nutrient limited media (Cajthaml et al., 2008).

The lignin degrading enzyme is divided into three groups which can act separately or in co-operation: 1. cellulose and hemicellulose complexes, laccase, different peroxidises, protocatechuate-3,4 dioxygenase etc (attack the wood constituent and their primary degradation products directly). 2. Aryl alcohol oxidase and gyloxal oxidase (do not attack wood component directly). 3. Glucose oxidase and cellobiose:quinine oxidoreductase (includes feed-back type enzymes). Peroxidise and laccase are extracellular oxidative enzyme which cleaves the carbon-carbon or carbon –oxygen bond in lignin polymer. Moreover, these enzymes have the ability to form radicals by catalysing one electron oxidation and thereby are extensively studied in bioremediation (Pollegioni et al., 2015). Fig. 9 shows the mechanism of degradation of ligninocellusic biomass by white rot fungi.

Laccases are important ligninolytic enzymes that can not only be constitutive but also be inductive and has these two properties: 1. the structural similarity between compounds and substrate for this enzyme 2. Similarity between substrate or compounds with natural growth substrates for fungi (Pozdnyakova et al., 2010). Laccase which is used for bleaching in pulp and paper industry provides a broad perspective in detoxification of organo-pollutants in soil (Gaur et al., 2018). The lignocelluloses constituents, cellulose, hemicelluloses and lignin are degraded by enzymes that convert cellulose and hemicelluloses into simple sugars. In addition, many bacteria, fungi and protozoans degrade the polysaccharide component of lignocelluloses into mono- and disaccharides by using a whole string of hydrolases. The white rot fungi have the capability to attack the lignin barrier efficiently because these groups of fungi have flexible machinery of enzymes co-operating with its certain secondary metabolites. These fungi transform and degrade polysaccharides and lignin by using multi-enzyme system (Shekher et al., 2011). Fungal laccase, also known as benzenediol: oxygen oxidoreductase, are also produced by white rot fungi or produced in the medium by mycelia of *Basidomycetes*, *Ascomycetes* and *Deuteromycetes*. Biochemically, it is an enzyme which oxidises a range of aromatic hydrogen donors. In addition, it forms free phenoxy radicals and amino radicals by catalysing electron and proton from phenolic hydroxyl and aromatic amino group respectively.

Lignin peroxidise (LiP), initially was known as ligninase cultured from *Phanerocharte chrysosporium*. After years of research, it was also isolated from *Phlebia radiate* and *Trametes versicolori* both strains belonging basidiomycetes. Its molecular weight is between 38 and 47 kDa and requires hydrogen peroxide (generated by other enzymes like oxidases) for its activation. The active site of the enzyme contains heme group while its catalytic site resembles horse radish peroxidise. For degradation of aromatic lignin, it does not requires any redox mediator and catalyse many oxidations on the alkyl side chains, cleavage of C–C side chains of lignin subunits. Although the enzyme is acidic (pI-3-5) but it shows low optimum activity in between pH 2.5–3.0 (Falade et al., 2017).

Manganese peroxidise (MnP) is an extracellular glycosylated enzyme that contains the heme as a prosthetic group having molecular weight from 40 to 48 kDa and pI between 2.9 and 7.0. *Phanerochaete chrysosporium*, *Trametes versicolor*, *Phlebia radiate*, *Cus bisporus*, *Nematoloma frowardii and Stroharia rugosoannulata* produces MnP. The catalytic cycle of MnP includes native ferric enzymes as well as MnP I and MnP II redox states and Mn^{2+} requires as electron donor in reductive reaction. Both the states (MnP I & Mnp II) are reduced by Mn^{2+} which is later oxidised to Mn^{3+}. In addition

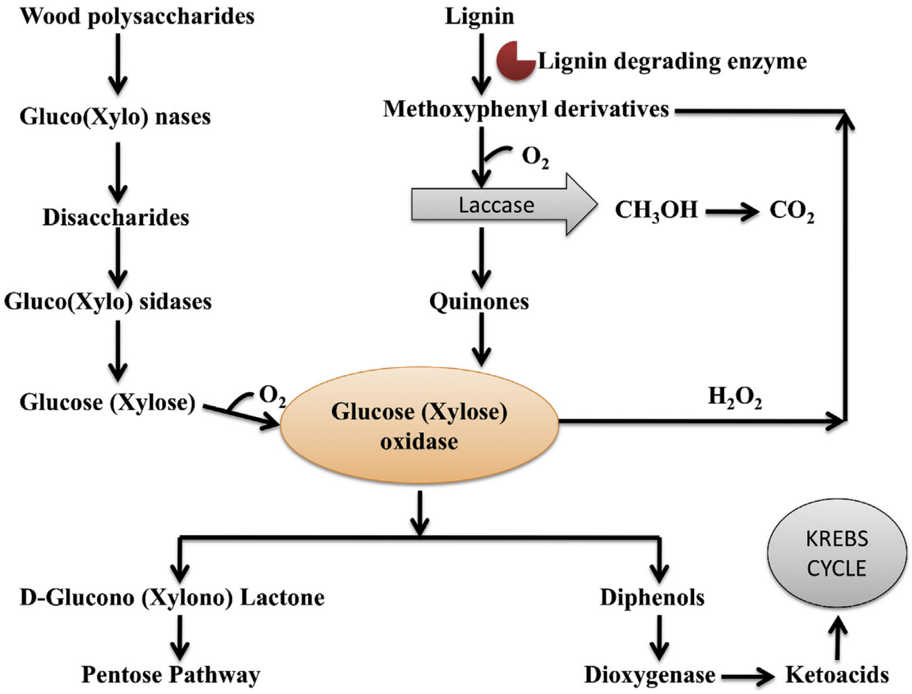

Fig. 9. Mechanism of lignocellulose biomass degradation by enzymes of white rot fungi.

Mn^{3+} ions are alleviated to high redox potential via chelation with organic acids (oxalate, malonate, malate, tartrate and lactate). Finally the chelated Mn^{3+} act as a diffusible redox mediator that oxidises phenolic compounds (Fig. 10) (Hatakka et al., 2003).

4.5. Pharmaceutical and personal care product (PPCPs) degradation

PPCPs are the group of compounds which consists of any substances used for personal care (used to maintain hygiene and general well-being such as cleansing products, fragrances and protective products) or medicinal (diagnostic chemicals, drugs, curative agents and preventive treatments) purposes. Their fate is dependent on parts of the application of product and its chemical properties. Products such as hygiene and fragrances are applied externally, typically enter the wastewater stream in the form of recalcitrant compound. So there is a need of degradation of these compounds through microbes as it is considered as most effective mechanism for organic pollutant removal (Wang and Wang, 2016).

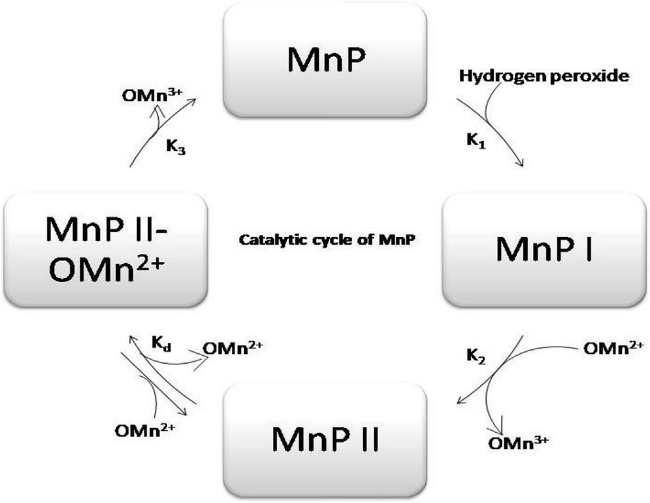

Fig. 10. Mechanism of MnP catalysed formation of Mn^{3+} oxalate complexes.

A number of studies have reported that frequently detected PPCPs such as sulfamethoxazole, iopromide, paracetamol, triclosan, diclofenac and carbamazepine can be degraded by pure cultures isolated from activated sludge, effluent or sediments. Pure cultures isolated from activated sludge process show the ability to degrade broad range of PPCPs. For example, *Achromobacter denitrificans* can degrade all sulphonamides including sulfamethoxazole. Furthermore, with different degradation mechanism, many pure cultures can use specific PPCPs as sole carbon and energy source such as paracetamol and can be degraded by *Stenotrophomonas Pseudomonas aeruginosa* and *Delftia tsuruhatensis*. Biosorption played an important role in removal of paracetamol for *Stenotrophomonas* while in case of *Pseudomonas aeruginosa* and *Delftia tsuruhatensis* it played a negligible role, this may be due to the presence and involvement of different enzymes in the degradation process. Enzymes plays an important role in biodegradation of PPCPs and its biodegradation can be determined by the production of specific enzyme (for decomposition) by the microorganism. For instance, ammonia monooxygenase can be produced by *Nitrosomonas europae* which can decompose triclosan but many recalcitrant PPCPs such as tetracycline, ciprofloxacin and trimethoprim cannot degrade properly by the microorganisms as these drugs cannot induce microorganisms to produce the specific enzyme. Therefore to improve the biodegradability of the refractory PPCPs, the main step is to induce microbes to yield particular enzyme (Daughton, 2001; Kagle et al., 2009).

White rot fungi (WRF) also plays an important role in PPCPs degradation. WRF removes PPCPs by any of the mechanism: (1) uses laccase, MnP and lignin peroxidase, (2) sorption onto fungal biomass and (3) degradation by intracellular enzymes. For instance, naproxen degradation by white rot fungi utilises laccase and cytochrome P450. In this process, 6-desmethylnaproxen and 1-(6-methoxynaphthalen-2-yl)ethanone, intermediates were observed possibly via P450-mediated desmethylation and laccase catalysis respectively. Additionally, from the reaction mixture naproxen and its associated intermediates were removed from the effluent completely. In another study, *T. versicolor* and *P. ostreatus* have been used for the degradation of carbamazepine and 10–11,dihydro-10-11dihydroxy-carbamazepine, acridone, acridine and 10,11-epoxy-carbamazepine were identified as a number of stable intermediate products. Remarkably, the treated effluent was less toxic (Asif et al., 2017).

Apart from these fungal degradation mechanism, bacterial enzymes such as monooxygenase, Flavin adenine dinucleotide binding domain, hydroxylation etc. are used for the degradation of PPCPs. The proposed catabolic pathways of ibuprofen and octylphenol (OP) by bacterial isolates are shown in Fig. 11. The proposed degradation pathway of OP by *Sphingomonas* sp. strain PWE1 is mentioned in Fig. 11a. Initiation of OP degradation was done by adding a hydroxyl group to the alkyl-substituted carbon of OP by using putative Flavin monooxygenase OpdA. This is followed by its (intermediate) conversion to either octyloxyphenol or hydroquinone and a carbocation corresponding to the octyl sidechain through type II *ipso* substitution. This pathway suggested that this mechanism may be conserved atleast within *Sphingomonads* (Kagle et al., 2009). Fig. 11b shows the proposed pathway of ibuprofen degradation by *Sphingomonas* sp. strain Ibu-2. The degradation of ibuprofen by Ibu-2 appears to be commenced by the formation of ibuprofen-CoA in the presence of *ipfF* (encodes coenzyme A ligase). This is followed by the formation of putative 1,2-*cis*-diol-2-hydroibuprofen-CoA by dioxygenase attack encoded by *ipfAB*. 4-isobutylcathechol is formed by the sequential removal of propionic acid side chain by the putative acyl transferase *ipfD*. Later the 4-isobutylcathechol via *meta* cleavage is further metabolized (Kagle et al., 2009).

5. Advanced oxidation process for wastewater treatment

Type and concentration of contaminants present, level of pollutants allowed in the discharge, volume of the wastewater to be treated and treatment procedure cost are the following criteria on which the wastewater treatment methodology depends. Effluent from chemical, agrochemical, pharmaceutical, cosmetic and pulp and paper industry contains several organic pollutants which are not easily degradable. Therefore conventional wastewater treatment plants are not sufficient to remove them to desirable level. Various physical, chemical and biological treatment methods have been applied for wastewater treatment. Though these methods have many disadvantages and cannot be implemented for large scale treatment. For instance, in precipitation method sludge formation occurs while coagulation and flocculation via chemical generates large amount of sludge and chemicals which contains hazardous materials. Adsorption process have been widely used for the treatment of various pollutants present in wastewater but the major drawback in adsorption process is the contaminant only transfer to the adsorbent and there is a need of regeneration of adsorbent regularly, resulting in additional cost. For full scale treatment and reuse of water and chemicals membrane technologies such as reverse osmosis, nanofiltration and ultrafiltration have been used. But in addition to high cost these methods have several operational difficulties. Therefore, for complete removal of contaminants from the environment physical methods may not be suitable (Chakraborty and Das, 2016; Krishnan et al., 2017; Muruganandham et al., 2014).

Similarly, aerobic and anaerobic biological wastewater treatment methods have been employed but these methods also do not completely remove the high concentration of organic contaminants present in the wastewater. In addition, chemical methods such as oxidation process is effective and relevant to large scale wastewater treatment. Chemical treatment methods generally uses air, oxygen, ozone and oxidants (NaOCl and H_2O_2). In natural also basic chemical oxidation process occurs with air and oxygen but for highly polluted wastewater it is no longer sufficient. Therefore, there is a need of simple, cost-effective and eco-friendly method which can effectively treat the wastewater (Wu et al., 2011).

Advanced Oxidation Process (AOP) is a chemical wastewater treatment process which has received a great consideration in recent years as this method efficiently removes the recalcitrant organic pollutant. AOPs work on the principle of hydroxyl radicals (HO·) production. Hydroxyl radicals can be produced from ozone, hydrogen peroxide (H_2O_2), oxidants or photo-catalysis in combination with using ultraviolet (UV radiation). In some cases, AOPs like ozonation (O_3), ozone combined with H_2O_2 and UV irradiation or

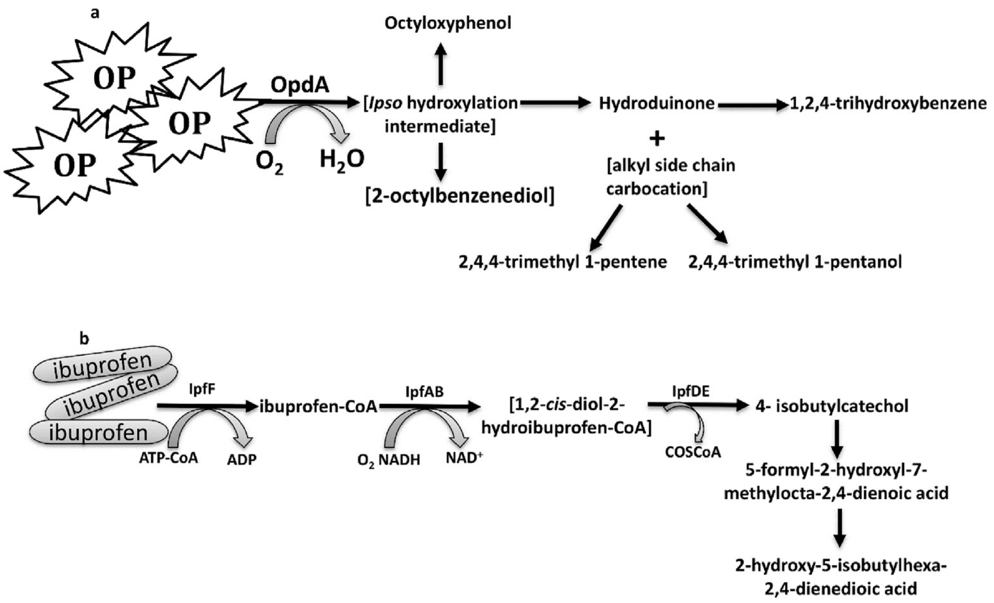

Fig. 11. Proposed pathway for (a) OP degradation by *Sphingomonas* sp. strain PWE1 and (b) ibuprofen degradation by *Sphingomonas* sp. strain Ibu-2.

both, O_3 combined with catalysts, UV/H_2O_2, Fenton and photo-Fenton processes and in all process HO· is primarily responsible for the organic pollutant degradation. Being a random strong chemical oxidant, HO^* on production attacks nearly all organic contaminants and breaks them completely. As a result the concentration of organic pollutant decreases from a few hundred ppm to less than 5 ppb. Studies showed that with AOPs, organic pollutant break down and become smaller and can be easily biodegradable. Organic radical (*R) is formed when HO^* takes away the hydrogen atom from an organic compound (R–H) as in equation (1). Later *R forms several products and by-products through a several successive chemical reactions (Matilainen and Sillanpää, 2010).

$$R - H + HO\ast \rightarrow H2O + \ast R \tag{1}$$

5.1. Ozonation

When ozone is added to water then HO^* and superoxide radical (O_2^{-*}) are formed though a complex series of reactions. At higher pH, the disintegration of ozone is better in water. The performance of the process can be determine by dose of ozone, alkalinity of water and contact time. Oxidation of organic species occurs when combination of reaction with molecular ozone and reactions with HO· takes place (Krishnan et al., 2017).

$$3O_3 + OH^- + H^+ \rightarrow 2HO^* + 4O_2 \tag{2}$$

Degradation of the organic compounds can be facilitated by the addition of H_2O_2 in the decomposition cycle of ozone which leads to the formation of HO^*. In water H_2O_2 partially dissociates to produce hydroperoxide ion which then rapidly react with ozone to produce HO^* (equation (3)).

$$2O_3 + H_2O_2 \rightarrow 2HO^{\bullet} + 3O_2 \tag{3}$$

By using homogenous or heterogeneous catalyst the ozonation process can also be speed up. The predominant factors for the enhancement of the degradation rate are the concentration of ozone in inlet gas and the ozonation time. Using F_2O_3, MnO_2, TiO_2–Me, Fe^{2+},Fe^{3+} and $Mn^{2+}$the oxidation of various contaminants can be studied. For the reduction of COD and TOC, the ozone/catalyst system appears to be more effective as compared to the oxidation with ozone alone at higher pH. Horakova et al. studied the application of the synergistic effects of various AOPs in wastewater treatment and they observed that decomposition of the Acid Orange 7, Hydrocortisone and Verapamil hydrochloride were strongly improved by synergistic effect of photo catalytic reactions occurring on TiO_2-photocatalyst (Horáková et al., 2014).

Ozonation process can be speed up when ozone decomposes readily and generates hydrogen peroxide as an intermediate by absorbing UV radiation (ƛ = 254 nm), which finally decomposes to HO^* (Equations (4) and (5)). Though several oxidation mechanism are present for disintegration of organic pollutants but HO^* is the predominant removal mechanism. This method is effective in degrading all organic pollutants and more efficient way of generating HO^* as it comprises H_2O_2/O_3, H_2O_2/UV and O_3/UV as compared to O_3 or UV alone (Krishnan et al., 2017; Muruganandham et al., 2014).

$$O_3 + H_2O + hv \rightarrow O_2 + H_2O_2 \text{at}(hv{:}\text{ƛ} < 300\ \text{nm}) \tag{4}$$

$$2O_3 + H_2O_2 \rightarrow 2HO^{\bullet} + 3O_2 \tag{5}$$

Ozone technology has been used in petroleum refineries, textile industries, pharmaceutical industries, food industry, pulp and paper industry, cosmetic industry, distilleries, olive mill and electronic chip manufacturing to treat pollutants present in wastewater.

5.2. Hydrogen peroxide

The photolytic dissociation of hydrogen peroxide in water forms the hydroxyl radicals by UV irradiation at a wavelength of 254 nm (Equation (6)). Studies has been done and it was found that the rate of photolysis of aqueous hydrogen peroxide is directly proportional to alkaline pH. The efficiency of the UV/Ozone system can be reduced as interfering compounds and turbidity absorbs the UV light.

$$H_2O + hv \rightarrow 2HO\ast \text{at}(hv{:}\text{ƛ} < 300\ \text{nm}) \tag{6}$$

UV/H_2O_2 system has many advantages like high reaction rate, flexible in the design of reactor, use of UV lamp (provides disinfection of the water), low cost, easy availability of hydrogen peroxide which leads lesser footprint in the treatment plant. Apart from these many advantages, this method of AOP has some drawbacks such as bromate formation hinder this process (reduced by lowering pH and increasing peroxide to ozone ratio), hydrogen peroxide has poor UV absorption characteristics etc. UV/H_2O_2 method have been used for the treatment of phenolic complexes present in olive mill wastewater. In addition, in textile industry also UV/H_2O_2 method has been used for the removal of dyes and it was found that increase in UV dosage and H_2O_2 concentration increases the rate of decolorization (Muruganandham et al., 2014; Vagı and Petsas, 2017).

5.3. Fenton's reagent, Fenton-like and photo-Fenton processes

When iron (II) reacts with hydrogen peroxide, Radicals are produced where Fe 2 + ion acts as a catalyst for this reaction. Fenton's Process is a simple method that takes place at ambient temperature and pressure and does not require any special apparatus or chemicals to produce $HO^{\bullet}$. As hydrogen peroxide and iron salts are easily available, easy to handle and environmentally safe, this method is an attractive way for oxidation. The destruction of organic compounds takes places by reacting with the $HO^{\bullet}$ (Equation (7)):

$$Fe\ 2+ + H2O2 \rightarrow Fe\ 3+ + OH^- + HO^{\bullet} \tag{7}$$

Irradiation with UV-VIS light at wavelengths greater than 300 nm strongly accelerates the rate of degradation of organic pollutants with Fenton–Fenton like reagents. Fe^{2+} is generated by the photolysis of Fe^{3+} complexes. equation (8) shows the occurrence of Fenton reactions in the presence of hydrogen peroxide (Karci et al., 2014; Krishnan et al., 2017).

$$Fe(OH)2+ h\nu \rightarrow Fe2^+ + HO^{\bullet} + OH^- \tag{8}$$

Similar to other AOPs, this process is initiated by the hydroxyl radical for the degradation of organic compounds, primarily by oxidation reactions. Though, to prevent precipitation of the iron, the Fenton process is strict and requires PH control. The reactor must be constructed so as to allow proper mixing of the Fe(II) and H_2O_2. Optimum hydroxyl radical formation, and degradation of the contaminants is achieved by this method. The cost of using this system would possibly be raised by the extraction of iron from the effluent water during the process. Elements with several redox states such as chromium and copper can be used to decompose H_2O_2 into $HO^{\bullet}$ through conventional ways for Fenton like processes.

However, each non-ferrous catalyst in the Fenton like system could counterbalance the practical gains of better catalyst stability and working at neutral pH. Hence, the activation process for H_2O_2 is influenced by the composition of the catalyst and is specific to its nature (Bokare and Choi, 2014; Karci et al., 2014).

By this method, toxic compounds such as phenols and herbicides in wastewater can be destroyed. However, the maintenance and operation cost increases because of the requirement of this system to keep the low pH value. For enhancing the biodegradability of wastewater containing surfactants, the advanced oxidation pre-treatment using Fenton reagent has been found to be very effective. Due to their flexibility, simplicity, and integration into existing water remediation processes such as coagulation, the Fenton, photo-Fenton and Fenton-like methods are popular methods for AOP (Bokare and Choi, 2014).

Also in this method, due to a rapid reaction between iron and H_2O_2, $HO^{\bullet}$ are generated in the shortest time compared to other AOPs. Since any excess H_2O_2 reacts with other inorganic matter, affecting the COD reduction, the optimum amount of H_2O_2 for this process needs to be determined beforehand. This method shows high elimination for the degradation of linear alkylbenzene sulfonates (LAS), and alkyl benzene sulfonate (ABS) surfactants. The production of sludge that contains iron hydroxide as a by-product is one major drawback of using the Fenton process. During a number of studies conducted, large quantities of flocs of various sizes have been observed (Bokare and Choi, 2014; Canizares et al., 2009). When estimating the cost of this process, the disposal of the sludge formed has to be included. Nonetheless, for the removal of the flocs, as well as COD, chemical coagulation has been found as an effective method.

Fenton and photo Fenton processes have been used to treat effluents from dye and chemical manufacturing, pulp bleaching, and agricultural processing until now. In addition to this, Fenton pretreatment can be used to improve biological wastewater treatment. Fenton's reaction has exhibited to be more efficient in terms of operating expenses for the treatment of toxic and food industrial wastewater as it has been considered as easy-to-handle (Heponiemi and Lassi, 2012).

5.4. Titanium dioxide (TiO_2)

For oxidation in industrial effluent treatment process, Heterogeneous photocatalysis using titanium dioxide (TiO_2) is an efficient and advanced method. A conduction band of electrons (ecb) and valence band holes (h+) (Equation. 9–11) are generated when the TiO_2 is illuminated by UV. Superoxide radical anions are produced when these band electrons interact with surface absorbed oxygen. When band holes interact with water, hydroxyl radicals are produced.

$$TiO2 + h\nu \rightarrow ecb + h^{+} \quad (9)$$

$$ecb + O2 \rightarrow O2^{-\bullet} \quad (10)$$

$$h^{+} + H2O \rightarrow H+ + HO^{\bullet} \quad (11)$$

It has been shown that in the presence of UV/TiO_2, many organic complexes can be degraded by oxidation. The degradation of organic compounds takes place by reacting with the hydroxyl radicals with rest of the processes in AOP. Also, because TiO_2 nanoparticles are non-toxic, chemically and biologically inert, and inexpensive, they are deemed suitable for wastewater treatment. Additionally, as compared to other oxidizing species, TiO_2 has a comparatively high oxidative power (Akpan and Hameed, 2009). In most of the studies that pertain to the photocatalytic oxidation of contaminants, suspended TiO_2 particles were used. A disadvantage of using suspended systems is that the recycling and recovery of these nanoparticles becomes cumbersome and expensive. This results in the requirement for inventing new methods for using immobilized TiO_2 to create systems with an immobilized active phase. Hence, using white plaster cement, different techniques to create immobilized TiO_2 have been studied for the photodegradation of surfactants present in produced water.

There aren't many industrial applications of the process yet as photocatalytic oxidation is considered as a developing technology. Though, many studies indicate successful use of the photocatalytic process in the treatment of effluents from winery and distillery, olive mill, dairy industry, molasses, candy and sugar industry, fresh-cut vegetable industry, etc. Photocatalysis was found to be effective for decreasing counts of bacteria, molds, and yeasts. In the study conducted by Kommineni et al., Hydroxyl Systems Incorporated stipulated the costs for TiO_2/UV AOP system. The estimated costs range between $1.01 for a flow 1380m3/h at 20 μg/L contaminant concentration and $5.17 for 13.8 m/h at 2000 μg/L per 3.79 m^3 of treated water. This system appears to be the least cost effective compared to the other processes (Kommineni et al., 2000). Table 6 showed the typical findings observed in the degradation of various organic pollutants by using AOPs.

6. Recent advancement

Recently, new approach as for the process of biodegradation and bioremediation have been revealed. Scientists have shown the application of genetically modified microbes and metagenomics, microbial fuel cell, nano-materials, biofilms and constructed wetlands for the degradation of persistent organic pollutants from different sources.

6.1. Genetically modified microbes

The main aim of biomolecular engineering in the field of bioremediation is to enhance the biocatalytic capability of microbes to degrade POPs. It is a relatively new field that exploits engineering biomolecules and biomolecular processes for development of genetically engineered enzymes or microbes for bioremediation purpose (Ang et al., 2005). Studies had been done on functional expression of fungal laccase in *Saccharomyces cerevisiae* which was from *Myceliophthora thermophila* (MtL) and previously expressed only in *Aspergillus oryzae* was subjected to directed evolution. It was found that directed evolution increased the laccase expression 8 fold and 22 fold increase in K_{cat} together with 170 fold increase in total activity. Due to high thermal stability of MtL enzyme it holds great potential to remediate PAHs (Bulter et al., 2003).

Out of large number of aforementioned enzymes that help in degradation of PAHs, Cytochrome P450 monooxygenase (CYPs) are one of the largest super families that degrade PAHs by forming catechols which is then further degraded by catechol dioxygenase to form various TCA cycle products in microorganisms. Wild type cytochrome P450 enzyme from *Bacillus megaterium* has been shown to have an inherently low activity towards naphthalene, fluorine, acenaphthene, acenaphtylene and 9-methlyanthracene. Therefore, several mutations has been done based on their crystal structure to obtain a cytochrome P450 BM-3, which showed the highest activity towards PAHs and found to have a great potential in degradation of PAHs in environment (Li et al., 2001). $P450_{cam}$ (CYP101) has been mutated to get the high oxidation activity towards PAHs. The wild type CYP101 from *Pseudomonas putida* had low activity ($<0.01\ min^{-1}$) but after mutation in the active site residues F87 and Y96, the activity greatly enhanced (Harford-Cross

Table 6
Typical findings observed in the degradation of organic pollutants by using AOPs.

S. No.	Pollutants	Initial concentration	Experimental setup		Conclusion	References
			AOPs applied	Optimum conditions		
PESTICIDES						
1	Carbofuran	20 mg/L	Fenton/Ultrasound	pH = 3.0, Temperature = 25 °C, Fe^{2+} = 0.8 mmol/L, H_2O_2 = 0–300 mmol/L	**Ultrasonic process**: carbofuran oxidised >40% in 120min. TOC = decreased less than 15%. **Ultrasonic/Fenton**: Degradation efficiency = increased by more than 99% with 40% mineralization in 30 min.	(Ma and Sung, 2010)
2	Fenthion	10 mg/L	UV/TiO_2 and UV/TiO_2/H_2O_2	TiO_2 = 100 mg/L, H_2O_2 = 5 mmol/L, UV = low pressure Hg lamp λ = 365 nm	**UV-TiO_2 illumination system**: decomposed its original concentration after 48 h of light exposure. **UV/TiO_2/H_2O_2 illumination system:** within 5 h target pesticide was decomposed.	(Petsas et al., 2013)
3	2,4-D Mecoprop 2,4,5-T Atrazine Terbutryn Metaldehyde	1 μg/L 1 μg/L 1 μg/L 2 μg/L 2 μg/L 2 μg/L	UV/H_2O_2 through pilot-scale experiment incorporating microfiltration and reverse osmosis (AOP1 and AOP2 respectively)	**Common for both AOPs**- Treatment capacity = 3m$_3$/h, contact time = 120s, UV = low pressure amalgam lamp λ = 254 nm **AOP1**: H_2O_2 dose = 16 mg/L, lamp power set-point = 100%; **AOP2**: H_2O_2 dose = 3 mg/L, lamp power set-point = 600%.	At an energy demand of 0.62 kWh/m^3 and H_2O_2 = 3 mg/L, 97% of pollutants were removed when applying AOP to the reverse osmosis permeate.	(James et al., 2014)
4	Dimethoate Triazophos Malathion	14.71 mg/L 5.87 mg/L 24.53 mg/L	Fenton, UV/Fenton and Microwave electrodeless UV (MWEUV)/Fenton	pH = 5.0, Temperature 25 °C, H2O2 = 100 mmol/L, Fe2+ = 0.8 mmol/L, UV= U-shaped MWEUV lamp made by quartz filled with 1 mg Hg and 0.66 kPa Ar with emission band at 254, 313,365 and 405 nm	Within 120 min complete removal by MWEUV/Fenton process	(Cheng et al., 2015)
5	Acetamiprid	100 μg/L	UV, UV/TiO_2, UV/H_2O_2/Fe, UV/$Na_2S_2O_8$ and UV/$Na_2S_2O_8$/Fe	pH = 7.0, Fe^{2+} = 1 mg/L, H_2O_2 = 50 mg/L, 3*30 W UV-C = low pressure lamp with emission at 254 nm (monochromatic light), UV light intensity = 20 W/m^2	Complete pesticide removal in 20min by UV/H_2O_2/Fe system (fastest method)	(Carra et al., 2016)
6	Atrazine	–	UV/TiO_2 and UV/Pt–TiO_2	UV light irradiation = 352 nm, Pt–TiO_2 = 1% wt/v coating of Pt on TiO_2	76% degradation in 3 h without adding H_2O_2 or aeration, which was more than 10% higher than the TiO_2– catalysed reaction and the degradation product was cyanuric acid.	(Chen et al., 2017a; b)
Phenols						
7	Phenol Solution	50–200 mg/dm^3	O_3 alone, UV alone, and O_3–UV, UV–TiO_2, and O_3–UV–TiO_2	Ozone flow rate = 0.013 mg/min, input power for O_3–UV–TiO_2 process = 10.5 W for a UV lamp	Phenol decomposition- 100% within 120min using O_3–UV–TiO_2 process, COD removal-100% within 240 min.	(Suzuki et al., 2015)
8	Phenol solution	100 mg/L	Electro-oxidation (EO), Ozonation-electro-oxidation coupled process (O_3-EO)	Temperature = 20 °C, pH = 7.0, current density = 60 mA/cm^2, flow rate = 0.05 l/min, ozone concentration = 5 mg/L	TOC removal = 99.8%, completely mineralise all phenol by coupled process.	(Amado-Piña et al., 2017)
9	Phenol solution	20 mg/L	Cobalt perovskite-based catalysts (P–Co), $ACoO_3$ (A = La,Ba,Ce,Sr)catalysts	Potassium monopersulfate (PMS) = 10^{-4}, pH = 7.0, catalyst loading = 0.3 g/L	Complete removal of phenol was achieved in 90min. 81% phenol mineralization yield was reached for 6 h heterogeneous P–Co/PMS system.	(Hammouda et al., 2017)
10	Phenol solution	–	H_2O_2, ZrMOF, Heme-ZrMOF as catalyst (100 mg)	pH = 3.5, temperature = 30 °C,	97.3% phenol removal after 2 h with heme-ZrMOF	(Jiang et al., 2018)
DYES						
11	Reactive green 19 (RG19)	900 mg/L	UV/H_2O_2	Temperature = 20 ± 2 °C, low pressure mercury lamp, UV source = power of 6 W and maximum emission at 254 nm	Decolorization was pseudo-first-order kinetics, complete decolorization was at 20min. 63% of TOC was removed in 90 min.	(Zuorro and Lavecchia, 2014)
12	Anthraquinonic dye Acid Blue 25 (AB25)	–	Non-thermal plasma at atm. Pressure with and without catalyst (TiO_2)	pH = 2–4.3 and pH = 10.3, catalyst load = 0.5 g/L	Plasmachemical treatment with catalyst- 90% degradation within 1 h treatment, plasmachemical treatment without catalyst-78% degradation within 1 h.	(Ghodbane et al., 2015)
13	Rhodamine B (RhB), Methylene Blue (MB), R6G	10 ppm	Pillared layer NNU-36, H_2O_2	30% H_2O_2,	NNU-36/visible light/H2O2 system-degraded 96.2% RhB after 70 min, MB-94.2% after 80 min and R6G-93.5% after 90 min of visible light irradiation,	(Zhao et al., 2017)
14	Acid Red 17 (AR-17)	100–500 mg/L	O3/UV	254 nm UV mercury lamp of 30 W power, ozone generator Model N1668A, power 18 W, AC 220 V/50 HZ and flow rate-500 mg of O_3/h, pH = 11.0,	Complete color removal and 72% COD elimination after 2 h and 50 min for 500 mg/L AR-17 initial concentration	(El Nemr et al., 2018a)
15	Direct Yellow 12 (DY-12)	100–500 mg/L	O3/UV, O3	Ozone = power: 18 W Vol AC 220 V/50HZ and flow rate 500 mg O_3/h. pH = 9,	Complete color removal = 750 min of AOPs (UV + O_3), more than 85% of the initial COD was eliminated for 500 ppm	(El Nemr et al., 2018b)
Pharmaceuticals and personal care products (PPCPs)						
16	ibuprofen	10 μM	UV/chlorine	pH = 6.0, H_2O_2 = 100 μM, chlorine = 100 μM, UV fluence rate = 1.05 mW/cm^2	Total organic chlorine yield = 31.6 μM after 90% degradation of 50 μM IBP.	(Xiang et al., 2016)
17	Diclofenac, Sulfamethoxazole,	5 mg/L	Photolysis, UV/H2O2	Low pressure mercury lamp, energy output = 83 W and intensity 1.04 W/cm^2		(Alharbi et al., 2017)

(continued on next page)

Table 6 (*continued*)

S. No.	Pollutants	Initial concentration	Experimental setup		Conclusion	References
			AOPs applied	Optimum conditions		
	Carbamazepine, and Trimethoprim				UV/H_2O_2 = TMP and CBZ degradation up to 91.2 and 99.7% respectively. DCF and SMX- completely degraded.	
18	Diclofenac (DCF) and ibuprofen	50 mg/L	Ozonation, Photocatalysis, and non-thermal plasma	Ozone generator = 130 ± 5 mg/L ozone gas at a power of 30 W and an oxygen gas flow rate of 10 L/h, pH = 5.6 (DCF), 5.7 (IBP)	Direct ozonation in darkness (effective in DCF degradation)- possesses the highest energy yield of 28 g/kW h but it was not effective for IBP (2.5 g/kW h)	(Hama Aziz et al., 2017)
19	Methyl paraben (MP)	32.8 μM	UV/persulfate	low-pressure mercury UV lamps = 254 nm, pH = 6.5, room temperature, persulfate = 1 mM	98.9% of MP was removed within 90 min using the UV/persulfate, TOC removal- 53%	(Dhaka et al., 2017)
20	Methylparaben Ethylparaben Propylparaben and Butylparaben	5ppm	O_3/Fenton, O_3/H_2O_2, O_3/UV, $O_3/UV/H_2O_2$, O_3/photo-Fenton, $O_3/UV/TiO_2$, and $O_3/UV/TiO_2/H_2O_2$	pH 8 and T = 20 °C, for O_3/Fenton and O_3/photo-Fenton systems, pH = 3.5,	Ozonation process = 94.85–99.22% removal of four parabens, $O_3/UV/TiO_2/H_2O_2$- most effective method.	(Cuerda-Correa et al., 2016)
PAHs						
21	Diesel oil	Density- 0.84 kg/L	Biological degradation followed by heterogeneous Fenton-like oxidation	pH = 3.0, nZVI dose = 2.0 g/L, H_2O_2 concentration = 15 mmol/L, temperature = 308 K,	*Acinetobacter venetianus* – degrade 78% diesel in 96 h, COD removal- 56.8%. Fenton like system-COD removal – 89%	(Chen et al., 2017a; b)
22	Total 27PAHs	Different concentration present in soil	Fenton process or successive permanganate ($KMnO_4$) oxidation and Fenton processes	TS = 30%, 7.5 times SOD, H2O2/Fe2+ ratio = 10, and added five times during 60 min	73% degradation- sequential application of Fenton process and $KMnO_4$ oxidation 43% degradation- either Fenton and $KMnO_4$ used alone	(Bendouz et al., 2017)
23	BaA, Chr, BbF, BkF and BaP	2000 mg/L	Fenton treatment, Ultrasonic treatment (US), Fenton/US	US alone- 360 W/L, H_2O_2 concentration = 100 mmol/L, pH = 3.0,	Fenton/US– 81.71% reduction of five Carcinogenic polycyclic aromatic hydrocarbon	(Zhang et al., 2017)

et al., 2000). Recently for the first time, the eukaryotic P450 CYP5136A3 enzyme from *Phenerochaete chrysosporium* has been mutated two times and the enzyme formed were expressed in *Pichia pastoris*. It was found that L324F and W129F/L324F showed the enhanced oxidation activity towards pyrene and phenanthrene (Syed et al., 2013).

PCBs present in the microorganisms are degraded by biphenyl dioxygenase via meta-cleavage pathway to yield TCA intermediates and chlorobenzoate (CBA). To reduce the accumulation of CBAs, the upper pathway enzyme genes for PCB degradation of RHA1 were introduced into *Burkholderia* sp. NK8 which is a CBA degrading bacteria. However, this recombinant strain exhibit no BpA activity. So to retain BpA activity of RHA1 in NK8, the BpA genes were constructed by combining the bphAaAbAcAd genes of RHA1 and bph3A4 of *Pseudomonas pseudoalcaligenes* KF707. The constructed plasmid were introduced into NK8 that efficiently degraded PCBs and reduced the accumulation of CBA (Ohmori et al., 2011).

Apart from these advantages there are several limitations. Construction of enzymes with new function represents a vast challenge in genetic engineering. It is very difficult to apply biomeolecular engineering to the bioremediation of novel pollutants because research is usually focused on altering the enzymes that can perform the desired function (Ang et al., 2005). Genetically engineered microorganism may not survive with the extra energy demand imposed by the presence of foreign genetic material when released into the environment.

6.2. *Role of metagenomics and metaproteomics for the assessment of organic pollutants bioremediation*

POP contaminated site is influenced by the indigenous microbial community in environment which establish a complex ecological niche. But these microbial populations are not easily cultured. Therefore to understand the detailed structure of community composition and their role in bioremediation of various complex compounds, direct DNA isolation from bacterial community will help understand the degradation mechanism of specific ecosystem. Simultaneously, the study of primary and secondary metabolites/protein will facilitate the understanding of the pollutant –microbe interaction, its function at molecular level and organism response to environmental factors such as abiotic stress due to pollution, temperature etc (Bundy et al., 2009; Lacerda and Reardon, 2009; Riesenfeld et al., 2004; Schloss and Handelsman, 2003; Singh, 2006). The organic pollutant exposure (especially high dose or repeated exposure) can elicit detrimental effects on life present on earth through diverse mechanism which leads to formation of toxic reactive metabolites and also disrupt endogenous metabolism due to change in their environment. Moreover, due to recalcitrant nature of pollutants, there may be possibility of incomplete mineralization by microbes or accumulation of sister metabolites in environment. Therefore, there is a need for prevention and treatment by more accurate method as compared to the traditional one. Because these methods lack the capacity to define global changes and unexpected events during metabolism and also exploring or engineering new catabolic pathway to study the primary and secondary metabolites for production of effective bioremediation reaction (Chen and Kim, 2013). Metagenomics and proteometabolomics would create a system wide approach for studying site specific microorganism during active mineralization process. In addition, the new generation sequencing technology i.e. next generation sequencing with its ability to sequence thousands of sequences concurrently and reduce the cost and time as compared to conventional sequencing method. Fig. 12 shows the workflow of metagenomics, metaproteomics and metabolomics approach expression profiling experiment.

Research has been done to identify the metabolic pathway of bacterial community from the environment and establish a link between taxonomic composition and the relative abundances of these metabolic pathways. On the basis of 16S rRNA the bacterial community were identified, some of them showed the greater degradability of xenobiotics while some bacterial genes are associated with metabolic pathways (Debroas et al., 2009). However, studies has been done where metagenomic approach were used to identify the bacterial community by cultivation, metagenomics and stable isotope probing that has the capability to degrade PAH (Gutierrez, 2011). In another study functional screening of

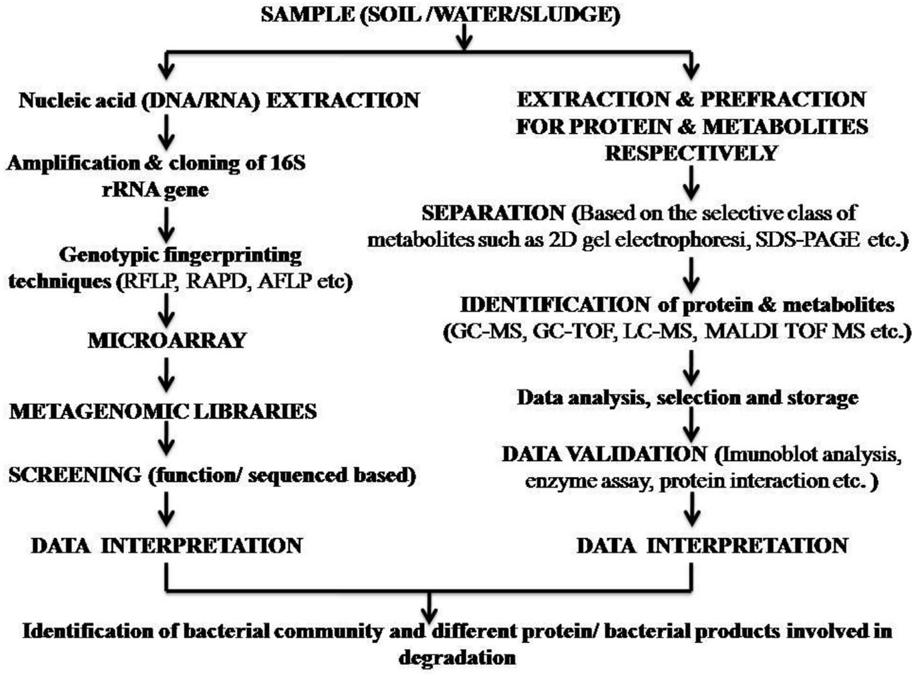

Fig. 12. Workflow of "omics" approach.

metagenomic library has been done for genes involved in microbial degradation of aromatic compounds (Reference). In addition, various Extradiol dioxygenases were retrieved, sequenced and characterised and also the evolution of these genes was discussed (Suenaga et al., 2007). Recent investigation on potential biodegradation pathways of persistent pesticides in fresh water and marine sediments through metagenomic approach has been done. It was found that *Plesiocystis*, *Anaerolinea*, *Jannaschia* and *Mycobacterium* were found to be an effective population present in all sediments out of 69 genera identified which help in biodegradation. In addition, complete degradation pathway of DDT and Atrazine (ATZ) and partial degradation pathway of hexachlorocyclohexane (HCH) were detected in all sediments (Fang et al., 2014).

6.3. *Microbial fuel cells*

Microbial fuel cells (MFC) are the device that uses biological pathways to convert chemical energy in influent matters to electricity. From decades, this device has been used as a renewable energy source which requires high power out rather than waste/wastewater treatment. To quantify the capability of the oxidization power of the pollutants, a unified index, chemical oxygen demand (COD) is adopted as most organic pollutants in waste or wastewater are in a reduced form. The anodic chamber of the MFC has the ability to convert COD to carbon dioxide (CO_2) and water (H_2O). Studies has been focused on the treatment of recalcitrant pollutants such as azo dyes, PAHs, inorganic wastewater containing sulphide and benzene derivatives by anodic treatment process. For decolorization of Acid Orange 7 (AO7) dye Thung et al. applied a single-chamber up-flow membrane-less MFC and found that both cathode and anode decolorize dye with the breakdown of azo bon and naphthalene compound in AO7 (Thung et al., 2015). For solid waste treatment, anodic oxidization of MFC is applied. Zhang et al. uses MFC for producing fuel by using dairy manure and they found by single feed of manure the tested MFC can produce electricity stably for over 110 days. They also determined that MFC converted the hydrophilic fraction and hydrophobic acid as fuel by anode (Zhang et al., 2015). Anodes embedded in the polluted matric with an external cathode exposed to air could be used to remediate contaminated soil/sediment/groundwater. For instance, Xu et al. noted that their tested sediment MFC in 60 days of operation could remove 58.91% TOC and 43.26% PCBs from contaminated sediment (Xu et al., 2015).

Cathode is the electrode where reduction reactions takes place. The oxidised substances can be reduced if the available electric potential on cathodic electrode surface exceeds their threshold. Cathodic chamber of MFC is widely used for removing organic substances (chlorobenzene and trichloroethylene), inorganic substances (ammonia) and heavy metal (Cr^{+6}) present in wastewater as it provides the reducing power. MFC as an integrated system (pre-treatment stage, post-treatment stage and parallel treatment) were widely discussed in literature work. To improve the efficiencies for the subsequent treatment unit, the MFC was applied as a pre-treatment unit for alter the characteristics of contaminants. For instance, studies was done to improve the removal efficiencies of COD and nitrogen from low strength municipal wastewater by using integrated MFC + membrane reactor (Ma et al., 2015). The influent compounds could be refractory to MFC biofilm and to increase the degradability of the contaminants pre-treatment could be applied for MFC. For example, researchers used *Aspergillus awamori* at pre-treatment stage to improve the COD removal and electricity quantity yield. This pre-treatment method before an MFC hydrolysed the insoluble and large molecules in distillery wastewater (Ray and Ghangrekar, 2015). In an another study, the COD removal was about 55% only without MFC while for the integrated reactor (continuously stirred sludge reactor + MFC) was about 90% (Wang et al., 2015).

6.4. *Nano-materials*

With high efficiency and low capital requirement, it's critical to develop and implement innovative wastewater treatment technologies. Researchers are showing interest in nanotechnology (works on nanometer scale) because of recent advanced processes in nano-material science. Nano-materials/nano-particles are the smallest structures having size of less than 100 nm. A variety of efficient, cost-effective and eco-friendly nano-materials having unique potential for wastewater treatment (industrial effluent, surface water, ground water and drinking water) have been developed. It is the most advanced process for wastewater treatment and several studies has been done on this. Based on the naomaterials nature it may be classified into three main categories: nano-adsorbents, nano-catalyst and nano-membranes. Using the atoms of those elements, nano-adsorbent can be produced which are chemically active and the surface of the nano-material has high adsorption capacity. For development of nano-adsorbents the materials used consist of activated carbon, silica, clay materials, metal oxides and modified compounds in the form of composites (Amin et al., 2014; Anjum et al., 2016).

In second class of nanomaterials (nano-catalysts) metal oxides and semiconductors have gained significant attention in developing technologies for wastewater treatment. Different type of nano-catalyst such as electrocatalyst, Fenton based catalyst (improve chemical oxidation of organic pollutants) and catalyst having antimicrobial properties have been employed for degradation of pollutants (Anjum et al., 2016). For instance, Amir et al. prepared the stable noble heterogeneous nanoparticle catalyst $MnFe_2O_4$@PANI@Ag for the degradation of azo dyes such as methylene blue, methyl orange, rhodamine B and eosin Y. They found that this nano-catalyst is effective in dye decolorizing and also can be recycled several times by magnetic separation (Amir et al., 2016). Similarly, in another study, efficient heterogeneous Fenton catalyst ($CuFeO_2$ [012]-H_2O_2) was developed for degradation of ofloxacin (OFX). The results indicated that $CuFeO_2${012} was degrading OFX four times faster than the $CuFeO_2$ [110] and in $CuFeO_2$ [012]-H_2O_2 system it was removed completely at a pH range 3.2–10.1 (Dai et al., 2018). For photocatalytic degradation of tetracycline novel $FeNi_3/SiO_2/CuS$ (FNSCS) magnetic nanocomposite was synthesized. The findings showed that the efficiency of FNSCS in tetracycline degradation reached almost 100% and the mineralization rate was 64.96% (Nasseh et al., 2018).

Nano-membranes is the third class of nano-materials which is a pressure driven treatment used in improving the quality if wastewater. Because of small pore size, low cost, high efficiency and user friendliness nano-filtration is extensively applied for treatment of wastewater in industries among various types of membrane filtration techniques available. Nano-metal particles, non-metal particles and nano-carbon tubes are the nano-materials can be developed from nano-materials (Anjum et al., 2016). Studies has been done for photocatalytic degradation of dairy effluent using silver-titanium dioxide nanofiber and silver-titanium dioxide nanoparticle nanofiber membrane. The results indicated that both nanofiber membranes showed maximum degradation of 75% (Polyurethane-$AgTiO_2$ NPs) and 95% (Polyurethane-$AgTiO_2$ NFs) after 2 h (Kanjwal et al., 2015).

6.5. *Biofilms*

The capability of the microorganisms to assemble in sessile biofilm structure allows for many advantages such as ability to communicate and exchange genetic material, protection from surrounding environment, persistent in different metabolic state and nutrient availability from the environment and each other. With varying environmental requirements (electron acceptor/donor) and nutrient conditions, biofilms can consist of single or multiple species of microorganisms originating from one or more kingdoms (bacteria, algae, fungi and arches). These properties of biofilms results in the development of physical biofilm structures. As high concentration of chemical would be detrimental to planktonic microorganisms when biofilms are applied for bioremediation and biotransformation purposes hence, the tolerance towards toxic and hazardous chemicals is of particular interest. Accumulation of microbes in floating (activated sludge) or sessile environment has major advantages of improved tolerance towards exposure to toxic chemicals (pollutants and antibiotics in higher concentration), change in environmental conditions (nutrients and predation) and other environmental stress conditions (change in pH, temperature, salt concentration and water content). Therefore, these natural properties and toughness of biofilm can efficiently be utilized to develop approaches for bioremediation of organic pollutants (Edwards and Kjellerup, 2013).

Recently naphthalene biodegradation in the presence of secondary carbon source such as glucose, starch, sucrose, and L-arginine were made. it was found that sucrose act as a bio-stimulating agent for PAH degradation. The PAH (naphthalene) degradation by the *Pseudomonas putida* KD9 strain was found to enhance the biofilm formation in the presence of sucrose (0.5 wt%) (Dutta et al., 2018). Isaac et al. demonstrated that the multi-species consortium of *Pseudomonas* strains enhanced the biofilm formation as compared with pure cultures. In addition, they found 100% removal of Phenanthrene and 78% pyrene after 7 days of incubation during biodegradation process. Phenanthrene and pyrene stimulate the biofilm arrangement and bioemusifier production (Isaac et al., 2017). In another study, biodegradation of PCBs containing wastewater was performed using a Moving Bed Biofilm Reactor (MBBR) and the removal efficiency of PCB77 in anaerobic and aerobic section were 73 and 84.4% respectively (Dong et al., 2015). The combined effect of activated sludge and biofilm process along with MBBR degrade the pharmaceuticals efficiently (Chhetri et al., 2015).

6.6. *Constructed wetlands (CWs)*

"CWs are the engineered systems that are designed and constructed to improve water quality with easy maintenance and operation and relatively low external energy requirements". These are also known as treatment wetlands and are alternative treatment to conventional mechanical system. CWs have been set up all over the world for wastewater treatment from small communities. The main types of CWs such as free water surface (FWS), horizontal subsurface flow (HF), vertical flow (VF), combined system (Cs) and intensified systems (IS) and are involved in treating numerous industrial wastewater with specific characteristics. Understanding on industrial effluent treatment through CWs is still inadequately understood. Chiefly, purification performance related to various plant species, soil materials, wetland types and their tolerance to different industrial chemicals are not systematically summarized, hence limiting the possible addition of the application of CWs to industrial wastewater treatment (Wu et al., 2015a; b). Since 2001, the Tuscan winery effluent has been treated with a multistage constructed wetland treatment system. This system consisted of primary treatment phase (connected with Imhoff septic tank) followed by single stage HF (480 m^2) and then by a FWS (850 m^2). In recent year, the flows to CW have increased from 35 to 70 m^3/d due to increased production at the winery which resulted in the severe clogging of the HF bed. This problem was solved by upgrading the existing system by IRIDRA srl, Florence (Vymazal, 2014). The influence on the detoxification of textile effluent by inoculation of textile effluent-degrading endophytic bacteria (enhance industrial effluent degradation) in a VF CW reactor was evaluated. *Typha domingensis* a wetland plant was vegetated in reactor along with *Microbacterium arborescens* and Bcillus pumilus PIRI30 (endophytic bacterial strains), which possessed plant growth –promoting activities and textile effluent degradation. The finding showed that plant growth, textile effluent degradation and mutagenicity reduction were improved by bacterial inoculation. Within 72 h, significant reduction in COD (79%), BOD_5 (77%), TSS (27%) and TDS (59%) were observed by the combined use of bacteria and plant (Shehzadi et al., 2014).

7. Challenges

- ❖ Microbial technology is restricted to those compounds that are easily biodegradable but there are many other compounds which cannot be completely or rapidly degraded.
- ❖ Sometimes the degraded product could be more persistent and toxic than the parent compound.
- ❖ From studies it was observed that the fungi do not use PAHs as a carbon and energy source therefore for their metabolism, additional carbon source is supplemented. In addition, it was also seen that bacteria metabolise and mineralise PAHs more rapidly than bacteria.
- ❖ The degradative pathway of many pollutants is not known and also many industrial pollutants are not identified.

8. Conclusion

Persistent organic pollutants are becoming a great concern due to increased industrial usage causing their accumulation, persistence in living beings and environment. Through several mechanisms, its exposure causes several fatal consequences to organs and tissues such as oxidative stress and finally leading to cell death. Several international strategies have been made to overcome the usage and complete elimination of POPs but still many developing countries across the world do not following the guidelines under Aarhus convection and Stockholm convection.

Presently, traditional treatment methods like incineration, solvent extraction and landfilling are used for the removal of persistent organic pollutants. But, these methods are insufficient to eradicate the problem and moreover the entire existing methods include high cost, incomplete degradation of POPs and production of more toxic compounds during degradation.

So, there is a need to develop an effective technique for bioremediation, capable of detoxifying them completely. In recent past, technology that uses plants, microbes and their enzymes for the degradation of POPs in an environmental friendly manner have been employed. Bioremediation involves microbial degradation approach which uses the microbes that have the capability to accumulate and degrade organic pollutants leading to upgrading the quality of soil and water. However, depending upon the type of contaminants (PAH, PCB or organochlorine pesticides) different mechanism of POP degradation (production of specific enzyme) has been implemented by microbes.

The latest addition has opened a broad perspective for the removal of different organic pollutants which are recalcitrant in nature. However, due to generation of several unknown pollutants from industrial process, the challenge is safe disposal. These pollutants cause mutagenic, carcinogenic and endocrine disrupting effect on human and aquatic life. Ultimately, it is microbial degradation armed with genetic engineering and meta-approaches that could direct us towards the elimination of POP from the environment in an eco-friendly manner.

9. Future prospects

Research has been going on continuously for finding the effective solution of increasing environmental pollution. So there is a need to adopt the following things:

- Isolation, characterization and purification of new enzyme and their role in the bioremediation of organic pollutants. But this a time consuming process and can be overcome by using metagenomics and metaproteomics approach.
- Many pathways of microbe related degradation are still unknown so there is a need of use of system biology approach such as genomics, proteomics, transcriptomics, phenomicsand metabolomics approach to study the complex behaviour of microbes and pathways related to it.
- Due to the unique properties of nano-material, they are of great interest in removing pollutants from industrial effluents. So there is a need of development of hybrid nanoparticle which can transform the pollutant in less toxic form or completely degrade it.
- Synergistic approach (i.e. use of all techniques step by step) should be used for treatment of POPs in a cost effective and eco-friendly manner.

Conflicts of interest

All authors mutually declare that they do not have any conflict of interest.

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