

THE BIODEGRADATION OF ORGANIC POLLUTANTS

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ABSTRACT:

A rise in environmental pollution in today's environment is a significant concern. Organic compounds may be controlled through physical and chemical methods but these procedures are harmful and not eco-friendly, as their finished output will stay hazardous until the very end. Biological methods would also be an acceptable solution to bioremediation activities, not just cost-effective but also eco-friendly. In comparison, the end result is less harmful than most methods. Microorganisms and plants (bioremediation) are used to fix contaminated conditions and have become an enticing and growing area in environmental biotechnology. In addition to the usage of all cell microorganisms, the use of their enzymes extracellular and/or cell-free is suggested as a creative emission control strategy. Extracellular enzymes have many benefits over the usage of entire microbial cells for the elimination of toxins. In the present paper several issues relevant to both cell-present and cell free extra-cell enzyme features and future capacities in the bioremediation of different organic contaminants has been highlighted.

KEYWORDS: Biodegradation, organic pollutants, microbial enzymes, extracellular enzymes.

INTRODUCTION:

Organic pollutants: Origin & Occurrence

In the late and early 1800s, the variety of chemically synthesized items like pesticides, fabrics, hydrocarbon oils, soaps, detergents and other valuable substances expanded significantly. The environmental consequences of these chemicals are a function of a series of processes dependent on the properties of each compound. Because of their longevity, bioaccumulation and possible exposure to animals and humans, halogenated chemical pollutant materials such as polychlorinated biphenyls, dichlorodiphenyltrichloroethane, polybrominated diphenylethers (PBDEs), dechlorane plus (DP) and dibromodiphenylethane are of considerable concern. In polybrominated diphenylethers including Penta, Octa and Deca-BDE, polychlorinated biphenyls (PCBs) were mainly used as dielectric and coolant fluids in sensors, textiles, thermoplastics and polyurethane. DP and decabromodiphenylethane (DBDPE) are some commonly used flame retardants (Xu et al 2015). In 2009, The Stockholm Convention List of new POP was upgraded with Penta and Octa-BDE, while in America and Europe, Deca-BDE technical mixture has been abandoned. In China, DP, DBDPE and Deca-BDE are still in use (Ratnakar et al 2016).

A wide variety of harmful substances of different mechanisms emerges from anthropogenic origins which constantly pollute the ecosystem. It is possible to classify three main causes of organic pollutants: agricultural practices, military waste and farming activity. Important organic toxins include gasoline, polycyclic aromatic hydrocarbons (PAHs), dioxins and chloroprene acetic acids (2, 4-D and 2, 4, 5-T), organophosphates, triazines and carbamates (Connel et al 2006). Four key factors rely on modern agriculture, including water, fertilizers, seeds and pesticides. Pesticides are a central component of industrial cultivation. About 35-45% of crop output is lost due to insects, weeds and diseases, whereas 35% of crop production is lost whilst it is processed. The scale of India's agrochemical industry is projected at US\$ 3.8 billion in 2012. The segment is projected to rise at 12-13 percent per year over the 12th plan era, hitting 7.0 billion (Indra Devi et al 2017). Indian domestic demand is increasing at 8-9% and export demand is at 15-16%. Motor vehicles are key sources of tar, polycyclic aromatic hydrocarbons and dioxins frequently emitted into the environment in particulate form. Urban and agricultural waste is frequently disposed of directly into the trenches sunk into the surface, contributing to land degradation and, in some instances, the surrounding soil water. Agricultural operations outside metropolitan centers are the primary causes of pollution.

Organic pollutants: Types and properties

Organic contaminants are carbon-containing chemical substances that have a demonstrably harmful impact on one or more environmental elements. Three wide groups can include organic pollutants: (i) hydrocarbons, (ii) oxygen, phosphorous and nitrogen compounds and (iii) organometallic compounds. Hydrocarbons and associated substances that include such substances as Dichloro-diphenyl trichloroethane (DDT), dioxins, and polycyclic aromatic hydrocarbons (PAHs) are the primary group of agricultural pollutes (Goodhead & Tyler 2009). These substances include carbon and hydrogen materials, including those that produce chlorine and oxygen. The number of chemical bonds that are mainly C-H, C-C, C-Cl, C = C and C = C (aromatic) are small. Both these bonds are reasonably stable and have minimal polarity and so the associated compounds are given this domain.

(1) Hydrocarbons are typically lipophilic, badly water soluble and stable in the atmosphere owing to low polarity. This includes: -2, 3, 7, 8-tetrachlorodibenzo dioxin (1,4) commonly known as 2, 3, 7, 8-TCDD or TCDD (TCDD), the most dangerous organic compound.

(2) A category of compounds containing oxygen, nitrogen and phosphorus can, in general, include compounds of relative high-water solubility, low fat solubility and relatively low environmental persistence. This may be attributed to the existence of reasonably strong polarity bonds because of the oxygen, nitrogen or phosphorus attachments to carbon and other atoms that provide a high degree to polarity to the corresponding compounds.

(3) The organometallic group is viewed as the least significant from an environmental standpoint which comprises substances that may be metal combinations such as lead which tin with carbohydrate-based organic constituents use (Ratnakar et al 2016).

Persistent Organic Pollutants (POPs)- Due to its fat solubility, bioaccumulation ability and environmental longevity, along with consumption trends, a category of chemicals has presented some environmental problems. These are considered persistent organic contaminants (POPs), and are also observed to be dispersed over large distances at a global extent. It has been found that they survive for a long period in the ecosystem and may grow up and migrate across the food chain from one animal to the next. Two types of essential compounds include: (i) polycyclic aromatic hydrocarbons and (ii) halogenated hydrocarbons as persistent organic contaminants. The above group consists of organochlorine, e.g., DDT (DichloroDiphenyl Trichloroethane)(El Shahawi et al 2010). The large-scale dioxins created are released into the atmosphere. The bacteria are not quickly killed. The abundance of strongly chlorinated biphenyls is more common than less chlorinated PCBs. In contrast to large chlorinated biphenyls, fewer chlorinated PCBs are quickly eliminated from the body. It is established historically that the more strongly chlorinated biphenyls appear to accumulate to a greater degree than less chlorinated PCBs; similarly, digestion and excretion for less chlorinated PCBs are more gradual than for strongly chlorinated biphenyls (www.epa.gov).

Under the Treaty, referred to as the Stockholm Convention, countries decided to minimize and/or exclude 12 main POP products (Table 1) development, use, and/or release and set out a scientific review mechanism under the Convention which has led to the inclusion of other POP chemicals of global concern (Ratnakar et al 2016).

Table 1: List of POPs Given by UNEP at Stockholm Convention(Ratnakar et al 2016).

S.N.	Agency	Name of Compounds	
		1995	2001
1.	UNEP at Stockholm Convention	Aldrin	Chlordecone
2.		Chlordane	α - Hexachlorocyclohexane and β -Hexachlorocyclohexane
3.		Dieldrin	Hexabromodiphenyl ether and heptabromodiphenyl ether.
4.		Endrin	Lindane
5.		Heptachlor	Pentachlorobenzene
6.		Hexachlorobenzene	Tetrabromodiphenyl ether and Pentabromodiphenyl ether.
7.		Mirex,	Perfluorooctane sulfonic acid
8.		Toxaphene	Endosulfans
9.		Polychlorinated biphenyls (PCBs)	Hexabromocyclododecane
10.		Dichlorodiphenyltrichloro ethane (DDT)	Tributyltin
11.		Dioxins	
12.		Polychlorinated dibenzofurans	

DEGRADATION OF ORGANIC POLLUTANTS:

In the world, organic compounds are exposed to many physical, biochemical, and biological processes that interconnect in environmental mechanisms to decide the ultimate fate of the substance. A great deal of acid is used when neutralized by chemical methods, which is neither economical nor healthy and poses significant health risks.(Sarnaik and Kanekar 1995). There are several mechanisms for organic pollutant degradation, of which, some are described below:

Physical processes- Physical methods have been employed for decades of organic degradation, and could involve different processes such as photocatalytic degradation by utilizing the Ag-modified Zn_2GeO_4 nanorods, the nano-composite graphene oxide hydrogels, the organic Silica, etc. Decomposition by catalytic / photocatalytic oxidation of these organic compounds is known to be the greenest approach for plastic waste management. Visible light reaction semiconductors have drawn attention as effective

photo catalysts from several researchers (Sun et al 2010). Many catalysts are used to degrade organic compounds photo catalytically. TiO_2 has been used as a photo catalyst owing to its low expense, chemical stability and non-toxicity. TiO_2 is favored since is a good photo-oxidation catalyst with a powerful photo-induced photo-oxidation ability. Many researchers paired TiO_2 with small strip-band semi-conductors, which increased the isolation of images by creating heterogeneous joints. Researchers changed the Ag PO surface using sol gel phase TiO_2 (Yao et al 2012).

Ag_3PO_4 was deposited on TiO_2 for heterostructure. Photoelectrodes utilizing a parallel chemical deposition and UV-reducing process of Ag / Ag_3PO_4 / TiO_2 hetero-structure. The TiO_2 nanoparticles as a photocatalyst are one successful tool for degrading organic compounds because of their non-toxicity, low expense, physical and chemical stability and high reactivity (Wang et al 2009).

Chemical Processes- Bioremediation approaches require electrical chlorinated benzene dehalogenation, such that chlorine is separated step by step from the heavily chlorinated benzene such order to create less chlorinated benzene and eventually converted to benzene. Chlorobenzenes and the cathodic route of reaction for hexachlorobenzenes were analyzed as follows: hexachlorobenzene, pentachlorobenzenes, 1,2,3,5 tetrachlorobenzene, 1,2,4-trichlorobenzene, 1,4-dichlorobenzene and monochlorobenzene. There are two catalytic degradation of organic modules by MnO_2 nanostructure, and numerous community mineralization's have been recorded for different organic compounds / dyes, for example, Rhodamine, MB, Benzyl alcohol at high temperatures with strong oxidants (Kargina et al., 1997; Guena et al., 2000; Miyoshi et al., 2004)

Biological processes- The bioremediation of polluted soil allows cost-competitive care for multiple locations facing expensive incineration or prolonged liabilities for land degradation at present. Technology was found to be cost-effective in the field under the circumstances of complete site remediation. Bio stimulation, bio-stimulation and bio-augmentation involve various forms of biological processes.

1. Bio-attenuation (Natural Attenuation): The toxins are converted into less noxious types or immobilized types of bio-attenuation. These mechanisms of transformation and immobilization are primarily attributable to biodegradation by microorganisms and, to some degree, reactions with natural chemicals and geologic medial sorption (Smet and Pritchard 2003).

2. Bio-stimulation: Bio-stimulation is a method of decontamination of degraded soils in which microbial development by altering the atmosphere is encouraged. The concentrations of microbial transformation of chemical contaminants are heavily influenced by the provision and supply of nutrients, such as carbon, nitrogen, potassium, oxygen required, appropriate pH, redox capacity, as well as organic pollutant sort and concentration. Nutrients in the form of manure, sluggish releases and oleophilic are applied to promote microbial degradation (Nikolopoulou and kalogerakis 2008).

3. Bio-augmentation: - Bio-enhancement is the incorporation of bacterial crops to improve the pace of contaminant depletion. The polluted soil sediments produce very well-equipped microflora for large levels of organic contaminants. The remediation of

soils freshly contaminated by hydrocarbons may involve microorganisms extracted from infected soil sediments. The 2% bio-remediated soil priming has been found to promote the biodegradation of soil PAH components treated with fuel oil (Lamberts et al., 2008)

TYPES OF BIOPROCESS FOR ORGANIC POLLUTANT REMEDIATION- The method of bio-remediation includes the collection of microorganisms from the infected locations. Toxic waste bioremediation may be graded as bioremediation in situ and ex situ. The key goal is to degrade organic chemicals below the acceptable limits set by higher authorities. Potential pressure inoculation improves the degradation of soil contaminants. Initially, these experiments were performed at depths of rhizosphere with 10-30 g of soil. In infected soil (e.g. 5.0 g parathion / kg, or more than 90 percent of parathion, direct *Pseudomonas stutzeri* and *Pseudo-monas aeruginosa* inoculation was removed within three weeks (Ratnakar et al 2016).

1. In-situ Bioremediation- On ground, procedure is implemented without extracting polluted content from its original location. Attractive technology is bioremediation which uses microorganisms to degrade toxic compounds. (i) bio-attenuation (ii) biological stimulus (iii) bioventing etc., including in-situ procedures. Full bioremediation at laboratory level of Tri Nitro Toluene indicated that initial anaerobic therapy before the aerobic stage was necessary. Researchers have documented the remediation of TNT by colonizing *Pseudomonas* in plant rhizosphere. Transgenic plants (tobacco) expressing the *Enterobacter cloacae* on gene were also engineered to bioremediate TNT (Siciliano et al 2001; French et al., 1998).

2. Ex-situ Bioremediation- The separation from the source (soil / water) and processing in bioreactors is done in this method of bioremediation techniques under regulated operating parameters (temperature, pH, and aeration). (ii) Soil bio-piles (iii) composting (iv) Phyto-remediation (v) biorestoration, and (vi) bio-stimulation. Nitro-aromatic explosives from polluted sediments have been documented to effectively degrade in the field through compost age. This method is more complex relative to the in-situ solution. In the method of Ex-situ bioremediation, highly polluted soil is contained in a soil: water rate of 1:1 (w / w) in reactor slurry and is contained under aerobic and anaerobic conditions (Esteve-Nunez et al., 2001). The key limitations to these methods involve lengthy cycles to incubation during composting and ineffective monitors. Contaminated soils are combined with minerals and moisture in land-farming and frequently aerated. Ex-situ therapy utilizes cell structures free and immobilized. Live bacteria / fiber or their consortia have been used as an inoculum in cell-free systems to destroy organic compounds. The efficiency of *P. putida* on a sintered-glass filter plate for bioremediation of 4-nitrophenol wastewater was examined. The effectively decontaminated the organophosphate pesticides from soils, utilizing immobilized enzymes on porous glass or silica beads (Ray et al 1999). Enzymes (hydrolases) adsorbed in soil have been studied to hydrolyze more than 90 percent parathion to non-toxic materials within 4 h. Similarly, laccases were also proposed for the oxidation of nitrophenol. In-situ and ex-situ bioremediation methods have been summarized in Fig. 1, in regard to biocatalyst immobilization.

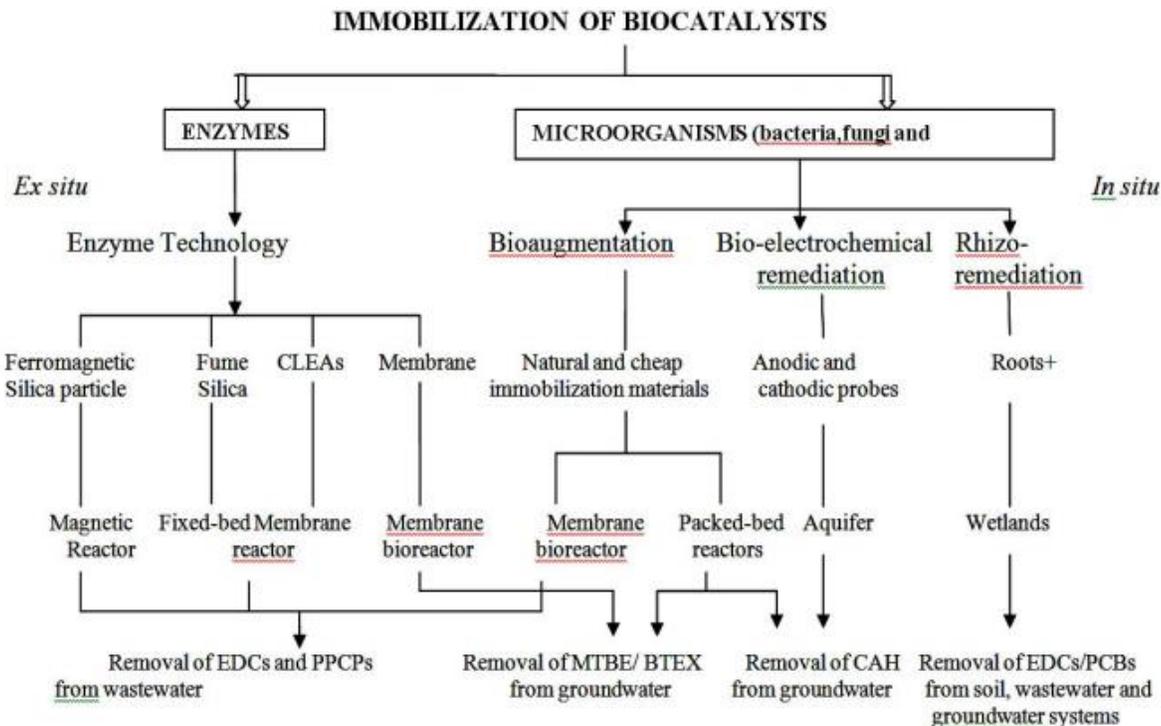


Fig.1: In situ and Ex situ Techniques(Ratnakar et al 2016).

ADVANTAGE OF MICROORGANISMS FOR ORGANIC POLLUTANT BIOREMEDIATION:

In recent decades intensive study has culminated in the isolation of a large array of organic compounds with new microbial strains. While many organic compounds are relatively new to the microbes, they have developed alternative paths for their metabolism to reduce these contaminants. Microbes are the only organisms that have an extraordinary capacity to utilize different organic / inorganic materials for development in the biosphere. Microbes can exist in different ecological niches and perform peculiar metabolism and physiological behaviors.

The bioremediation and biotransformation process, which aims to exploit the shocked, naturally occurring, microbial catabolic variety of hydrocarbons (e.g. oils), polychlorinated biphenyl (PCBs), polyaromatic hydrocarbons (PAHs), radionuclides and metals, to dissolve, convert or absorb a broad range of compounds is outlined in Figure 2.

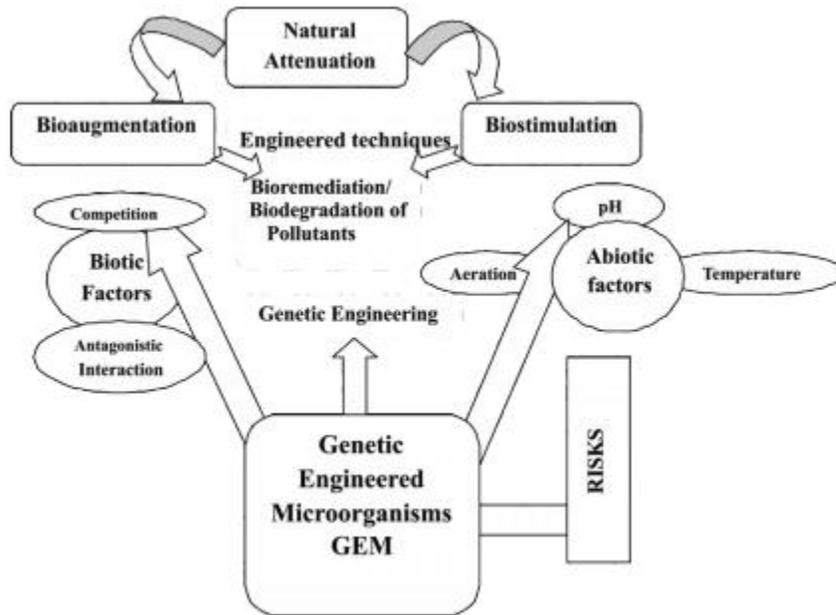


Fig. 2: Bioremediation of pollutants utilizing biodegradation abilities of microorganisms(Ratnakar et al 2016).

PROCESS/ MECHANISM OF BIODEGRADATION OF ORGANIC POLLUTANTS

Enzymes are present in the soil in large, three dimensional assemblies of mineral and organic particles that inhibit and influence their mobility (Fig. 3)

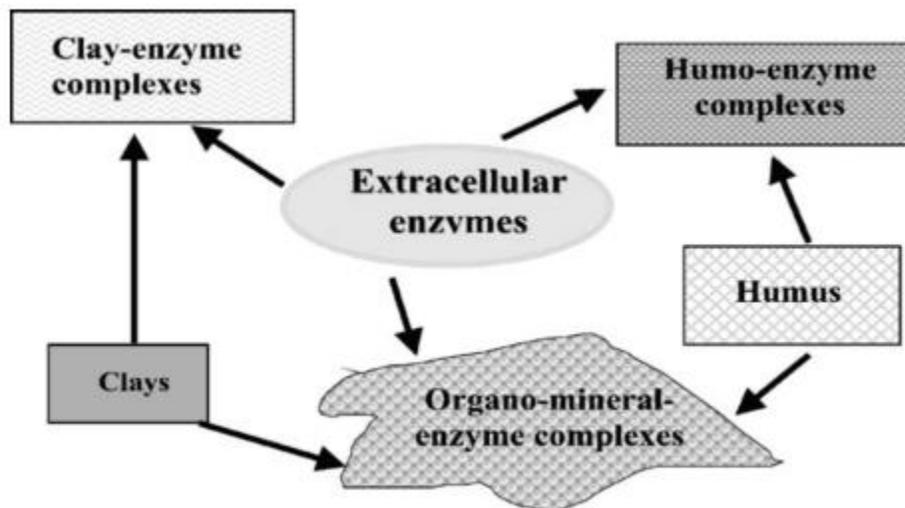


Fig. 3: Soil Bound Enzymes (Connell et al. 2006)

Enzyme molecules can be adsorbed, immobilized or stuck in these materials that contribute to the production of so-called spontaneously immobilized enzymes (Gianfreda 2004).

Aromatic hydrocarbons are popular poisonous, genotoxic, mutagenic and carcinogenic environmental contaminants. The microorganisms were found to be very helpful in the bio remedy of petroleum hydrocarbons as a carbon supply for growth and production by microbes. Pseudomonas species from the polluted collection of soil of petroleum hydrocarbons; these isolates have been shown to degrade hydrocarbon. Multiple petroleum hydrocarbon bacterial degradation requires more than only a pressure to degrade it. In petroleum-contaminated soil or water, microbial communities of strains belonging to different genres were selected on the basis of parameters showing strong growth in crude oil, individual hydrocarbon compounds or both. Strain potential to degrade organic hydrocarbon pollution was examined with soil samples polluted by gasoline, fuel oil or motor oil. Textile performance care using biological methods was more appropriate than chemical and physical methods. The usage of biological discoloration approaches primarily includes microbes, fungi and plants. Textile dyes have been decolorized for the use of the number of microorganisms.

CONCLUSION:

The best way to treat contaminated organic pollutant sites via bioremediation is because it is not only sustainable but also eco-friendly. In addition, there is no collateral habitat loss quality. The microorganism in our environment offers greater potential to transform toxic compounds into less toxic by-products. Microbial enzymes play a major and vital role in the biodegradation of organically contaminated soils such as diesel, petroleum or PAHs etc. In future, these enzymes will be opened up which are likely to open a new era of microbiology to support different technologies for cleaning up the environment.

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