

# Phytomechanistic Processes in Environmental Clean-Up: A Biochemical Perspective

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**Abstract** - Plant plays important roles in environmental clean-up geared towards a sustained eco-friendly environments. Myriads of environmental pollutants from natural and anthropogenic activities are mopped up by certain plants via phyto-based mechanisms. This processes are highly regulated by phytoenzymatic and non-enzymatic activities. The uptake of contaminants via the plant roots for further biochemical processes within the plant tissues utilizes apoplastic pathway (passive diffusion process) and symplastic pathway (an energy dependent process). However, certain pollutants that are not taken up by plants are transformed into less harmful and eco-friendly molecules by the activities of endophytes within the plant roots. Phytomechanistic processes utilized by plant to remediate contaminated environments include; phytoextraction where pollutants in soil, sediments and groundwater are taken up into plant tissues or adsorbed into the roots for storage and further biochemical activities; phytodegradation where toxic pollutants taken up by plants are metabolized by phytoenzymes into non-toxic molecules; phytostabilization where the environmental pollutants are immobilized, precipitated and adsorbed within the root zone via the release of plant exudates in synergy with endophytic activities; and phytovolatilization which involves pollutant uptake and subsequent transformation into an eco-friendly compounds that are released into the atmosphere. Phytoremediation strategy for remediating contaminated environments has enormous merits over other conventional environmental remediation techniques. However, by understanding the mechanisms and the phytometabolic events occurring within plants used in phytoremediation, a new paradigm geared towards effective phytotechnological advancement and application with high ecological impact can be gained, hence the focus of this review.

**Keywords** – Allelochemicals, Apoplastic pathway, Endophytes, Phytometabolism, Phytoremediation, Phytotoxicity, Symplastic pathway, Xenobiotics.

## I. INTRODUCTION

Environmental pollution by allelochemicals and xenobiotic pollutants of both organic and inorganic compounds has become a worldwide menace, posing threats to living organisms, affecting agricultural productivity and ecosystem disruption [1], [2], [3], [4]. As industrialization continues to persist to meet the demand of an ever increasing populations of living organisms (e.g. humans), environmental contaminations by xenobiotic organic and inorganic pollutants

evolving from industrial activities are also at higher degree. Hence, the quality of the environments remains indispensable to the growth and survival of species in the ecosystem. Natural and anthropogenic activities (Fossil fuel burning, industrial emissions, oil and gasoline loses, auto-vehicle exhausts, fertilizers, electroplating, sewage sludge, metal mining and smelting, miticides, insecticides and pesticides application etc.) have resulted in large-scale contamination of soil and water with detrimental effects on ecosystems and human health [4]. [5], [6], [7]. The world has never before seen or experience increase in anthropogenic activities such as exploration and usage of petroleum products during the last century as it is of today leading to ecosystem pollution [8]. Remediating environments form these noxious organic and inorganic pollutants remains a great challenge as industrializations are keen to human sustainability. However, incessant increase in anthropogenic activities geared toward human development and sustainability has continued to alter the natural habitat, thus making life perilous for living organisms.

The knowing that plants has an inherent ability to remediate inorganic pollutants (such as heavy metals etc) and organic pollutants (e.g. dioxins, polyaromatic hydrocarbons, pesticides, chlorinated solvents, polychlorinated biphenyls, etc) from the environment evolved few decades ago. Since then, studies on plants remediation mechanisms has continue to receive tremendous attention from researchers as a promising phytotechnology also known as “phytoremediation” that can be geared towards addressing an ever increasing menace of organic and inorganic pollutants in the environments. Phytoremediation has been recognized for more than 300 year ago, however no research was carried out on the suitable plants until the early 1980s [9]. The effectiveness of phytoremediation has been demonstrated with all kinds of xenobiotic and allelochemical contaminants of both organic and inorganic molecules [7].

Phytoremediation, an *in situ* green remediation technology that uses plants (trees, shrubs, grasses and aquatic plants) and their associated microorganisms to remediate contaminated soil, ground waters or sediments through degradation, extraction, stabilization (immobilization), transformation or

volatilization [9], [11]. According to United States Environmental Protection Agency (USEPA) [12], plants can help clean up contaminants as deep as their roots can reach using natural processes to store the contaminants in the roots, stems, or leaves; transformed them to less harmful chemicals within the plant or more commonly the root zone; convert them to vapors which are released into the air; sorb (stick) contaminants onto their roots where microbes (such as bacteria) that live in the soil transforms the sorbed contaminants to less harmful compounds. Removal of organic and inorganic pollutants through phytoremediation emerges as a sustainable technology for contaminated soil as well as wastewater. However, phytotechnology can also be used to provide an active form of controlled natural attenuation [1], [11].

Phytoremediation of organic and inorganic pollutants has high performance results when compared with other conventional technologies such as pneumatic fracturing, soil flushing, solidification/stabilization, vitrification, chemical reduction/oxidation, soil washing and excavation used *in situ* and *ex situ*. These conventional methods can generate secondary waste and are cost prohibitive [1], [13]. Some of the advantages of phytoremediation over other conventional remediation techniques are: cost-effective due to the absence of energy-consuming equipment and limited maintenance; eco-friendly due to its *in situ* nature; and large public acceptance as an alternative remediation strategy [4], [14], [15]. Site restoration, erosion control, carbon sequestration, and feedstock for biofuel production are the common beneficial effects of phytotechnology [14], [16], [17]. However, lack of some biochemical pathways for complete degradation of pollutants; slow remediation rates; undesirable effects such as phytotoxicity and environmental recontamination poses a serious challenge in phytotechnology [18], [19], [20].

Plants are known to possess myriads of cellular structures and physiological processes to maintain homeostasis and detoxify certain organic and inorganic contaminants in the environments [21]. According to Vangronsveld et al., [11], commonly used plants in phytoremediation includes; Poplar (*Populus* spp.), Willow (*Salix* spp.), Maple (*Acer* spp.), grasses (*Festuca* spp., *Agrostis* spp., *Molinia caerulea*), leguminous plants (*Medicago sativa*, *Lotus* spp., *Trifolium* spp.), agricultural and horticultural crops (*Zea mais*, *Brassica juncea*, *Heliantus annuus*, *Triticum* spp. *Cucurbita* spp.), metal hyper accumulators (*Nocceaei caerulescens*) and aquatic plants (*Phragmites* spp., *Thypha* spp.). The selection of plants with increased pollutant tolerance, production of sufficient root and shoot biomass, suitability for various soil types, effective pollutant uptake mechanisms, appropriate metabolic capabilities to degrade organic pollutants, and association with active degradative microorganisms are required in phytoremediation processes [22], [23]. Rapid growth, high biomass, hairy and deep-root system, and high

bioaccumulation coefficient are some of the major phytoremediation plant qualities [24].

Phytoremediation mechanisms adopted by plants to remediate contaminated environments from adamant xenobiotics and allelochemicals includes phytodegradation, phytostimulation, phytoextraction, phytostabilization, and phytovolatilization as shown in Fig. 1. In some cases, depending on the chemical nature and properties of the contaminants in polluted areas, more than one phytoremediation mechanisms may be used by plants simultaneously for effective remediation processes. However, certain phytoremediation applications are used whether or not in combination with other remediation techniques for the remediation of contaminated soils, groundwater and sediment as a main remediation technology, while others can be used after applying traditional remediation methods as aftercare (e.g. after excavation) [11].

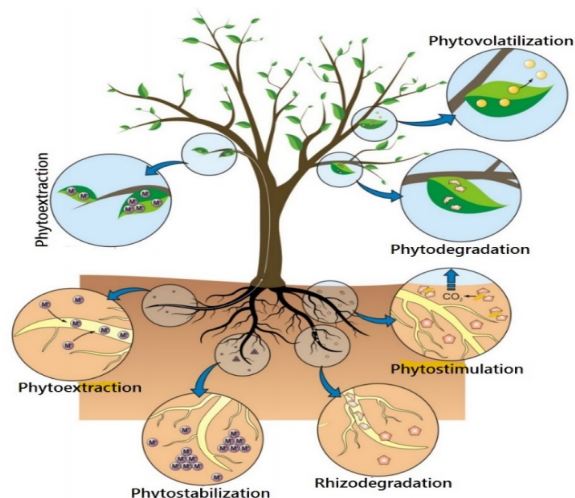


Fig. 1 Plants adopted phytoremediation mechanisms against organic and inorganic pollutants [25].

In determining the most efficient phytoremediation mechanism, it is essential to ascertain biochemically if the contaminants can be mop-up by plants and/or is biodegradable or not, as depicted in Fig. 2. Phytodegradation, phytovolatilization and rhizodegradation mechanisms are commonly employed separately or in combinations to degrade biodegradable contaminants. Rhizo-degradation is employed in degrading biodegradable contaminants that cannot be taken up by plants. However, degradable contaminants taken up by plants that are not volatile in nature undergoes phytodegradation while volatilized contaminant taken up by plants undergoes phytovolatilization. Non-biodegradable contaminants taken up by plants which are not volatile in nature undergoes phytoextraction while volatile contaminants taken up by plant employs phytovolatilization. Phytohydraulica is employed against non-biodegradable contaminants that cannot be taken up by plant but are present in ground water pollution while phytostabilization is employed against non-biodegradable contaminants that cannot be taken up by plants and are not available in ground water pollution but present in the soil.

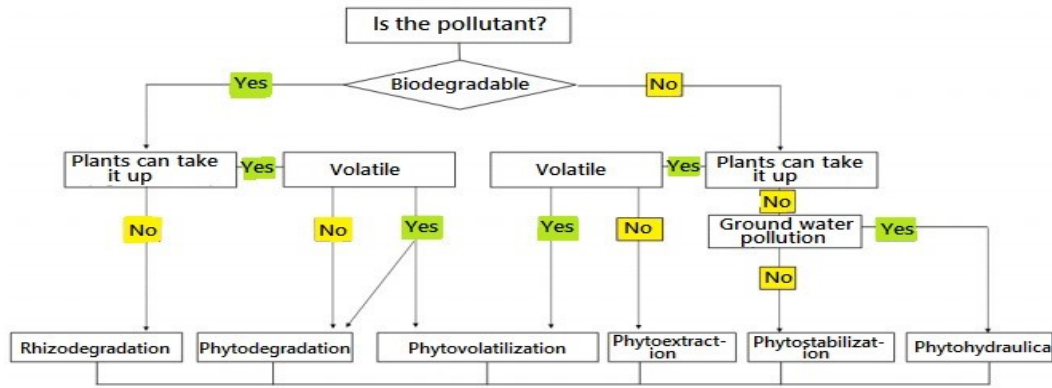


Fig. 2: Schematic representation of decision model of phytoremediation mechanism [11].

Phytotechnology (phytoremediation) are influenced by certain environmental conditions such as soil type, organic matter content, pH, cation exchange capacity, presence of impenetrable layers, the depth and flow rate of the groundwater and the climate [11]. The time required for phytoremediation depends on several factors such as: the remediation objective; the concentrations and extent of the contamination; the bioavailability of the contamination; the depth of the contaminated zone; the growth rate of the plants; the growing season of the plant; the climatic conditions; the soil conditions; the accessibility of the contamination [11].

It is without doubt that living organisms are constantly exposed to a variety of allelochemicals or anthropogenic toxic chemicals (xenobiotics) released into their environments. To circumvent the hazardous effects, living organisms developed myriads of inherent defense mechanisms against toxic pollutants. However, persistent exposure of living organisms to toxic environmental contaminants may overrides their inherent defense mechanisms, hence leading to extinction of species in the ecosystem. Research over the years have demonstrated that certain plants are able to remediate contaminated environments from myriads of exogenous organic and inorganic toxic pollutants evolving from both natural and manmade activities through the induction of phyto-based mechanisms (phytodegradation, phytoextraction, phytostabilization, phytostimulation and phytovolatilization). However, a detailed review on the mechanistic insight utilized by plants in the remediation processes remains scarce. Reviewing the phytoremediation mechanisms as a technological helpful alternative for cleaning up contaminated environments remains the objective of this work.

#### *Overview on the General Mechanistic Events of Phytoremediation*

Biochemically, certain plants are capable of utilizing an intrinsic phyto-based mechanisms involving contaminant uptake, transport, transformation and sequestration to remediate both organic and inorganic contaminants from the environments (soil, ground water and sediments) [11], [26]. In ideal cases, some plants enhance remediation processes in the environment by releasing degrading enzymes to

detoxify/metabolize organic pollutants in the soil or by extracting organic contaminants and degrading them inside their own tissues. Phyto-metabolism of organic pollutants into a less toxic compound for bioaccumulation or to an eco-friendly volatile compound for excretion are essential phytotechnological process for remediating environments.

Research findings reveals that increased accumulation of organic or inorganic in plant cytoplasm induce reactive oxygen species (ROS) generation leading to oxidative stress. This triggers phytotoxicity such as inhibition of cellular processes, DNA damages, protein oxidation and disruption of cell homeostasis [27], [28]. In circumventing organic and inorganic-induced oxidative damage, plant cells activate the ROS-scavenging machinery by inducing antioxidant enzymes, such as superoxide dismutase (SOD), catalase (CAT), peroxidase (POD), and glutathione reductase (GR), as well as non-enzymatic antioxidant compounds including tocopherol, ascorbate, carotenoids, glutathione and flavonoids [28], [29].

The biochemical processes observed in phytometabolism of organic xenobiotic compounds are similar with xenobiotic metabolic processes in mammalian liver which includes the ability to detoxify contaminants, utilization of specific enzymatic pathways, and removal of the compounds from the susceptible organelles. However, the differences observed is in the ultimate fate-storage as opposed to excretion in mammals [30]. On the other hand, inorganic compounds (e.g. heavy metals) are non-degradable by any biological or physical process [2], however, certain plants are able to remediate inorganic pollutants from the environment through various phyto-based mechanisms. In addition, plants facilitate remediation in contaminated areas by providing essential nutrients for soil microorganisms to mop up organic and inorganic pollutants [31].

#### *Step 1: Phyto-uptake and translocation of allelochemicals and xenobiotic contaminants*

Myriads of environmental contaminants, both organic and inorganic (e.g. chlorinated solvents, herbicides, pesticides, insecticides and explosives, etc.) compounds are mopped up by some plants [11]. Plant roots represent the major routes by

which both organic and inorganic contaminants in the environments can be mopped up by plants and subsequently translocated to the above-ground parts of the plants followed by accumulation or evapotranspiration/degradation as shown in Fig. 3 and 5. The series of biochemical processes involve in the uptake, translocation and accumulation of organic or inorganic contaminants in plants includes: pollutant mobilization, root uptake, xylem loading, root-to-shoot transport, cellular compartmentalization, and sequestration [4].

Organic and inorganic pollutants are absorbed at the root surface and moves across the cellular membrane into the root cells. The uptake of organic and inorganic pollutants into roots occurs mainly via two pathways viz; *apoplastic pathway* (passive diffusion) and *symplastic pathway* (active transport against electrochemical potential gradients and concentration across the plasma membrane). Symplastic pathway is an energy dependent process mediated by metal ion carriers or complexing agents in which inorganic pollutants are taken up via the plant roots while organic pollutants commonly undergo apoplastic pathway due to their hydrophobic properties [4], [32].

Inorganic pollutants (e.g. heavy metals) mostly are not bioavailable to plants due to their insoluble state in the soil. However, plants increases their bioavailability by releasing a variety of plants exudates (e.g. organic acids and amino acids) which can change the rhizosphere pH and increases inorganic contaminant solubility by acting as an inorganic ligand to form a soluble inorganic complexes in the rhizosphere [4], [33].

Uptake and translocation of inorganic pollutants in plant are mediated by specialized metal ion transporters and complexing agents such as organic acids. These specialized transporters (channel proteins) or  $H^+$  coupled carrier proteins are found in the plasma membrane of the root cell and are essential for the uptake of inorganic pollutants (heavy metal ions) from soil [4], [28]. Plant releases various exudates or

chelators (e.g. organic acids, *phytochelatins*, *metallothioneins* etc) to form complexes with inorganic pollutants in the cytosolic compartment after entering into the root cells. The inorganic pollutant complexes (transformed pollutants) are immobilized and translocated from the cytosol into inactive intracellular compartments (symplastic compartments such as vacuoles) or to the extracellular compartments (apoplastic cellular walls) where they are stored [34], [35].

In addition, to prevent pollutant accumulation leading to phytotoxicity, the transformed pollutants sequestered into the extracellular compartments (cell walls) or plant vacuole can further be sequestered and compartmentalized into other location such as leaf petioles, leaf sheathes, and trichomes via apoplast or symplast where phytotoxicities induced by inorganic and organic pollutants can be mitigated [4], [34], [36], [37]. The inorganic ions sequestered inside the vacuoles may be transported into the stele and enter into the xylem stream via the root symplast and subsequently translocated to the shoots through xylem vessels [38].

Organic pollutants uptake by plant utilizes *apoplastic pathway* (passive diffusion) due to the hydrophobic nature of organic pollutants. Hydrophobicity of the contaminated molecules as well as the plant species and the environmental conditions remains the sole determinants of organic pollutant uptake via plant roots [11], [14], [39]. Hydrophobicity of organic pollutant is expressed as the log Kow (logarithm of the octanol water partition coefficient) [15]. According to research findings, a log Kow of 0.5 - 3.5 means good uptake by plants, while substances with a higher log Kow value will mainly adsorb to plant roots with no or very little translocation to the above-ground parts [39]. However, water soluble contaminants, on the other hand, penetrate the xylem vessels fairly quickly before they can be degraded by microorganisms in the rhizosphere. Thus, a crucial role in the degradation of this type of contaminants is observed in Endophytes (the bacteria and fungi that live in the plant) [11].

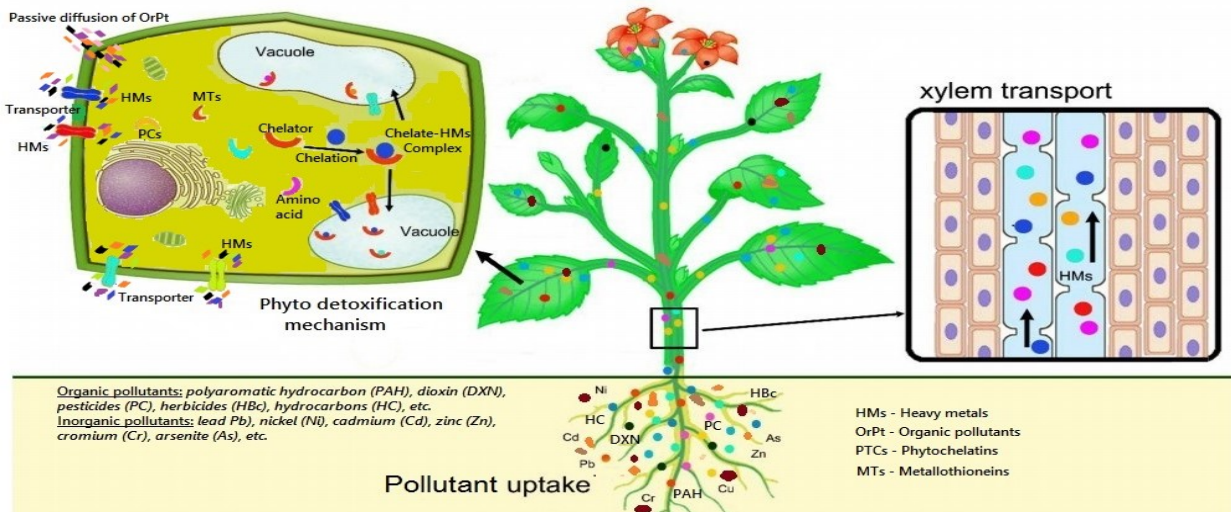


Fig. 3: Phyto-based mechanisms of pollutant uptake, translocation and sequestration [4].

Step 2: Phytotransformation of contaminants

Plants are able to transform organic and inorganic xenobiotic contaminants into more H<sub>2</sub>O soluble and less toxic forms. This are carried out through sequence of enzymatic reaction as show in Fig. 4 and Fig. 5. First, the unreactive groups of contaminants undergoes phase 1 functionalization reaction to become activated by redox reactions. The functionalization/activation reaction introduces functional groups such as hydroxyl, amino or sulfhydryl group to unreactive contaminants, thus becoming reactive which are then subjected to phase two reaction. However, functionalized contaminants bypasses phase 1 reaction to undergoes phase 2 reaction. In phase two reaction (conjugation reaction), the activated contaminants in phase 1 or the functionalize contaminants can be conjugated with sugars by glutathione and UDP glycosyl transferases. Subsequently, they are sequestered usually in the vacuole or cell wall and finally stored in less photosynthetically active tissues including old leaves in the roots or in the woody material of the plant [11], [14], [39]. Depending on the nature of contaminants, plant can adopt different phytomechanistic processes such as phytodegradation, rhizodegradation, phytovolatilization, phytostabilization, phytohydraulics and phytoextraction to remediate environments from contaminants.

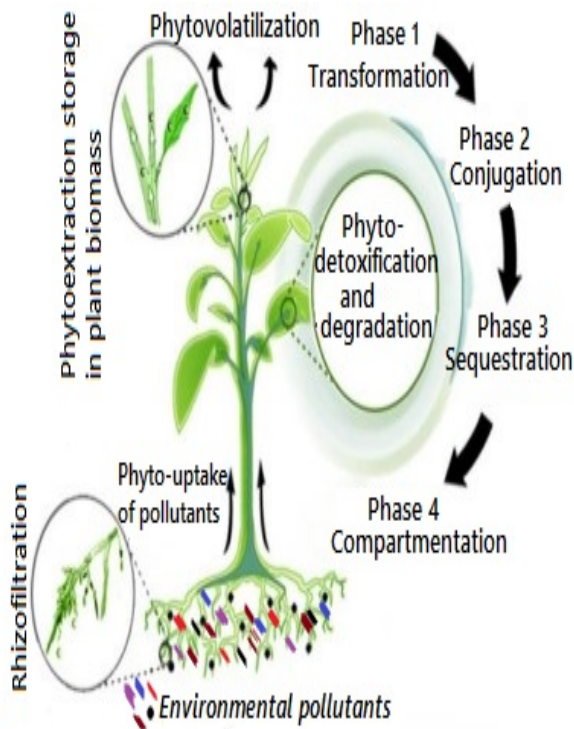


Fig. 4: Uptake of environmental contaminant via plant roots and subsequent phyto-transformation processes [14], [39].

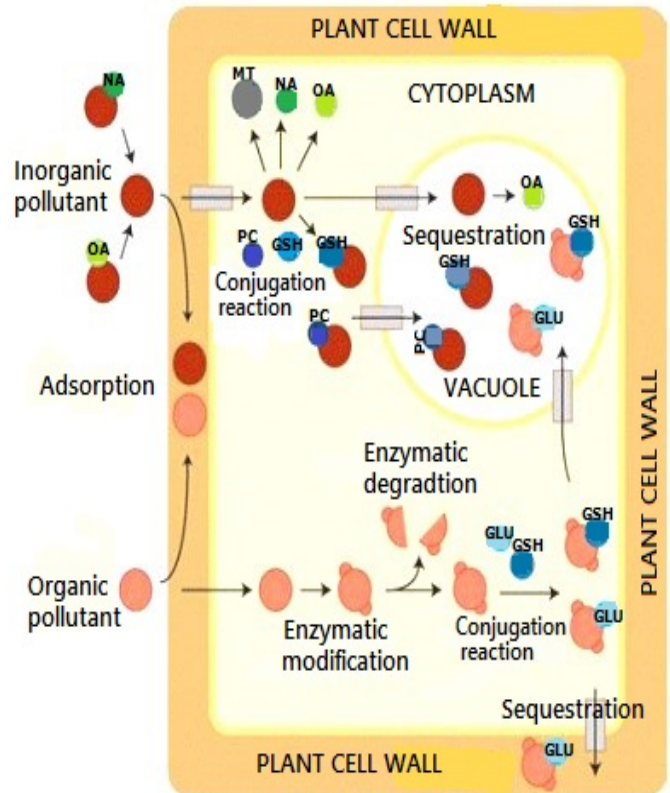


Fig. 5: Mechanisms for the phyto-uptake, transformation and sequestration of organic and inorganic contaminants. PC: phytochelatins, OA: organic acids, GSH: glutathione, MT: metallothioneins, NA: nicotianamine, Glu: glutamic acid [11].

Biochemically, organic and inorganic pollutants are taken up by adsorption via roots into the plant cytoplasmic compartment. The inorganic pollutants are capable of bypassing phase 1 reaction upon their adsorption and subsequently undergoes conjugation reaction and sequestration into the plant vacuole. However, organic pollutants are adsorbed into the plant cytoplasm where the pollutant undergoes enzymatic modification known as phase 1 reaction, the enzymatic modified organic pollutants can be degraded or undergoes further conjugation reaction known as phase 2 reaction. Subsequently, the conjugated pollutants will then undergoes sequestration into the plant vacuole or cell wall.

It is without doubt that plants (a photoautotrophic organism) are not evolutionarily endowed with myriads of enzymes to metabolize organic molecules and contaminants as compared to heterotrophic organisms such animals. However, the plants-roots associated microorganisms (endophytes) possesses as wide variety of metabolic enzymes which in synergy with plants collectively catalyze complete degradation of organic contaminants into CO<sub>2</sub> and H<sub>2</sub>O and also facilitate the sequestration of inorganic pollutants as depicted in Fig. 6 [40].

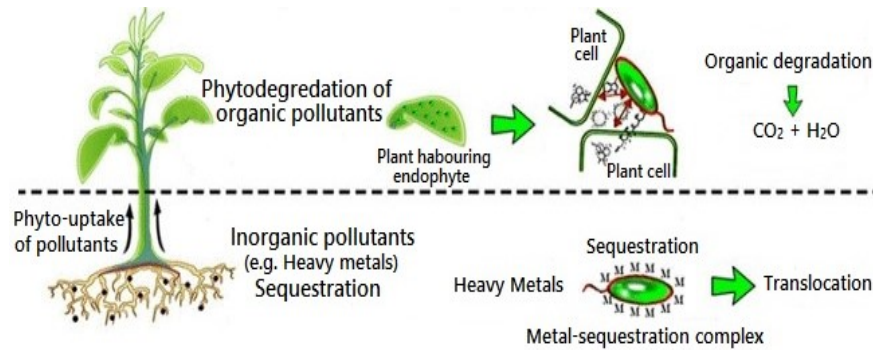


Fig. 6: Endophytic mechanisms against organic and inorganic contaminants [40].

Certain bacteria and fungi lives and interact with plants both above and below ground [40], [41]. Plant associated microorganisms can transform contaminants, fix metals and protect the plant against stress and phytotoxicities. In addition, they can also stimulate plant growth through the synthesis of plant hormones, the release of poorly soluble iron and phosphate, and help with the absorption of non-bioavailable elements [11]. A collective role has been observed among phyto-associated microbes and plants in enhancing phytoremediation of contaminated sites [42], [43].

Findings from research reported a mutual interaction between endophytes and their host plant, benefiting from a less competitive environment for nutrients and niches compared to the very diverse complex and dynamic environment of the soil and rhizosphere [11]. Endophytes invades their host plants via roots mainly at the junctions between root hairs and at the level of the lateral root formation, they are store in the root cortex or the xylem after translocation through the apoplast or vascular bundle system as represented in Fig. 7 [11], [44].

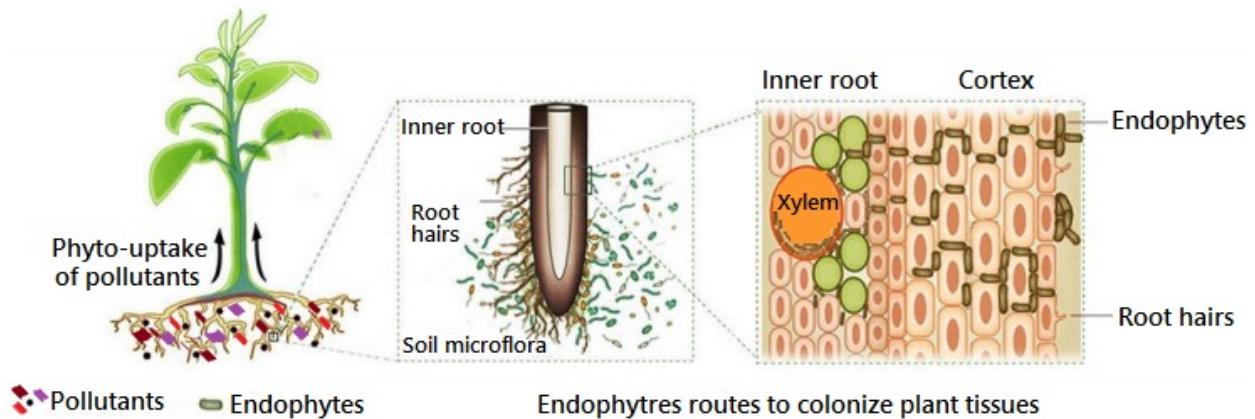


Fig. 7: Endophytes invasion and colonization [11].

The physiology of plant and the nature of the released plant-specific mixture of exudate determines the harboring specific microbiome for each plant. Remediation expert reported that the interactions between plants and their harbouring microorganism often lead to an improved efficiency of phytoremediation [11], [26], [45].

## II. PHYTOMECHANISTIC STRATEGIES ADOPTED BY PLANT FOR ENVIRONMENTAL CLEAN-UP

1. *Phytodegradation*: it is a process in which organic allelochemicals and xenobiotic contaminants can be biochemically degraded by phyto-based mechanisms following a sequence of enzymatic reactions. It is a process in which plants and their associated microorganisms absorb and degrade contaminants in plant tissues through enzyme mediated metabolic processes. Organic contaminants are taken

up by plants via the roots for degradation [4], [11]. After uptake, xenobiotic degrading enzymes are secreted by the plant in synergy with endophytes to degrade complex organic contaminants into simpler molecules which can then be utilized or released by plant. Some of the phytoenzymes involve in phytometabolisms of organic allelochemical and xenobiotic contaminants includes dehalogenases, nitroreductases, oxophytodienoate reductases, polyphenol oxidases, peroxidases, laccases and dehydrogenases. These enzymes often have a spatial effect because they work on their own outside the plant, and a temporal effect. However, they can still be active even after the plant dies [11].

Plants are capable of degrading organic pollutants inside the plant or within the rhizosphere of the plant as shown in Fig. 8 [46]. Poplar, Leuceana, Brassica, Herbaceous plants, Alfalfa,

Helianthus are some of the plants known to degrade organic pollutants [46], [47], [48], [49].

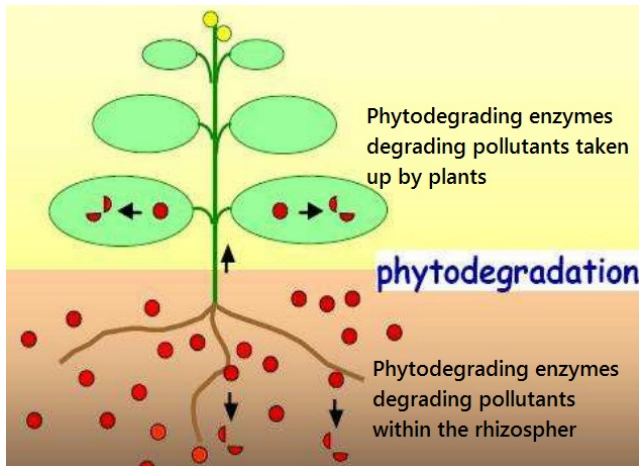


Fig. 8: Schematic illustration of phytodegradation [50].

Biochemically, the sequential events observed in phytodegradation of both organic allelochemicals and xenobiotic contaminants utilizes the three phases of phytometabolism as proposed in the green liver model. Phase 1 reaction known as the activation reaction oxidizes organic pollutants to generate various hydroxylated molecules that are highly soluble and reactive; the activated molecules in Phase 1 undergoes Phase 2 reaction known as conjugation reaction where they are conjugated with phyto-based molecules (e.g. amino acids or glutathione) to form a more soluble and less toxic molecules; In Phase 3, the conjugates are sequestered into plants vacuole or incorporated into plant cell wall [14], [51], [52]. An example of this biochemical events of phytometabolism of organic pollutants can be elucidated as observed in phenolic degradation. Phenolic contaminants are catalyzed by oxidase enzyme to produce an oxidized molecule (e.g. quinone) which can further be condensed with amino acids and peptides to form humic acids. Phytodegradation applies only to organic pollutants as inorganic molecules (e.g. metals) cannot be degraded [11], [53].

2. *Rhizodegradation*: Certain degradable environmental contaminants are degraded in rhizosphere, outside the plant but within the plant roots. In the rhizosphere, microbial activity is stimulated by the presence of plant roots and by the supply of oxygen, water and rhizodeposits. Plants associated microbes are the major key players in rhizodegradation process. Rhizodegradation occurs when certain degradable contaminants cannot be taken up by the plants, the contaminants are degraded via endophytic activities in the soil within the plants roots [11], [54]. The sequence of enzymatic reactions in degrading contaminants by rhizodegradation are similar to phytodegradation. However, with every application of phytodegradation (degradation in the plant), part of the contamination is also degraded by rhizodegradation (degradation in rhizosphere, outside the plant) [11].

An additional merit to rhizodegradation process is that the micro-organisms present in the rhizosphere can spread through the soil at a faster rate if absorbed to the roots. Hence microorganisms adapted to contamination can colonize a larger portion of the contaminated soil. This is important for degradation of petroleum hydrocarbons and explosives etc. [55], [56].

3. *Phytoextraction*: In phytoextraction, inorganic contaminants often metals, are taken up by the plant tissues from soil or water and subsequently translocated and stored preferably in the above ground biomass of the plants [4], [57]. It is a process in which plants and their associated microorganisms absorb contaminants and fix them in plant tissue. According to Vangronsveld et al., [11], uptaking of the contaminants and accumulation/storage are highly dependent on the plant species, the type and concentration of the contamination, the pH and the bioavailability of the metals in the soil to plants.

Primarily, phytoextraction of inorganic contaminants (heavy metals) proceeds via the following steps: (i) mobilization of heavy metals in rhizosphere, (ii) uptake of heavy metals by plant roots, (iii) translocation of heavy metal ions from roots to aerial parts of plant, (iv) sequestration and compartmentation of heavy metal ions in plant tissues as shown in Fig. 9 [35], [50]. However, phytoextraction efficiency depends on certain factors such as plant selection, plant performance, heavy metal bioavailability, soil, and rhizosphere properties [4]. Rye, Parrot feather, Canna and Curcubita are some of the plants known for uptake of organic pollutants [46], [58], [59], [60].

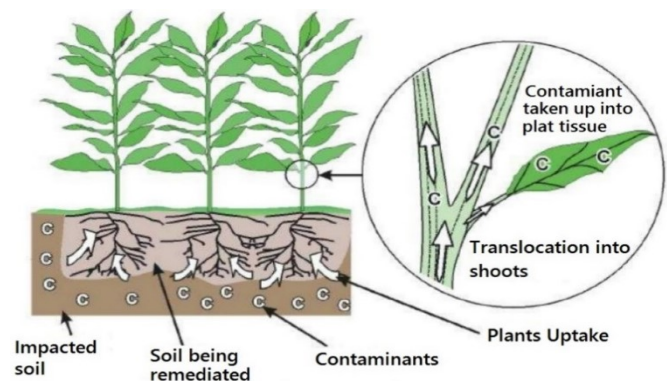


Fig. 9: Schematic illustration of phytoextraction [50].

Various mechanisms have been reported to play a role in the uptake of metals by plants, e.g. exudation of protons and organic acids promotes the bioavailability and mobilization of metals in the rhizosphere [11]. In addition, phytochelatins and siderophores are plants associated chelators that are known to form metal complexes which can be taken up by the plant and subsequently translocated above the ground parts. Harvesting plants accumulating inorganic and organic pollutant byproducts has to be often and carefully to avoid recontamination of the soil when plants die or trees lose their leave [11]. Among the common plants used in phytoextraction

are Sunflowers, Indian mustard, Rape seed plants, Barley, Hops, Crucifers, Serpentine plants, Nettles, Dandelions [11].

Endophytes can induce inorganic and organic extraction from the soil through a biological process such as the secretion of acids and hydrogen ions ( $H^+$ ). Phyto-associated microbe enhances metal detoxification and improve the plants biomass production as well as reducing stress. The main advantage of endophytes induced mobilization of the contaminants is the fact that this happens in balance with the activity of the plant [11].

4. *Phytostabilization*: a phytotechnological process in which plants are used to immobilize contaminants by adsorption, absorption, accumulation and precipitation in the root zone. It is useful in mopping up inorganic and organic contaminants in the soil, thus reducing the spread of contaminants into the groundwater or the atmosphere [4], [11]. In remediating inorganic contaminated environments, metal-tolerant plant species are used to immobilize heavy metals belowground and reduce their bioavailability, hence halting their migration into the ecosystem and reducing the likelihood of metals entering into the food chain [61], [62], [63]. According to Gerhardt et al., [64] and Kumpiene et al., [65], phytostabilization occurs via precipitation of heavy metals or reduction in metal valence in the rhizosphere, absorption, and sequestration within root tissues, or adsorption onto root cell walls.

Contaminants in the rhizosphere can be sequestered by plants through adsorption and precipitation into less soluble forms like carbonates and sulphides of metals as shown in Fig. 10. The contaminants complexed with organic compounds are adsorption on root surfaces and stored in root tissues [61]. Mycorrhizae can modify the rhizosphere and also induced the excretion of organic acids to stabilize inorganic contaminants in the rhizosphere by interacting with hyphae and some mycorrhizae like ericoid and *Ectomycorrhizal fungi* colonizing in *Cynodon dactylon* [66].

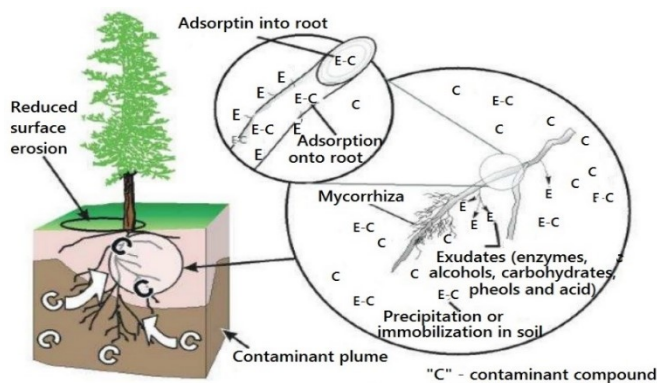


Fig. 10: Schematic illustration of phytostabilization [50].

One of the notable challenge in phytostabilization is excessive phytotoxicity. However, working with certain stabilizing soil additives (mineral oxides, lime, phosphates, organic substances) help to reduce the amount of contaminants to be absorb by plant thereby mitigating phytotoxicity.

5. *Phytovolatilization*: in phytovolatilization, certain plants are able to take up pollutants (both organic and inorganic) from contaminated environments (soil, sediments and groundwater) which are transformed into less toxic volatile compounds, and subsequently releases them into the atmosphere by transpiration process through the leaves or foliage system [4], [67]. This phyto-based remediation approach can be applied for detoxification of organic and inorganic pollutants in contaminated environments [67]. Organic pollutants, especially volatile organic compounds (VOCs) are passively volatilized by plants as depicted in Fig. 11 [50]. For example, hybrid poplar trees have been used to volatilize trichloroethylene (TCE) by converting it to chlorinated acetates and  $CO_2$  [46], [47], [68]. In addition, Brassicaceae family plants such as *Brassica juncea* are also commonly used in phytovolatilization [69].

One of the major advantage of phytovolatilization is that organic and inorganic pollutants are extracted and transform into an eco-friendly volatile molecules which are released as waste products of environmental pollutants into the atmosphere without plant harvesting and disposal [4]. However, depending on the nature of the contaminants and its adverse effects after being transformed into volatile molecules, phytovolatilization is applied if the volatilized contaminants are rapidly degraded once it enters the air or if the release can occur under controlled conditions without toxicity [11].

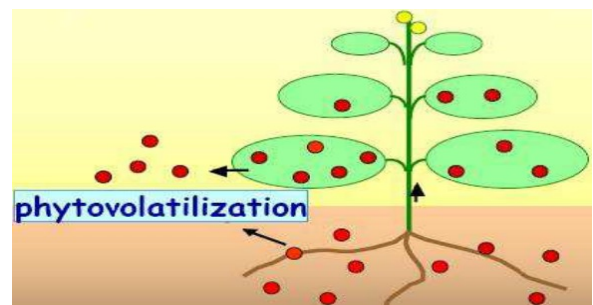


Fig. 11: Schematic illustration of phytovolatilization [50].

6. *Phytohydraulics*: It is based on the ability of the plants to carryout evapotranspiration on the surface or ground water. In phytohydraulics, plants and their endophytes take up and evaporate water thereby influence the groundwater level, the direction and velocity of the groundwater flow [11], [70]. Horizontal migration of groundwater can be controlled and contained by deep-rooting plant species such as phreatophytes that can absorb and transpire a lot of water. Trees that are classified as phreatophytes are deep-rooted, rapidly transpiring trees that prefer wet soils and can tolerate temporary periods of water saturation. Typical phreatophytes are poplars and willows, these can limit the spreading of the contamination [11]. Planting of phreatophytes at contaminated groundwater sites can serve as a groundwater treatment system. Phytohydraulic strategy can be used to address a wide range of contaminants in soil, sediment, or groundwater [11], [70].



### III. CONCLUSIONS

Certain plants are capable of utilizing phyto-based mechanisms in synergy with their endophytic processes to extract/remove, detoxify and metabolize myriads of allelochemicals and xenobiotic organic and inorganic contaminants from polluted environment. Phytoremediating plants are able to extract, immobilize, stabilize, degrade and volatilize both organic and inorganic pollutants in the environment. However, extracting contaminants from the polluted environments, concentrating the contaminants in the plant tissue, immobilization of the contamination in the root zone or rhizosphere, and transforming pollutants into eco-friendly volatile compounds as waste products which released into the atmosphere represents the phyto-based mechanisms utilized by plants in cleaning up contaminated environments. In addition, plants possess an inherent defense mechanisms against pollutant-induced phytotoxicity through the activation of both antioxidant and non-antioxidant enzyme activities. Understanding the mechanisms of phytoremediation of both allelochemicals and xenobiotic pollutants will proffer an insight geared towards developing an effective strategy to remediate contaminated soils, sediments and water, aiming at restoring the disturbed ecosystems.

### CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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