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Mode of Action, Toxicity and Biodegradation of Organchlorinated Pesticides: A Mini Overview

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ABSTRACT

Organochlorinated pesticides OCs are highly toxic due to their persistence and severe ill effects on ecosystem. OCs were used extensively for agricultural as well as for health purposes like DDT, used for controlling malaria etc. OCs persistence and bioaccumulation create lot of health hazards including cancer, nervous system disorders, and tumor etc. Due to their recalcitrant nature there is a need to develop some effective technologies for the remediation of these compounds. Traditional methods physical or chemical to treat these compounds are not much effective. Mostly these methods require some high tech instruments which makes the process very expensive. Additionally, most of these treatments never give the desired solution. In contrast to these methods the biological ways of treating these types of compounds are proved to be quite promising and effective. Biological methods do not require highly sophisticated instruments as well as they are low cost. This review explains the importance of bioremediation in treating OCs.

KEYWORDS: Biodegradation, enzyme, microorganisms, organochlorinated pesticides, persistence, toxicity.
Running Title: Biodegradation of organochlorinated pesticides

1. INTRODUCTION

Pesticides are a group of chemicals made for the purpose of killing and destroying "pest" species. The pesticides comprise insecticides, herbicides, fungicides, or other pest control compounds. These are extremely toxic and are related with adverse health effects in non-target organisms. Hence, the fate of synthetic pesticides is uncertain; they can contaminate other land surface that is far off from where they were originally utilized. Then these organic chemicals enter down in water bodies at detectable level.[1]

Pesticides including organochlorinated pesticides are widely used throughout the world for last 50 years. This is a large group of chlorinated hydrocarbon that includes chlorinated derivatives of diphenyl ethane DDT dichloro diphenyl trichloro ethane and its metabolites, hexachlorobenzene HCB, hexachlorocyclohexane or lindane, cyclodiene including aldrin, dieldrin, endrin, chlordane, nonachlor, heptachlor and heptachlor epoxide, and chlorinated hydrocarbons.[2]OCs were first introduce during 2nd World War in early 1940 and after that used extensively in agriculture, home and forestry. These chlorinated hydrocarbons have some common physical features such as low water solubility, and ability to adsorb organic materials in soil that make them highly persistent. Their accumulation has several negative impacts on the soil fertility, crop productivity, ecological imbalance and human health.[3] Due to their high persistence and severe toxicity these are mostly banned through out the world specially in developed countries but still in use in under developed countires like Pakistan because of their low cost and easy availability.[4]

2.0 TOXICITY OF ORGANOCHOLRINATED PESTICIDES

Organochlorinated OCs pesticides reconsidered to be highly noxious, harmful and persistent in the environment. Toxicological properties of OCs are related with substituting chlorine in the molecule.[5]Itcan accumulate in human as well as in animal bodies because it has ability to solubilize in fats and causes health problems such as cancer and hematopoietic, nephrotoxic, hepatotoxic, and reproductive diseases. Moreover they also affect hormonal system, and may have interactive effects by producing both androgenic and estrogenic responses in vertebrates. Even in invertebrates, causing endocrine disruption, neurological and immunodeficiency disorders.[6]DDT like other OCs is not acutely toxic which the major reason of its widespread use. It persists for a

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long time in environment, and accumulates in food and animal tissues. The inadequate use of DDT resulted in worldwide pollution which makes it a threat for whole web of life. The residues of DDT mainly its metabolite DDE was observed in all fish eating birds, in fishes it is the major cause of reproductive failure.[7,8,9]DDT persists for very long time and stored in various tissues with highest accumulation in fat where repeated exposure accumulates high concentration. This property of storage in all tissues causes serious health issues mostly in occupational exposure to DDT. Various reports have confirmed its carcinogenic effects as it is the major cause of pancreatic cancer, liver cancer and multiple myeloma.[10,11,12,13] Endosulfan is one of the OCs that has found to use very extensively. The enormous use of endosulfan makes it vulnerable for the whole environment. The extensive use of endosulfan deteriorate soil quality, it's biology, fertility, health and productivity..[14]Toxic effects has also been observed in aquatic ecosystem and fish is the one in which extremelytoxic effects of endosulfan has been reported.[15]Severely toxic effects of endosulfan are also observed in mammal with genotoxic and neurotoxic symptoms.[16]The most alarming chronic symptoms, like testicular and prostate cancer, breast cancer, sexual abnormality, endocrine disruption and stomach contact poison, has also been reported by endosulfan. Lindane is use as an insecticide on fruits and vegetables. It is anorganochlorinated insecticide has severe health effects. It's adverse effects has been found in African catfish by damaging important organs like kidney, liver, gills, stomach, brain, muscle and genital organs. In humans it also causes induce membrane perturbation, functional impairment in blood brain barrier, disturbance in glutathione homeostasis and alteration in cyt P450 monooxygenase enzymes,[17]which ultimately causes neurotoxicity.

2.1Toxicity and exposure in Pakistan

Pesticide consumption in Pakistan is increasing significantly like in other South Asian countries. In 1960s thousand tons of pesticides were introduced in Pakistan during the green revolution and for malaria and locust control.[18]Most of these were widely used in Sindh and Punjab provinces. Some pesticides are biodegradable while others persist in the soils for longer times. The lack of legislation for the use and registry of pesticides in Pakistan makes them a vulnerable problem for the environment. The residues of organochlorinated pesticides were measured in detectable amounts in samples of food products such as milk, fruit and vegetables[19,20,21,22]due to their intensive use. Residues of OCs and of their metabolites were also been observed in water, surface soil and even in human blood serum.[23,24,25]Due to illiteracy and lack of guidance to the users especially the farm workers have high risk of pesticide exposure.[26]According to survey only 19% farmers getting training in handling of pesticides while only half are using defensive measure during pesticide application in Pakistan. Although the most persistent and toxic organochlorinated pesticides like DDT has been banned in Pakistan like other countries but still they are available in local markets.[27]Moreover the local farmers have misconception that the direct spray is long lasting for macro fauna.[28]There are various reports that claim lethal effects of pesticide poisoning in Pakistan, annually 500,000 populations is suffered by various types of pesticides out of which 10,000 peoples were died.[29]

3.0 MECHANISM OF ACTION OF OCs IN HUMAN

Many organochlorinated compounds, such as DDT, PCBS, and Dioxions are known as hormone disrupting chemicals or as endocrine disrupters. A wide range of living organisms including aquatic, insects and humans are affected due to non-target mechanism of action. These disturb the endocrine system by different ways i.e. it acts on nervous system by depolarization of the nerve membranes, while some compounds act on the picrotoxinin site in the γ-amino butyric acid GABA and inhibits the GABA chloride channel complex.[30]Thus preventing the normal transmission of nerve impulse, leads to uncontrolled neuronal excitation. Many OCs are hydrophobic molecules which has ability to accumulate in lipid rich tissues. [31]They are also involved in sensitization of the myocardium to endogenous as well as exogenous catecholamines and predispose to arrhythmias. Insecticides containing cyclodiene are also involved in the inhibition of Ca^{+} Mg^{-}- ATPase and Ca^{+2}ATPase. Thus organochlorinated insecticides interfere primarily with the plasma membrane and changing cell permeability, which alter cellular physiology.[32]

4.0 BIOREMEDIATION

Various solutions has been proposed to degrade organochlorinated pesticides that includes physical, chemical and biological methods but the most promising one is Bioremediation i.e. remediation by the use of living organisms or their products. This technique attracted attention over physical and chemical processes because of their environmental friendly and cost effective characteristics.[33]Biological processes generally produce benign end-products; unlike conventional methods that may produce some more notorious products such as emission of lethal bi-products from incineration and leaching of toxic substances from land disposal. Most hazardous organic compounds can be biologically detoxified or mineralized by establishing microbial communities and environmental

conditions necessary for biodegradation. Similarly, some of the microorganisms can convert or transform organic compounds, not essentially completely but to such form which has low toxic rate.[34]

Bioremediation are classified as *in situ* or *ex situ*. *In-situ* bioremediation is natural process in which biologically organic containments are degraded or treated at the site and convert into CO_2 or H_2O or harmless compounds. It is cost effective and environment-friendly method for the removal of environmental contaminants. *Ex-situ* bioremediation involved the elimination of the polluted material at the site where it is generated and then treated somewhere else. The process of excavation and transportation of contaminated material to other site makes *ex-situ* process expensive. Particularly the transportation cost effects a lot in making it expensive. Thus *ex-situ* is comparatively expensive than *in-situ* one. Interdisciplinary approach for bioremediation makes the process very fruitful such as microbiology, engineering, ecology, geology, and chemistry is vital, because bioremediation has to be designed in light of environmental conditions and microbial populations.[35]

5.0 ROLE OF MICROORGANISMS

Microbes are considered as the key players that determined the fate of different organic and inorganic compounds in the environment. Microorganisms play a considerable role in the metabolism of organochlorinated pesticides. However, some of the OCs are extremely stable in water and soil, this is due to the transformation of pesticides into toxic metabolite or complex compound which is resistant to microbial attack.[36]Microbial degradation is a cost-effective, environmentally sound, and efficient way of remediating contaminated environments. Microorganism degrade organic chemicals into two ways i.e. catabolism and anabolism. In catabolism organic compounds are completely or partially mineralized or degraded by microbes and energy released is utilized by cell growth. While in metabolism or co-metabolism, the partial removal of an organic compound occurred without any benefit to the organism. OCs degradation by bacteria occurs in both aerobic and anaerobic conditions.[37]Numerous workers isolated and identified many microorganisms and their genes capable to degrade OCs. Generally it is believed that the chlorinated hydrocarbons mostly undergo anaerobic degradation first and after dechlorination they go to aerobic phase for further transformation. Both the aerobic as well as anaerobic pathways for the DDT degradation have been proposed. The aromatic nature along with chlorination of DDT and DDE makes it more persistent against the attack of microbes. Therefore DDT and its metabolite DDE is consider to be the most recalcitrant but still few of the microbes has been reported that can be able to transform DDT and their metabolites by using it as their sole source of carbon. A bacterium *Alcaligenes denitrificans* isolated from contaminated soil can degrade DDT in both aerobic as well as anaerobic conditions. [31]A *Pseudomonas* species has ability to degrade DDT yielding 4-chlorobenzoic acid.[38]Another bacterium *Staphylococcus haemolyticus* isolated from agricultural soil can transform DDT into p,p′-DDT while using it as a sole carbon source.[39]Mwangi *et al*[40] studied that *Bacillus spp.* has ability to degrade DDT into l, l-dichloro-2,2-bis p-chlorophenyl ethylene DDE which cannot be further utilized by the same strain. He also reported that degradation rate of mixed bacterial culture is higher than individual strain. Liang *et al.*[41] has found that the anaerobic-aerobic cycle of degradation enhanced the transformation process of DDT as well as HCH, after anaerobic dechlorination of compounds, aerobes i.e. *Pseudomonas* sp., *Bascillus* sp., and *Sphingomonas* sp. actively enhance the degradation of both compounds in aerobic phase.HCH belong to OCshave proved history of persistent and recalcitrant in environment but fortunately there are microbes that can able to utilize it as sole source of energy and nutrient. Thomas *et al.*[42]isolated a bacterial strain by enrichment technique which was identified as *Sphingomonas paucimobilis* has capability to mineralized γ-HCH. It was further confirmed that this bacterium has *Lin A* and *Lin B* which is responsible for γ-HCH degradation. *Bacillus circulans, Bacillus brevis, Alcaligenes faecalis* and *Pseudomonas aeruginosa* has ability to mineralize HCH completely along with its isomers. [43]In 2006 Manickam and his co-workers[44]reported that *linA, linB* and *linC* genes in *Xanthomonas* spp.is responsible for lindane degradation. S*phingobium indicum* B90A*, S. japonicum* UT26and *S. francense* has potential to degrade HCH. The strains B90A and UT26 can rapidly mineralize γ-HCH, while *S. francense* sp. has low efficiency towards HCH.[45]Like other OCs endosulfan is also one of the persistent pesticide and particularly its metabolite endosulfan sulfate is more notorious and recalcitrant. But the microbial community also take part here again as like other OCs and numerous bacterial as well as fungal strains has been observed that can able to detoxify endosulfan along with its persistent metabolite i.e endosulfan sulphate. Bacteria belong to various species able to use endosulfan as sole source of carbon and sulphur, and able to mineralize endosulfan via intermediates including endosulfan sulfate, diol, lactone, hydroxyl ether, and dialdehyde.[46]Previous studies has shown that many bacterial strains including *Klebsiella pneumonia, Rhodococcus sp., Rhodococcus erythropolis, Pseudomonas spinosa, Burk Holderia cepacia, Pseudomonas aeruginosa, Chromobacterium violaceum Ochrobacterum* sp*., Arthrobacter* sp., *Burkholderia* sp, *Stenotrophomonas maltophilia Pseudomonas* sp*., Alcaligenes* sp*., Klebsiella* sp*., Bacillus* sp*., Staphylococcus* sp*., Bacillus circulans*–Iand *Bacillus* can able to degrade endosulfan without producing any toxic metabolite.[47,48,49,50,51]Although there are numerous reports of bacterial degradation of organochlorinated pesticides

but still the problem persist due their recalcitrant nature. Few of the OCs such as dieldrin, aldrin, DDT is consider to be in class of Persistent Organic Pollutants POPs. The major constraint in their degradation is halogenated group which make them highly persistent and unable to detoxify them via aerobic pathway. Anaerobic detoxification helps to decontaminate them but still the way is not very promising if these persistent in upper layers of soil as in case of dieldrin that binds strongly with soil layer and not percolate down.[52,53]The only way to degrade them in aerobic condition is the presence of hydrolytic pathway, so the need is to find some efficient bacteria that have ability to hydrolyze them and substitute hydroxyl group in place of "chlorine" moieties. The DDT and its metabolite DDE is found to be highly recalcitrant different microbial strains has been reported as we have discussed earlier but still the problem persist. The microbial degradation of DDT is still scarce and till now there is need to discover some more promising bacteria that can able to metabolize DDT and its metabolites.

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