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Rhizoremediation and Phytoremediation Action In The Bioremediation Of PCB-Contaminated Soil

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Abstract-This paper described the biological methods of the cleaning of the environment especially our soil that has been receiving increasing attention especially in the past two decades. Bacteria, plants, and fungi have been the natural detoxification agents for contaminants in the environment. Substantive research in this field of study sparked as a result of the shortcomings of the conventional methods of remediation of POPs including PCBs. Although PCBs and other POPs have continued to be less responsive to various bioremediation strategies, however recent studies have proven that the combination of plants and microorganism in the right proportions and technique, could lead to the detoxification of PCBs in the environment. In this paper, rhizo/phytoremediation carried out synergistically was agued as the most effective biological method for the remediation of PCB contaminated soil. Rhizoremediation and phytoremediation was reported to both play their individual role and has its specific advantages in the remediation of PCBs, but each has certain demerits and could be provided for by the effective utilization of the symbiotic relationship of both plants and microbes. Different methods of PCB remediation was discussed including their merits and demerits, narrowing to the biological remediation. However, the advantages of harnessing rhizoremediation combined with phytoremediation for an effective PCB remediation was elucidated.

Keywords: bioremediation, phytoremediation, PCB, biodegradation, environmental pollution, rhyzodegradation, dechlorination, contaminated soil.

1.0 Introduction

Polychlorinated biphenyls (PCBs) represent a certain number of recalcitrant pollutants in the environment. They differ in number of chlorine substitution attached to the biphenyl nucleus forming the congeners and therefore conforming to their excellent physico-chemical properties (Mackova et al., 2007). PCBs are representatives of a group of compounds known as Persistent Organic Pollutants (POPs). This persistence is as a result of their physico-chemical characteristics. PCBs compounds are mixtures of aromatic chemicals produced by the chlorination of biphenyls in the presence of suitable catalyst. The chemical formula of PCB can be represented as thus:-

$C_{12}H_{10-n}Cl_n$ (Erickson, 1997),

Where n is the number of chlorine atom within the range of numbers from 1-10. i.e., from monochlorobiphenyl through decachlorobiphenyl. The relative molecular weight of PCBs depends on their degree of chlorination.

1.1 Properties of PCBs

The properties of PCBs bring about the understanding of their analytical, physiological and environmental effects, these properties however vary widely across the class of the compounds. PCBs are characterised by two linked aromatic rings substituted by 1-10 chlorine atoms. There are about 209 of its congeners identified as a function of chlorine numbers and position Erickson, 1997).

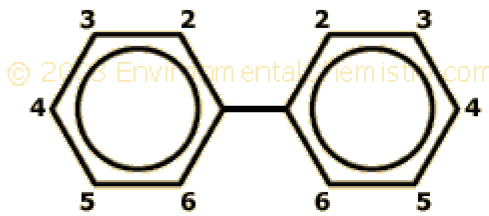
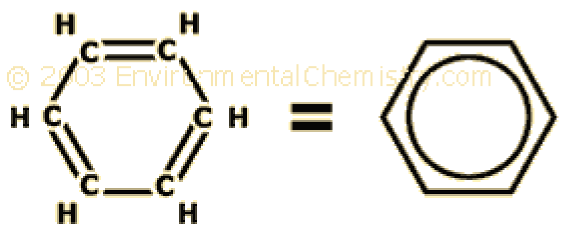


Figure 1. Structural formula of PCB showing the number and location of a Cl groups (Barbalace, 2000)

Most PCB congeners posses colourless and odourless crystals, and the most commercial mixtures are usually viscous liquids; though the highly chlorobiphenyls are more viscous for example Aroclor 1260 which is a sticky resin. PCBs are very insoluble in water and have low vapour pressures, it is however, very soluble in aqueous substances. These properties of the compound tend to change as the number of abounding chlorine substitute changes (Anyasi and Atagana, 2021). The molecular weight of PCBs are usually presented in two forms; based on the atomic of the abundant common isotopes as well as the average atomic weight of the ratios of the ones that abound naturally in their different isotopes. While the initial corresponds to the least mass in the molecular cluster of the spectrum, the other signifies the average molecular weight. The boiling point, melting point, octanol water partition coefficient as well as its bioconcentration factor in aquatics all increases as the number of chlorine atoms abounding in the biphenyl nucleus increases. Evaporation rate on the other hand, at room temperature reduces as the number of chlorine increases (EPA, 1996). The interaction of the physico-chemical properties of PCBs and their relevance to specific application of the compound could be complex, however many of the references that were cited in this review use their properties to derive bioconcentration ability in the biosphere (Erickson, 1997).



Basic Aromatic structures

Figure 2: Basic Aromatic conformation and PCB congeners (Barbalace, 2000)

Meanwhile, the behaviour of individual PCB congener is much influence by its physic-chemical characteristics; take for instance its volatility, lipophilicity, aqueous solubility, as well as the ability to rotate around the phenyl-phenyl bond (Annema et al., 1995; Andersson, 2000; Anyasi and Atagana, $_{2022(1)}$). These properties moreso depend on the degree of chlorination of PCB molecule. Most PCBs are highly mobile colourless and oily liquids through the increasingly darker and more viscous liquids, to the yellow and black resins. The monos-, di-, tri-and tetra-chlorinated PCBs regarded as the lower ones are colourless, oily liquids (Anyasi and Atagana, 2011). The heavy PCBs are honey-like oils. The most highly chlorinated PCBs are waxy and greasy substances. PCBs have a low flash point ranging from 140^0 C to 200^0 C, but most of them have no flash points according to standard tests (Wiegel and Wu, 2000). The vapour of PCB is usually invisible and has a very strong odour; this is one of the characteristic properties of the compound. The partition coefficient and water solubility of PCBs is low, while octanol partition is high as well as its solubility in fats and oil. The solubility in water decreases with increase in the degree of chlorination. This solubility is known to vary among congeners of same number of chlorine atoms (Borja *et al*., 2005).

1.2 Sources of PCBs

No evidence has supported the natural occurrence of PCBs although they continue to exist in many environmental matrices (Borja et al, 2005). Majority of the PCBs in the environment finds its way during their manufacture, usage as well as during disposal (EPA, 1996). Human activities influence the concentration of PCBs especially close to shorelines and in water (Borja et al., 2005), this could be attributed to human occupation as well as the use of PCB-containing products. The major source of PCB in surface water is from environmental cycling (i.e. from sediments, air and land). Sediments at the bottom of a water body can act as a reservoir from which PCBs can be released in small amounts to water. PCBs in fish can be hundreds and thousands of times higher than in water because they bioaccumulate in the fish (EPA, 1993a). PCBs are versatile and synthetic chlorinated compounds, though its production was banned years ago, they are still contained in most of the finished products that are used by man. PCB attaches strongly to soil and may remain there for several years as a result of its lipophilicity it is for this reason that environmental cycling is expected in disposal and spill sites. Another possible source of PCB exposure is the workplace, these occurs during the course of maintenance and repair of PCB transformers, accidents, fires and spills (Yang *et al*., 2006). It also occurs during the disposal of PCB-containing materials by breathing contaminated air and by making contact with materials containing PCBs (Borja *et al*., 2006). Old appliances and electrical equipments are also believed to be the primary source of household contamination, since they may contain PCBs. Meanwhile, PCB levels in indoor air are often much higher than outdoor air (Borja *et al*, 2005).

1.2.1 PCB release into the environment- PCBs are largely generated as by-products of other chemical production. Dating from 1929 until 1970s, they were commercially produced as complex mixtures (Erickson, 1997), such production were stopped in some of the producing countries in 1970s because of the harmful effect of the compound. However, production continued in some areas till 1984 (Erickson, 1997). Each country of production of PCBs adopt different methods and name to the compound, for example, In USA, Monsanto Industrial Chemicals Company, produced PCBs as Aroclor; in Germany, Bayer produced as Clophen; Caffaro produced as Phenoclor in Italy; Japan as Pyralene by Kanegafuchi Chemical Company; Kanechlor in France by Prodelec; Fenchlor in Czechoslovakia by Chemko; and Delor in USSR by Sovol. During the period of production especially in the US, about 571,000 metric tons ($1{,}250x10^6$ pounds), were produced and or were used in the United States (Erickson, 1997; Hamlin, 1999). In 1976, the US government banned the manufacture, processing, distribution in commerce and use of PCB under Toxic Substance Control Act (TSCA), and The Reserve Conservation and Recovery Act (RCRA). Exemptions could be granted to individual practitioners for use with optical microscopy and for research and development (EPA 1998u). However, production of PCBs in Europe, USA and Canada ceased years ago as a result of its toxicity and persistence (Pross *et al*., 2000)

1.3 Uses of PCB

PCB are valuable for industrial applications as a result of the following properties in which they posses: chemical inertness, high electrical resistivity and dielectric constancy, thermal stability, non-flammability and low acute toxicity (Hutzinger, 1974). The aforementioned characteristics of PCB instil their usefulness in various industrial applications, these ranges from liquid components of transformers, heat exchangers, capacitors as well as vacuum pumps. PCBS are also found in open systems such as in plasticizers, sealing liquids, water proofing agents, deinking solvents, pesticides and in water retardants (Andersson, 2000; ; Anyasi and Atagana, $2022_{(2)}$).

1.4 Health and environmental effects of PCBs

The toxicity of PCB varies considerably among congeners. The coplanar PCBs are known as non-*ortho* PCBs because they are not substituted at the ring positions to the other ring, (i.e. PCBs 77, 126, 169 etc.). They tend to have dioxin like properties, and are generally among the most toxic congeners (UNEP Chemicals, 1999). PCB health effects on human ranges from the skin conditions to the acute liver damage as a result of man’s exposure to the chemical. Animals that eat PCB contaminated food even for a short period of time surfers liver damage and may die (UNEP Chemicals, 1999). About twenty nine of PCB congeners are of environmental interest when considering its toxicity (Figure 1).

Toxicological problems of PCB which are associated with its co-planar congeners have been studied extensively in vitro and in vivo using animals as well as well as humans that were exposed to the compound through occupation or perhaps incidents for example the Yusho incident of Japan in 1968, the Hudson River incident in the US in 1979, the New Bedford Harbor incident also in the US, in the 1970s, and in the Great Lakes incident of 1988 in Canada (Erickson, 1997). Lethality, toxicity on reproduction, growth inhibition, porphyria, immunotoxicity, induction of enzyme, hepatotoxicity, endocrine effects, neurotoxicity, thymic atrophy, dermal toxicity, carcinogenicity and other biochemical responses have all been implicated in almost all the multiple PCB studies in the laboratory. This laboratory exposure is subject to some questions as a result of the purity of the compound. However, the possibility of other POPs present in the studies, make the assignment of the observed effects to PCBs liable to criticism (Safe, 1992; species (Anyasi and Atagana, 2011). The toxicological effects of PCBs relates directly with their structures. The most important of the congeners is that containing no ortho-chlorine substituents or single ortho chlorine substituents which can assume a co-planar configuration with shapes similar to 2,3,7,8-TCDD (Erickson, 1997).

1.4 PCB regulations

As a result of the adverse health effects caused by PCBs and their persistence in the environment, the Toxic Substances Control Act (TSCA), enacted on October 11, 1976, banned the manufacture of PCBs after 1978 [Section 6(e)]. The first PCB regulations were in the Code of Federal Regulations, promulgated at 40 CFR Part 761, and were finalized on February 17, 1978. These PCB regulations include requirements specifying disposal methods and labelling procedures, and controlling PCB use (Rahuman et al., 2000). PCBs have been assigned a hazardous substance in accordance with the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) of 1980 and as a toxic chemical under Section 313 of Title III of the Superfund Amendments and Reauthorization Act (SARA) of 1986. Section 121(b) of this act requires the EPA "conduct an assessment of permanent solutions and alternative technologies or resource recovery technologies." Special emphasis was placed on those technologies which could permanently decrease the level of pollutants. Congress further provided for a "program of research, evaluation, testing, development, and demonstration 7 of alternative or innovative treatment technologies" in section 311(b) of SARA (Timian and Connolly, 1996). PCBs is one of twelve (so called dirty dozen) Persistent Organic Pollutants (POPs) governed by UNEP (United Nations Environmental Program) according to the outcome of the Basel Convention that was held in March 1999 and the treaty that was ratified in Sweden in May 2001, with South Africa being a signatory.

CERCLA instituted the National Contingency Plan (NCP) in order to establish a framework for identification and remediation of the nation‟s most contaminated and hazardous sites. The national goal of the remedy selection process is to select remedies that are protective of human health and the environment, that maintain protection over time, and that minimize untreated waste (U.S. EPA, 1997). Section 121(d)(2)(A) of CERCLA requires adherence to other Federal and State laws through the identification of and compliance with applicable or relevant and appropriate requirements (ARARs). Overall, the NCP has implemented CERCLA requirements involving the protection of human health and the environment, compliance with ARARs of Federal and State laws, be cost-effective, utilize long-term permanent solutions, have short-term effectiveness, reduce the toxicity, mobility, or volume through treatment, implementable, and attain state and community acceptance (Table 1) (U.S. EPA, 1990; U.S. EPA, 1997).

1.5 Biological PCB transformation

Various literatures have dealt critically with the biological degradation of PCB by plant as well as with microorganisms both referred to as phytoremediation and bioremediation respectively. Although both concepts seem to be synonymous with each other as the former is a component of the later, however, each of the concepts is a technique which can be used independently. While Bioremediation specifically investigates the natural capability by living organisms to degrade toxins, phytoremediation on the other hand entails the use of plants to remediate environmentally toxic compounds (Newman and Reynolds, 2005; Aken et al., 2010). Conventional remediation of PCB-polluted sites requires excavation and transportation of the soil, prior to in situ treatment by solvent extraction, thermal alkaline dechlorination, incineration, or landfilling. These mentioned techniques are bemoaned with a lot of disadvantages culminated to the rise in the search for alternative remediation techniques (Anyasi and Atagana, 2011).

The ability of PCBs to be degraded or be transformed in the environment depends on the degree of chlorination of the biphenyl molecule as well as isomeric substitution pattern. However, the process of putting biochemical capabilities of microorganisms into use has become the technique of interest in the bioremediation of contaminated soil (Semple *et al*., 2001). Microorganism, more so than any other class of organisms, have a unique ability to interact both chemically and physically with a huge range of man-made and naturally occurring compounds leading to a structural change to, or the complete degradation of, the target molecule (Borja *et al*., 2005). Recent improvement on bioremediation technique has increased the existing clean-up processes currently available for the restoration of contaminated sites. It can be done either *in-situ* or *ex-situ*. *In situ* remediation entails the remediation of soil at its point of contamination. This include: bioventing, biosparging, bioslurping and phytoremediation along with in situ physical, chemical and thermal process (Koning *et al*., 2000). *In situ* remediation is less costly as the cost of excavation and transportation is avoided, it is easily controlled and managed (Idris and Ahmed, 2003). *Ex situ* remediation however, is the situation whereby the contaminated soil is taking to the remediation plant or center to be remediated. They include: land farming, biopiling, *ex situ* thermal, chemical/physical process. A major advantage of *ex situ* technique is the fact that most of the decontaminated soil can be reused (Dobbins, 1995; McEldowney *et al*., 1993; Aken *et al*., 2010; Furukawa *et al*., 1985).

The optimization of bioremediation is dependent on many environmental factors, and the rate of such optimization depends on the environmental condition at which such action was carried out. These factors are:

(a). the structure of the compound.
(b). the presence of foreign substituent and their position in the molecule.
(c). Solubility of the compound and
(d). Concentration of the pollutants.

Phytoremediation as a technique involves a whole range of processes which acts to remove contaminants from soil using plants. It goes beyond plants uptake of metabolism of chemicals from soil hence includes the whole process as described in Figure 1.

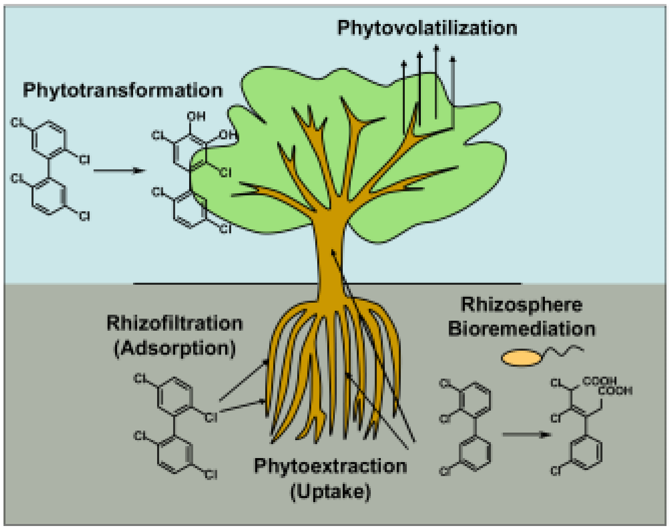


Figure 2: Phytoremediation processes of PCB remediation (Aken et al., 2010)

This ability of PCBs to constantly persist in the atmosphere requires a more environmentally friendly alternative dissipation method having been failed by the conventional methods of incineration. The environmentally friendly alternative mentioned above is bioremediation. Bioremediation involves the use of biological means to destroy, transform or deactivate environmental contaminants as to protecting potential sensitive receptors (ENTACT. www.entact.com/26/03/11). It could also be referred to as any process that uses microorganisms or their enzymes to return the environment altered by contaminants to its original condition (Brazil *et al*., 1995). Bioremediation is sometimes used to attack contaminants like PCBs that are degraded by bacteria. Various forms of bioremediation technique include:

- Land farming
- Bioventing
- Biosparging
- Bioslurping
- Phytoremediation
- In situ/ex situ remediation

This chapter shall elaborate only on those that are within its.

1.6 In situ remediation technique

In situ remediation is a phenomenon used to treat pollutions on site devoid of significant disturbance. It is a biological technique which incorporates the use of either physical extraction, biological activities, chemical modification or other processes to remove, stabilize or degrade pollutants in soil and groundwater. In *in-situ* processes, result is usually accomplished by the introduction of exotic substances into the site.

1.6.1 Bioventing- This bioremediation technique that allows only the treatment of unsaturated soil. It is an *in situ* remediation technology that uses indigenous microbes to biodegrade organic constituents which were adsorbed to the soil especially in the unsaturated zones (www.sci.ccny.cuny//bioventing). Bioventing is mostly used in the remediation of petroleum products because it induces airflow as a provision of oxygen which promotes the biodegradation of the pollutants. Some factors referred to as site characteristics support the practicability of bioventing technique, they are:-

(a) Intrinsic permeability-this means that there should be enough oxygen supply to the system. The air flow rates also should be in 1 order of magnitude less with corresponding less pressure.

(b) There should be enough microbial presence.

(c) Supply of appreciable sources of energy which depends on whether the microbes and system is heterotrophic, autotrophic, aerobic, anaerobic or facultative.

(d) Optimal soil pH which ranges between 6 and 8, moisture content of 40-60%, soil temperature between 10^{o}C and 45^{o}C, enough nutrient concentration and also the depth to groundwater.

Advantages of bioventing include- the system makes use of readily available equipments which are easy to install, minimal disturbance to its site of operation, short time of treatment, less expensive, ability to combine with other technologies etc. But this technique is disadvantaged in that it is not effective if the water table is within several feet from the surface, high constituent concentration usually toxic to microbes, requires certain site conditions, and cannot achieve low clean-up standards (Van Deuren et al., 2002).

1.6.2 Biosparging- Biosparging is an in situ remediation technique which exploits and stimulates the use of indigenous microbes to degrade organic contaminants in soil. This is the injection of atmospheric air into the aquifer to stimulate the activity of microorganisms by increasing oxygen dissolution which by so doing enhances biodegradation of the contaminants present in the soil (www.remedios.uk.com). Biosparging is used in both saturated and unsaturated soil zones hence was designed to augment for the shortcomings of bioventing process meaning that reduction of energy consumption is reduced (Held and Dorr, 2000). The injection of air into the aquifer results in small channels for the air to move to the unsaturated soil zone. Therefore, in order to form the necessary numerous branches in these channels, the air must be pulsed into this soil. This then result in volatile contaminants being transported to the unsaturated zone. Finally soil vapour extraction is then used to extract the volatile vapours and treat them at the surface. In order for biosparging to be effective, the sparge point must be below the contamination zone because air always flows upwards (EPA, 1994).

1.6.3 Phytoremediation- Phytoremediation is a recent development in green technology that uses plants to remedy soils, sediments, surface water and ground water, when contaminated with metals, organics and radionuclides (Alkorta and Garbisu, 2001). Phytoremediation is an effective, environmentally friendly, and inexpensive means of remediating soil (Wiltse *et al.*, 1998; Alkorta and Garbisu, 2001; Dietz-Annette and Schnoor, 2001). It is a more cost effective method than the conventional mechanical and chemical methods of removing hazardous compounds from the soil (Trap and Ulrich, 2001; Bhandry, 2007). Apart from these, phytoremediation is a natural, aesthetically pleasing low-cost technology which is socially accepted by surrounding communities and regulatory agencies as a potentially elegant and beautiful technology (Chekol *et al.*, 2004). Phytoremediation of contaminated soils offers an environmentally friendly, cost effective, and carbon neutral approach for the cleanup of toxic pollutants in the environment. Plants with abilities to hyper accumulate heavy metals, uptake volatile organic compounds, and sequester pollutants have been proposed as a solution to the treatment of toxic contamination *in situ*.

Plant remediates organic pollutants by:

1. Direct uptake of contaminants, their conversion and accumulation of non-phototoxic metabolites;
2. Releasing exudates and enzymes enhancing microbial activity and biochemical transformations (Mackova *et al*., 1997);
3. Enhancement of mineralization in the rhizosphere.

There is suggestion that plant enzymes released into the environment have a significant catalytic effect (Cunningham *et al*., 1997). After screening of freshwater sediments, it was shown that five specific enzymes- dehagenase, nitroreductase, peroxidise, laccase and nitrilase- were of plant origin. Though there has been scarce detailed description of enzymatic reactions leading to the degradation of PCBs in plants. But the metabolic pathways of PCB degradation in microbial cells has been intensively studied; this showed that bacterial degradation occurs via two main routes, highly chlorinated PCB congeners can be dechlorinated under anaerobic conditions to form less chlorinated ones which are more susceptible to aerobic degradation. Lower chlorinated PCBs on the other hand, can be degraded by aerobic bacteria via a well-documented pathway (Abramowicz, 1995) to chlorobenzoates.

1.6.3.1 Direct benefits of phytoremediation. Phytoremediation is an in situ, solar driven technique, which limits environmental disturbance and reduces cost (Smith *et al*., 2007). Moreover it is particularly well suited to the treatment of large areas of surface contamination, especially where other methods may not be cost effective (Schnoor, 1999). In general both public and government regulators look favourably upon phytoremediation because it involves exploiting the natural ability of the environment to restore itself (Cunningham *et al.,* 1997). There has been a wider support from the public on the use of plants for remediation. This was cited at a series of public focus group meetings to gauge public perceptions and awareness of environmental applications of bio-technology especially in Canada (Carrillo-Castaneda *et al*., 2001).

Plant samples can be harvested and used as indicators of the extent of remediation or, conversely contamination. Similarly, a field of plants may serve as a direct, visual bioassay (Shimp et al., 1993). There is also the potential to grow various phytoremediator species together on the same site in an attempt to simultaneously remediate various contaminants, including salts, metals, pesticides, and petroleum hydrocarbons. Plants help to contain the region of contamination by removing water from soil, thereby keeping the contaminants from spreading or confining them within or near the root system (Quiping *et al*., 1992). Some wetland plants can transport oxygen to the rhizosphere under conditions that may otherwise limit the amount of oxygen available to soil microorganisms, as in the case in soils and sediments saturated with water or contaminated with oil (Schnoor, *et al*., 1995). For this reason, microbial communities in the rhizosphere may be able to biodegrade wide variety of organic contaminants. Finally, using existing agricultural practice in a contaminated site, application of phytoremediation could be done at ease (Haritash and Kaushik, 2009).

1.6.3.2 Indirect benefit of phytoremediation. Phytoremediation leads to improvement of soil quality by improving soil structure (aggregates and pads), increasing porosity/aggregation and therefore water infiltration, providing nutrients (nitrogen fixing legumes), and accelerating nutrient cycling, and increasing soil organic carbon (Schnoor *et al*., 1995; Cunningham *et al*., 1997). The use of plant in remediation efforts stabilizes the soil, thus preventing erosion and direct human exposure (i.e. inhalation of soil particles carried by the wind (Carrillo-Castaneda *et al*., 2001). Phytoremediation eliminates secondary air-or water- borne waste, example the accumulation of PAHs from the atmosphere (Bock *et al*., 2002). It also has the potential to eliminate green house gas emission because it does not require the use of pumps or motors that give off green house gases and plants used in phytoremediation may serve as sinks for the green house CO_2 (Schnoor *et al.* 1995). Reduction of noise level from industrial sites is achieved because phytoremediation is less noisy than the other reclamation alternative. Another indirect benefit of phytoremediation is that the growths of high hardy plants gives room for growth of lower ones also (Germida *et al*., 2002; Frick *et al*., 1999).

1.6.3.3 Limitations of phytoremediation. Petroleum hydrocarbon contamination must occur at shallow depths for phytoremediation to be effective. There is generally decrease in root diversity with depth as most plants do not have high root depths like the trees (Frick *et al*., 1999: Germida *et al*., 2002). Consequently, as depth increases beyond one or two metres, relatively immobile contaminant- those that cannot migrate to the plant roots during water uptake are increasingly unlikely to be affected by phytoremediation. Phytoremediation requires more than annual planting seasons for site clean-up hence slower than *ex-situ* methods (Frick *et al*., 1999; Germida *et al*., 2002). Because it is slow, phytoremediation is not an appropriate solution where the target contaminant presents an immediate danger to human health or the environment. If the contaminant is bound tightly on soil particles or organic matter, it may not be available to plants or microbes for degradation (Olsen *et al*., 2003). Bioremediation is a required option especially where sediments are contaminated with PCBs (Furukawa and Fujihara, 2008). However, thermal and chemical processes have always been the method used to decontaminated highly polluted sites until bio-technology offered a more economically friendly alternative for diffuse pollution (Furukawa *et al*., 2004). The aim of all thermal, chemical/physical methods of remediation is to change the chemical environment in a way that prevents the transport of toxic substances to other elements of the soil system; examples can be given by the transport of pollution to plants, to ground water, or to soil organisms. Such preventive measures may include decreasing mobility change of chemical constitution or any of the factors on which it has been elaborated by various researchers (Aken *et al*., 2010).

1.7 Phytoremediation of PCBs

PCBs are exotic compounds of note which spreads widely in the environment (Toro *et al.,* 2006). A review of literatures indicates that PCBs are not leachable in soils and that they are readily adsorbed by soil constituents. It appears that lower chlorinated PCBs are less adsorbed and thus slightly mobile in soils. There have also been reports of absorption of PCBs by plants, but in very low amounts as PCBs appears to have some effects on photosynthesis and respiration in plants (Toro *et al*., 2006). As a result contradictory evidence ensures thus; while some studies report that there is little or no active transport, others showed evidence of an active uptake and translocation. According to Quiping *et al*, (1992), an investigation into the possible effects of PCB congeners in tomato and barley plants, showed a lack of active transport or metabolism of PCBs. From the study, 95% of the injected PCBs were retrieved from stem section within 5cm of point of introduction after 55 days.

Phytoremediation is referred to as the use of plants to dissipate organic compounds like PCB from the soil (Ferro *et al*, 1994). It is an in situ technique which is most suited for sites where other remediation options are not cost effective, low-level contaminated sites, or in conjunction with other remediation technique. Deep rooted trees, grasses, legumes, and aquatic plants all have application in the phytoremediation field. The ultimate aim of this review is to highlight bioremediation technologies with plants and microorganisms that have proven successful in the remediation of PCB. It will then compare the two mechanisms, describing the positive impacts of combining the two processes in the remediation of PCBs

2.0 Rhizo/phytodegradation of PCBs.

The rates of removal of pollutants in bioremediation are usually slower than those that can be achieved by the conventional methods. This is purely shown in remediation by plants in which its growth depends on some environmental factors. Therefore, the need arises for finding ways to enhance the entire scope and rate of bioremediation in order to propel them as a competitive commercial technique (Chaudhry *et al*., 2005). PCBs are hydrophobic hence sorbs strongly to soil particles rendering its biotransformation property. The compounds are poorly taken up by plants tissues, but in the rhizospheres microbes play a dominant role in their remediation. They have been many reports of recent, showing significant increase in the reduction of PCBs in soil with different plants grown in it compared to unplanted soil (Chaudhry *et al*., 2005; Gerhardt *et al*., 2009).

This section of the chapter reviews the interactions of plants and microorganism in a rhizosphere looking at the effectiveness of remediation of PCB-contaminated soil with microorganism and plants explaining the differences between the two. It will also throw more light in the combination of the two techniques using rhizodegradation technology of microorganisms and phytoremediation of plants.

2.1 Degradation of PCBs by microorganisms

Recalcitrance of PCBs to biodegradation by microbes was as a result of its chemical stability (Furukawa and Fujihara, 2008). Just as higher chlorine constitution increases chemical stability and lowers water solubility; it makes higher chlorinated congeners more resistant to remediation. Metabolism of PCBs is usually unfavourable energetically, thus requiring additional source of carbon to aid its co-metabolism. PCBs are regarded as POPs, however; its degradation by microbes has been well reported (Brazil et al., 1995; Pieper and Seeger, 2008; Borja *et al.,* 2005; Field and Sierra-Alvarez, 2008; Vasilyeva and Strijekova, 2007). There are two known metabolic pathways of microbes in PCB- aerobic and anaerobic, these depends on the degree of chlorination of the congener, the types of microbes involved as well as the redox conditions (Borja *et al*., 2005: In Aken *et al.,* 2010)

2.1.1 Anaerobic PCB-dechlorination. PCB congeners that contain four or more chlorine substituent undergo anaerobic reductive dechlorination (Aken *et al*., 2010). This is an energy yielding process in which PCBs serves as the electron acceptor for the oxidation of organic substrates. Anaerobic bacteria possess characteristics that are suited for high carbon-concentration pollutants because of the limitation in oxygen diffusion in a high concentration system (Borja *et al.,* 2005). A predominant anaerobe environment is conducive for the reductive transformation resulting in the displacement of chlorine by hydrogen (Borja *et al.,* 2005). These compounds that are dechlorinated are however substrates for oxidative attack of the anaerobes. Aerobic bacteria grow faster than anaerobes and can sustain high degradation rate resulting in mineralization of the compound. Theoretically, the biological degradation of PCBs should give carbon dioxide, chlorine, and water. This process involves the removal of chlorine from the biphenyl ring followed by cleavage and oxidation of the resulting compound (Boyle *et al*., 1992).

2.1.2 Aerobic biodegradation of PCB. Sparsely chlorinated PCB congeners which form as a result of dechlorination of the higher congeners are substrates for aerobic bacteria (Komancova *et al.,* 2003) Those PCB congeners undergo cometabolic aerobic oxidation which is mediated by an enzyme deoxygenases, bringing about a ring opening hence completing mineralization of the molecule (Kohler *et al*., 1989; Vasilyeva and Strijakova, 2007; Furukawa and Fijihara, 2008). A lot of bacterial strains are implicated in oxidative degradation of PCBs; among them are *Pseudomonas*, *Burkholderia, Comamonas, Rhodococcus,* as well as *Bacilus* (Aken *et al*., 2010). Obviously, chlorine numbers per molecule and its placement are important factors in aerobic biodegradation (Furukawa *et al*., 2004). PCB congeners with three or less chlorine atoms per molecule are easily degraded, but ones with more are recalcitrant, therefore requires reductive dechlorination prior to oxidative mineralization (Aken *et al*., 2010). PCB-destruction in the presence of oxygen involves two gene clusters (Borja *et al*., 2005). The first one enables transformation of PCB congeners to chlorobenzoic acid and the second involves degradation of the chlorobenzoic acid. A common growth substrate for PCB –degradating bacteria is biphenyl or monochlorobiphenyls. During utilization of biphenyls, a yellow *meta*-ring cleavage product is formed as observed in most studied bacteria like the *Pseudomonas sp. (*Boyle *et al*., 1992), and *Micrococcus sp*. (Benvinakatti *et al*., 1992)

3.0 Phytoremediation and PCB

The inability of PCBs to be leached in soil has been reviewed by literatures. PCBs are also reported to be readily absorbed by soil sediments (Strek and Weber, 1982). These indicated the difficulty in the removal of PCBs from the soil. It appears that lower chlorinated PCBs are less absorbed and slightly mobile in the soils. Meanwhile, total organic matter content of the soils seems to be a more important than total clay content or total surface area in explaining adsorption of PCBs by soil. There have been various work on the effect of PCBs on plants, the results of those work indicated that plants absorb PCBs, but in a very slow amount. PCBs therefore appear to have some effects on the photosynthesis and respiration in plants (Strek and Weber., 1982). Reports on the potential of plants for phytoremediation of PCBs started during the late 70s and early 80s. (Aken *et al*., 2010). From then, a lot of significant advances have been made to elucidate the potentials of plants and microbes for the metabolism of PCBs. Some processes are known to be involved in phytoremediation of PCBs; they are rhizoremediation, phytoextraction and phytotransformation.

3.1 Rhizoremediation

PCBs are hydrophobic, hence possesses high affinity for soil particles. There are therefore taken up into the plants tissues sparingly. However, microorganisms in the rhizosphere play a dominant role in the biodegradation of PCBs (Aken *et al*., 2010). Reports have continued to show significant improvement in the reduction of PCBs in a soil planted with different types of plants as compared with non-planted controls (Campanella *et al*., 2002; Chaudhry *et al*., 2005; Gerhardt *et al*., 2009; Wood *et al*., 2000). The mechanisms by which plants can stimulate microorganism activity in the soil to enhance the biodegradation of PCBs include:

(a) The release of organic compounds like suger, amino acids, and organic acids by plants root used as electron donor support for either aerobic or anaerobic metabolism of chlorinated compounds. In certain instances, microbial aerobic degradation consumes energy resulting in anaerobic processes which is usually favourable for PCB dehalogenation. (Chaudhry *et al*., 2005).

(b) Extracellular enzymes that cause transformation of PCBs leading to further microbial metabolism are secreted by plants (Fletcher *et al*., 1995).

(c) Microbial degradation of PCBs are speed up by inducers which are secreted by plants., however, Hedge and Fletcher (1996), reported that *B. Xenovoransvorans* LB400 and its activity as a PCB degrader was induced by plants phenolic exudates.

(d) The effects of plants root increases the permeability of the soil and also oxygen diffusion in the rhizosphere. These induces microbial oxidative transformation by certain enzymes (Chaudhry *et al*., 2005)

(e) Growth factors are also known to be secreted by plants (Campanella *et al*., 2002).

(f) Organic acids and molecules that act as surfactants comes from the roots, they therefore help to mobilize PCBs making them more susceptible to plants tissues (Chaudry *et al.*, 2005).

4.0 Difference between PCB metabolism in bacteria and plants

Plants are implicated in the increase of both microbial numbers and activity in the soil, which usually results to an increase in the biodegradation of PCB (Limbert and Betts, 1996). Nevertheless, endogenous microbes capable of maintaining symbiosis with plant are however attracted to the rhizosphere by plants secretions. Although plants have shown capability of degradation of PCBs, it has rather been slowly achieved in field trials leading to accumulation and volatilization of compounds that are toxic (Aken *et al*., 2010). Metabolism of PCB by plants is represented conceptually by a three way process of activation, conjugation and sequestration (Sandermann, 1994; Subramanian *et al*., 2019). Generally, the first stage of detoxification of PCBs called activation usually involves oxidation or hydroxylation reaction. It is a high reactive process producing soluble hydroxylated products (Aken *et al*., 2010). Following activation stage is the conjugation reaction involving endogenous hydrophilic molecules including glutathione, glucose or malonate that helps to increase the hydrophobicity of the parent compound (Rezek *et al*., 2007; Anyasi and Atagana, 2022b).

6.0 Conclusions

In conclusion, Schnoor and his co-workers evaluated applicability of phytoremediation (Schnoor et al., 1995; Schnoor, 1997). They found out that the technique is most successful when top soil is polluted with chemicals being either degraded in the rhizosphere or effectively taken up by plants for too high pollutants concentrations. Toxic effects may occur, and phytoremediation therefore is restricted to lower medium contaminated level. There is need for phytoremediation to be used in combination with an alternative treatment method, for example harnessing the symbiotic relationship between plants and microorganisms in rhizoremediation for hot spots (Schnoor, 1997Therefore, the remediation of PCBs from the soil should be facilitated using the synergistic effects of plants and microbes in the rhizosphere (Chaudhry *et al*., 2005). This co-effect enables them to cope with the toxicity and recalcitrance of the pollutant that would otherwise be difficult for either plants or soil microbes to do alone. In that line also, more research is however important to throw more light into the feedback processes that regulate the interaction of plant and microbes in the root zone of the soil during PCB remediation. The study of Mackova *et al*, (2007), highlighted on the subject, but suggested that more effort be directed towards proper elucidation of the possibility of interactions between plant and bacteria in a model PCB-contaminated environment. Therefore, all hands should be on deck by all environmental toxicologists towards achieving an effective solution to PCB contamination.

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