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PHYTOREMEDIATION: AN ENVIRONMENTAL DETOXIFICATION TECHNOLOGY USING PLANTS

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ABSTRACT

Phytoremediation is a green technology that uses plant to remove, detoxify and clean up some selected environmental contaminations inside the soil, waste water, ground water and sludge that are contaminated through human, economic, agricultural and industrial activities. Excessive contaminations of the soil usually pose significant health hazard to human and plants life, hence it is imperative to adequately and carefully remove all these toxic substances from the soil leaving the soil free of contaminations. They are usually less expensive and eco-friendly. These pollutants are usually remediated using five different applications; Phyto-extraction, phyto-stabilization, phyto-filtration (Rhizo-filtration), phyto-volatization, phyto-transformation (Phyto-degradation). Different plants have been identified as phyto-remediators and are capable of bio-accumulating shallow contaminants, toxic metals, organic and nutrients pollutants into their different harvestable body parts; like the leaves, root, shoot and stem thereby stabilizing the soil of variety of pollutions. The plants that are efficient in remediating the soil are also called 'Hyper-accumulators' they thrive well in a toxic environment. They concentrate heavy metals like; Pb, Ni, Co, Cd, Co and lots more into their body parts and the plant biomass are carefully disposed and incinerated in an enclosed medium. United States Environmental Protection agency reiterates that phytoremediation is a clean and cheap technology that can be used in remediating our polluted sites.

Contribution/Originality: This study contributes in the existing literature on how to make use of green plants to effectively remove, cleanse, restore and remediate soils contaminated with metals, pesticides, solvents, crude oil, waste water, sludge and sediments without disrupting the structure, texture and quality of the soil.

1. INTRODUCTION

A major environmental concern due to disposal of industrial waste produced anthropogenically is soil contamination. Monitored and unmonitored waste disposal, sewage, accidental spillage, mining of metallic ores, lead pollution produced by industries is responsible for the contaminations of non-contaminated sites. Some metals like Chromium, Lead, Mercury, Cadmium are dangerous to human life [1]. So, contaminated soils with metals must be remediated using an eco-friendly method. In this modern years, the use of metal hyper-accumulator plants shows that the green technology is promising for cleaning up sites that are contaminated. Plants are useful in cleaning and stabilizing contaminated heavy metals soils [2]. Currently the phytoremediation technology now focuses on expanding the contaminated soil and air pollutants to preserve the soil bio-diversity [3]. From this phytoremediation technology, the technique is eco-friendly, cheap and has a very high bio-recovery potential for heavy metals. Moreover, the soil still maintains its physical and biological properties after remediation. Natural environmental pollution caused by the excessive concentration of the metals is a global problem because they have toxic effects on living things and are indestructible. Some contaminated soil frequently possesses some heavy metals like; Pb, Cu, Fe, Cd, Cr, Zn [4]. Numerous researchers have explored a less expensive technique to phytoremediate heavy metal contaminated soil [5]. Therefore, the use of metal hyper-accumulator plants to remove heavy metal polluted soil is called Green Solution [6]. The aim of phytoremediation is to remediate, reclaim, and clean up soils containing unusual high heavy metal concentrations. Plants that are of high metal tolerant potential are normally used for remediation processes [7]. The physical and chemical characteristics of contaminated soils with heavy metals always hinders the growth of the plant [8].

2. PHYTOREMEDIATION

Phytoremediation (from Greek word *(phyto)*, means "plant", and Latin *remedium*, means "clean up") describes a process where plants cleanse and restores soil purity without excavating or disposing the contaminated materials in the soil. Phytoremediation requires green plants planted in the media (soil) to remove pollutants that are in excessive concentrations in the environment and could eliminate or degrade pesticides, metals, solvents, crude oil and solvents. Remediation uses green plants to 'vacuum' metals from the soil through the root. While removing the metals, the plants must act efficiently as hyper metal accumulators and could tolerate and survive metal accumulation [9]. It is fully or considerably used to remediate some selected contaminants in soil, waste water, ground water, surface water, sludge and sediment. Phytoremediation can also be referred to as agro-remediation, green remediation and botano-remediation [10]. The plants are very effective in remediating soils with metal, organic, nutrient that are of shallow contamination. Phytoremediation is a modern technology used due to its versatility and low cost to remediate polluted sites [11]. Phytoextraction, that is one of the effective environmental phytoremediation process depends on numerous factors like; availability of metal uptake into roots, shoots and leaves (bioavailability), extent of contamination, plants ability to accumulate metals, intercept and absorb metals in the shoots.

2.1. Phytoremediation Processes

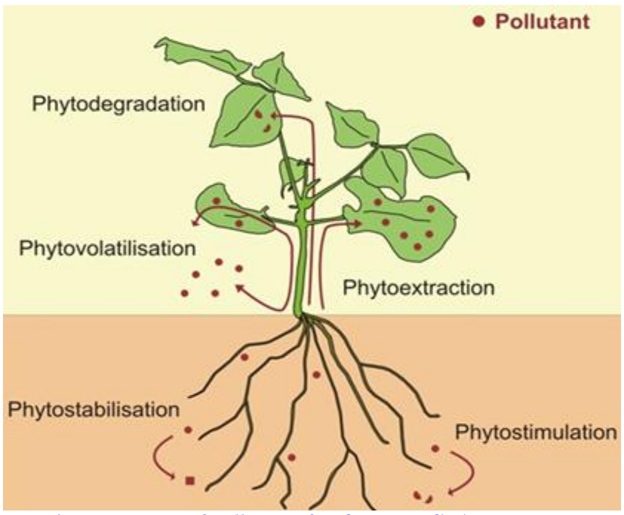

Figure-1. Fates of Pollutants for phytoremediation processes.
Source: Pilon-Smits [12].

2.1.1. Phytoextraction

Phytoextraction is when contaminants are being absorbed and translocated by plant into the aerial portions like shoots and leaves. The accumulated biomass can be recycled using the ash content [13]. The harvested root and shoot containing the contaminants are expunged from the soil. The conventional technique of remediating the soil is ten times more expensive than the cost involved in phytoextraction [14]. A very low chemical oriented technology involved in phytoextraction contributes to its environmental friendliness attributes. Furthermore, during phytoextraction, leaching and erosion are well reduced because the plant covers the soil. With successive phytoextraction processes, the contamination soil level can be drastically reduced [15].

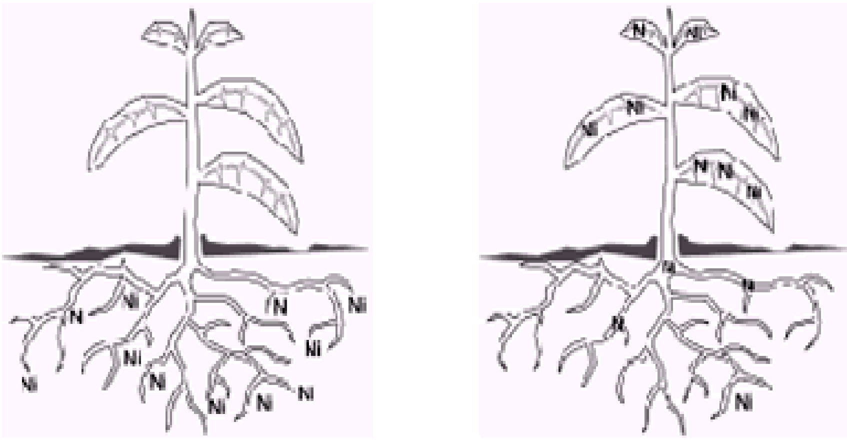

Figure-2. Uptake of Metals (Nickel) by Phytoextraction.
Source: United Nations Environment Program (UNEP) [16].

Nickel is removed from soil by moving up into plant roots, stems, and leaves [15] . The metal accumulated plant is then harvested and disposed of and a successive planting was done until all the nickel in the soil is permanently cleaned to an acceptable level.

2.1.1.1. Importance and Barriers of Phytoextraction

Phytoextraction is known for its environmental friendliness. Compared to the former methods, in the bid to remediate the soil ended up disrupting the soil structure, texture and quality, whereas phytoextraction cleanse without altering the quality of the soil. Another importance is that it is less expensive than any other remediating process. Unlike anthropogenic activities, phytoextraction takes longer time to clean up because they are controlled by plants. Also they cannot remediate a heavy contaminated site.

2.1.1.2. Types of Phytoextraction

2.1.1.2.1. Natural Hyper-Accumulators

These type of plants naturally remediate the contaminated soil without been assisted by any agents. They are commonly called natural metal hyper accumulators (metallophyte) that accumulates and tolerate the heavy metal absorbed until they are harvested.

2.1.1.2.2. Induced Hyper-Accumulation

These type of plant requires the effect or addition of a chelating agent that is added to the soil to increase its metal solubility and absorption so, the plant can be easily remediated or absorbed. An induced plant does not possess the ability to phytoremediate naturally unless with the aid of a chelating agent.

2.1.2. Phytostabilization

These focuses on the stabilization of the plant that enables it withstand and reduce erosion, act as wind breakers, prevent wind erosion. It contains the pollutants by absorbing and immobilizing them and provide a rigid zone beneath the root that enables the pollutant to stabilize and precipitate. Phytostabilization mainly brings together all the far pollutants that are close to the roots but in the soil thereby rendering them harmless and less bioavailable to human beings and animals [17]. Metals or contaminant removal is not of utmost importance in phyto-stabilization. It focuses more on stabilizing the root, the area, and the soil rather than removing the metals. The plants actually provide a barrier to animal and human contact and do not exhibit any role in stabilizing the area. Soil amendments chemically helps to make metals insoluble and gather them in the soil [18]. It requires the use of plants to accumulate various contaminants that are present in the groundwater and soil through the accumulation in the plant tissues and root zones hereby inhibiting their movement [19]. Phyto-stabilization is actually used for the cleansing of soil, sludges and sediment [20]. The plant root is used to hinder the mobility and movement of available contaminants in the soil. They are commonly called in-place inactivation. The main function of the plant is to reduce the volume of water entering through the soil, hence, result in the hazardous leachate formation. The plants action as a barrier helps in the prevention of a direct contact with the contaminant, helps in the prevention of soil erosion and channel the heavy metals to other areas [21]. It occurs through complexation, bonding, sorption, precipitation and reduction of metal [15]. The disposal of the contaminated material accumulated (biomass) is not required in phytostabilization. The rapid immobilization of the contaminant is important in the preservation of the contaminated waters. Phyto-stabilization minimizes soil erosion and reduces the availability of water in the soil medium [20].

2.1.3. Phytofiltration

This is the cleaning, sieving and filtering of water using plants. It is also the use of plants, both terrestrial and aquatic, to precipitate, purify and remediate contaminants from polluted aqueous sites in their roots. It is also termed as Rhizofiltration. Like phytoextraction, they utilize the hyper accumulating plants and at times, it is unnecessary that movement to the aerial part (above ground) should take place and possibly a biomass of the contaminated plants. In phytofiltration, the root sucks the metal contaminant, because the clean water is absolutely removed from the system and not the plant [22]. Metals that are phytoremediated, filtered and retained within the root includes; Ni, Cd, Pb, Cu, Cr and Zn [20]. Phytoextraction and phytofiltration explore similar method to accumulate and purify metal abundance. This is usually done by the combination of some phytochelating agents and metallothioneins proteins that handle the detoxification and purification of metals both in the plants tissue and cells. Few of these kinds of proteins have found a wide area of research and they are much efficient and refined [23]. Rhizofiltration uses plants to reclaim and purify groundwater, wastewater and surface water with little contaminations [24]. Some plants like spinach, corn, Indian mustard, tobacco, sunflower and rye have been studied by different researchers for possessing the ability to expunge and reclaim lead from water. Sunflower and Indian mustard has a strong potential and has been researched to remove lead effectively [15]. It has an accumulation coefficient for the removal of lead from water and also has a large concentration range of lead (4 mg/L -500 mg/L) [20, 21].

2.1.3.1. Importance of Rhizofiltrations

Rhizofiltration has the ability to utilize aquatic and terrestrial plants for phytoremediation applications. Another importance is that in this process, contaminants are not transferrable to the shoots because the roots has filtered them away and are not present in the soil. The only preferred plants are the terrestrial plants because they have long and fibrous root system [21]. From the research conducted by Dushenkov, et al. [25] it was observed that the root of many terrestrials grown plants such as Indian mustard and Sunflower removed heavy metals effectively from aqueous sites.

2.1.4. Phytovolatilization

It is a process through which a plant uptake and transpires a contaminant into the atmosphere. Some contaminants enter through the higher plants in the growing trees and volatilize at a considerably low concentration into the atmosphere [13]. Another important role performed by plant is the stabilization of the root system thereby hindering the occurrence of erosion, preventing the washing away of the soil surface and reduce rain impact. Also, nutrients are released by plant root to sustain the community of microbes in the rhizosphere. The community are usually affected by soil type, root zone, and plant species. Microbes in the rhizosphere are higher generally than in the root of the soil. This is because of the mutual bond between the plant and the microorganism in the soil. This mutual relationship strengthens bioremediation process. The roots of the plants usually provide avenue for precipitation and sorption of contaminants from toxic metals [26]. In phytoremediation, the most important part of the plant is the root and often, they absorbed contaminants, metabolised and store them. The harvested contaminants are usually degraded by the plant enzymes extracted from the root, this is another mechanism of phytoremediation Merkl, et al. [27]. USEPA [20] explains plant volatilization is the transforming of contaminants present in the soil into volatile compounds and which are transpired into the atmosphere making use of plants. A particular chemical contaminant that explains these process is mercuric mercury, because the mercuric ion could be transformed into a less harmful substance, reducing it totally to becoming an element (Hg) [15]. The limitation of these mechanism is that the atmospheric mercury i.e the mercury transpired into the atmosphere are been recycled and precipitated back into our soil, oceans, lakes, thus repeating the methyl mercury production by anaerobic bacteria [28]. The yellow poplar (*Liriodendron tulipifera)* plant similarly, can survive very well in a toxic environment containing ionic mercury. The plants volatility is ten times stronger in its elemental form than the elemental mercury. Also Indian mustard and canola (*Brassica napus*) are very good plants that is used for phytovolatilization accumulation and transpiration of selenium [29].

2.1.5. Phytotransformation

It is also named as Phytodegradation. It is a process whereby the contaminants taken up by plants are broken down by some enzymes produced by same plant and transformed through physiological activities that occurs in the plant. Complex organic pollutants are degraded into smaller and simpler molecules, incorporate them into plant tissue to enable them grow faster [16].

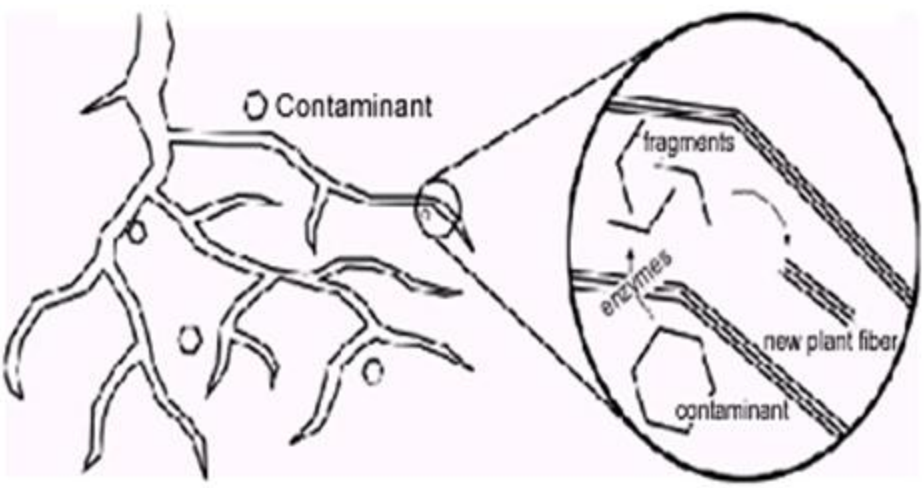

Figure-3. Enzymatic compositions in Plant root break down (degrade) organic contaminants.
Source: United Nations Environment Program (UNEP) [16].

Cannas, a very good remediating plant renders the organic pollutants like; industrial chemicals, pesticides, solvents, pesticides, xenobiotic compounds non-harmful by the plants metabolism. At times, microorganism living in the plant roots may degrade these toxic substances that is present in the water and the soil. The complex pollutants cannot be degraded to simpler and smaller units such as (carbon dioxide and water) by the plant, but can only be transformed from one chemical structure to another without breaking the compound. hence the term Phytotransformation. The action of plants when linked with the xenobiotic substances (Foreign pollutant) in the human liver is used in describing phytotransformation as a 'Green liver' [30].

Table-1. List of some plants used for phytoremediation

Plant	Metal	Method of Extraction	References
Brassica juncea	Lead	Phytoextraction	Raskin and Ensley [21]
Helianthus annuus	Uranium	Rhizofiltration	Dushenkov, et al. [25]
Impatiens balsamina	Cadmium	Phytoextraction	Liu, et al. [32]
Jatropha curcas	Cu, Pb, Cr, Ni, Zn	Phytoextraction	Awotedu and Ogunbamowo [33]
Jatropha multifida	Cu, Pb	Phytoextraction	Awotedu and Ogunbamowo [33]
Jatropha gossipifolia	Zn, Cr, Ni	Phytoextraction	Awotedu and Ogunbamowo [33]
Althaea rosea	Cadmium	Phytoextraction	Liu, et al. [32]
Pteris vittata.L	Arsenic	Phytoextraction	Ma, et al. [34]
Eichhomia crassipes	Cd, Zn	Phytoextraction	Lu, et al. [35]
Apium nodiflorum	Cu, Pb	Phytoextraction	Vlyssides, et al. [36]
Myriophyllum spicatum	Pb, Zn, Cu	Phytoextraction	Keskinkan, et al. [37]
Lemma trisulca. L	Cd	Phytoextraction	Kara and Kara [38]
Helianthus annuus	Pb, Cu, U, Sr, Cs, Co, Zn.	Rhizofiltration	Dushenkov, et al. [25]
Nicotiana tabacum	Hg	Phytovolatization	Rugh, et al. [1]
Brassica juncea	Se	Phytovolatization	Pilon-Smits [12]
Brassica juncea	Cu, Cd, Zn, Pb, Ni, Cr.	Phytovolatization	Dushenkov, et al. [25]
Salix viminalis	Cd, Zn, Cu	Phytoextraction	Seth, et al. [23]
Helianthus annuus	As	Phytoextraction	Han, et al. [18]
Pteris vittata	As	Phytoextraction	Clemens, et al. [22]
Helianthus annuus	Cs, Sr	Phytoextraction	Rascio and Navari-Izzo [39]

The polarity of the xenobiotics after been taken, is been increased by enzymes present in plants by adding hydroxyl groups (OH). This is called the Phase I metabolism, and it is synonymous to how human liver increases its polarity for drugs and xenobiotics. Whereas cytochrome P450s, an enzyme located in the human liver is responsible for the enzymatic reactions such as esterases, nitroreductases, peroxidases and phenoloxidases. In phase II metabolism of phytotransformation. The biomolecules of plants such as amino acid and glucose are added to the polarized foreign substances which then increases its polarity. This aligns with the metabolic process of glutathione and glucuronidation that occurs in the liver. Both metabolic phases always increase the polarity and limit the effectiveness of the toxic substances but some exceptions have been discovered. The higher the polarity of the pollutants, the easier the passage through the aqueous medium. The last stage of transformation which is the Phase III metabolism involves the xenobiotic compound was eliminated from the plant. The foreign compounds condensed together in a lignin form manner and later form a complex structure that is removed from the plant. This insure that the toxic compounds do not hinders the normal metabolic activity of the plant. However, research shows that plants containing these harmful substances are dangerous to small animals like snail. Plants that are used for phytotransformation should be gotten rid of in an enclosed medium to minimise the exposure of the harmful substances [31].

2.2. Importance of Phytoremediation Technology

The most important factor in phytoremediation technology is the ability to minimize heavy metal concentration to a very low amount using a less expensive absorbent material [40]. Phytoremediation is a very cheap and clean method used in reclaiming and purifying a contaminated site [20]. There are diverse methods used in purifying the contaminated sites [41]. It usually detoxifies a contaminated media that has little contamination and operates under a less costly approach [42]. This green technology has lately been given a very wide publicity as a cost effective method to reduce harzardous waste [20]. It effectively offers a unique environmental clean-up for contaminated toxic compounds and radionuclides [43]. It cleanses diverse range of organic and inorganic pollutants [44]. It purifies multiple range of toxic contaminants, air and water borne waste and heavy metals [43]. The contaminants may be precipitated to carbondioxide and water thereby reducing environmental pollution [44]. Compared to the conventional remediation technologies that involves soil washing, solvent washing, thermal vaporization which alter the chemical and biological composition of the soil, phytoremediation on the other hand, purifies, detoxifies and reclaim the soil's purity without affecting or altering the chemical composition of the soil, even the soil is made more improved, pure and cleaner at a low cost. For contaminated soil, phytoremediation is the most ecologically suitable remediation technology. The recycling of the accumulated plant biomass generates a metal rich ash residue [43]. In the phytoremediation process, hyper metal-accumulating plants are always suitable for use [41]. In biodiesel production, oil rich plants could be used for phytoremediation of contaminated soil, however, the matured plant could also be used in generating energy [42]. Also in thermal energy production, the energy stored through the plants can be utilized, but the production must be in large scale [44].

2.3. Limitations of Phytoremediation Technology

One of the crucial limitation affecting phytoremediation is that it consumes a lot of time, the harvested and disposal of the accumulated and produced biomass, the extent of contamination, the maturity (age) of plants, the depth of the root, the climatic condition and the soil chemistry [45]. It takes several seasons to clean up a contaminated site. The accumulated pollutants like heavy metals may be injurious to plants [44]. Where the contamination level is very high, stunted growth of plants is imminent and possibly longer time will be required to clean up. The disposal and excavation of contaminants may take months to achieve, while several years is needed for phytoextraction. For heavily contaminated sites that poses serious health challenge, phytoremediation may not necessarily be the best option [20]. It may be considered for remote villages where there is little soil contamination and human contact [45]. The harvested plant biomass could reach 100 t/ha/y under a normal irrigation and fertilization condition. The harvestable plant biomass of 10 to 20 t/ha/y would likely be feasible when the plant are metal accumulators. There is always a reduction in the amount of biomass produced which depends on the amount of contamination, plant species and climatic factors. The annual remediation from 2.5-100ppm in soil contaminated medium is targeted for a soil depth of 30cm (4,000t/ha). This is a well approved rate of remediation technology, where the contamination rate is reduced to regulatory standards. The annual pollution removal capacity of 10-400kg/ha/y will be reduced to the barest minimum if the harvested biomass is increased. This depends on the plant species. For effectiveness of the phytoremediation technology, the plants root must be in contact with the contaminants in the soil [20]. Generally, the age of a plants affects its potential as a strong remediating plant. It is noteworthy that young plant filters more contaminants than the old plants, the metabolic and biological activity of young plants most especially the roots are efficient in the removal of contaminants [46]. However, the matured plants can still remediate but not as much as the young plants. The phyto-toxicity of the highly contaminated harvested biomass may be handled with a very sensitive approach that will reduce its polluted risk, while the in-situ detoxification and purification is done over for a long period to reclaim low contaminations. Physical exposure to harvested metal hyper accumulating plants are of great concern and the disposal too should be handled properly. The harvested biomass should be gotten rid of by following some regulatory guidelines [20]. Consumption of the matured contaminated hyper accumulating plant is a very big concern because if it is not properly disposed it can find its way into our food and will be consumed again by humans or animals [44].

3. REMEDIATION MEASURES

Remediation of soil is the reclaim and repositioning of soil back to its normal purified stable state. The detoxifying method through the conventional approach usually destroys the soil's quality structure [14]. Precipitation of metals by the addition of calcium carbonate ($CaCO_3$), Phosphate and lime has been a very unique remediation technology too [47-49]. These unique approach has a way of lowering the health challenges arising from heavy metal contamination immediately after application. However, it is a temporary remedy because it has not removed totally the metals present in the soil. Because of the increasing environmental and industrial pollution, there is a dire need to detoxify, clean, and purify the contaminated wastewater, leachate, soil, ground water using in situ and ex situ technology [50]. Two or three combinations of approach may be needed to clean up a contaminated site, in other to allow a safe and maximum purification of the polluted site. BIO-WISE [51] described various conventional method in remediating a heavily contaminated site like vitrification, stabilization, thermal desorption, soil flushing and encapsulation.

4. FACTORS AFFECTING THE UPTAKE MECHANISMS OF HEAVY METALS

4.1. The Plant Species

Different plant species are screened for phytoremediation potentials and plants that are effective 'hyper accumulator' are chosen. A particular clean-up process will attract a specific plant species [52]. For a successful clean up or green technology, suitable plant that could accommodate heavy metals and produce large volume of biomass of the contaminant is used [41].

4.2. Properties of Medium

Several environmental protection practices have been discovered that could help in the remediation process. For example, addition of chelating agents, fertilizer, P^H adjustment, microorganism (Bacteria and fungi). The properties of the soil medium are important in the cleaning process. The quantity of lead removed by a plant is dependent on the availability of its PH, phosphorus and organic matter of the soil. To minimize the activity by which plants will uptake lead, with the addition of lime, the soil's PH is adjusted to 6.5-7.0 [53].

4.3. The Root Zone

In remediation process, plant root remains a special point of reference because the contaminants are absorbed, filtered and translocated by the root. The accumulated contaminants catalysed by plant enzymes are done mainly by the roots. It has this prolong adaptation to drought [27].

4.4. Vegetative Uptake

The removal of contaminants through vegetative means is usually affected some environmental factors [52]. The length of the root and the temperature are factors to be considered in remediation process. The root activity of a plant placed inside a greenhouse is far different from the root activity of a plant on the field. Also temperature plays an important role in the growth of a plant [27]. The effectiveness of phytoremediation, most especially phytoextraction is using the best plant species (hyper accumulator) to remediate a contaminated soil [46]. Finding an environmental friendly method of disposing the harvested accumulated biomass is a major key in phytoremediation [44]. The interaction of the absorbed metal and water in the soil is another crucial factor to be considered. If a contaminated metal did not exist in watery form, the tendency of been extracted or detoxified is very low. The attachment of the metal to the organic matter, changes the PH, soil medium of the soil and redox potential and definitely reduce the existence of the metal to occur in an ionic form and if the metal did not exist in an ionic form, it makes it unavailable and un-removable for the plants. If a plant can reduce the PH and oxygenate sediment, then, it will affect the presence of heavy metals in the soil [54]. The addition of a chelating agents can make available the heavy metals and nutrients present in the contaminated soil [42].

4.5. Addition of Chelating Agent

The remediation process can be induced or influenced by the addition of a biodegradable physicochemical agent also called chelating agent which in turn will increase the bioavailability of the contaminated heavy metal. The application of the chelating agent will quicken the rate at which the heavy metals will be remediated and then reduce the period of remediation. The consequence associated with the addition of chelating agent is that it causes leaching, and they are required in alkaline soils with a pH of 5.5-6.0, so as to make the heavy metals accessible to the plant, and this must be properly considered before use [42]. The addition of EDTA (chelating agent) at 5 mmol/kg for some weeks after application will remove, detoxify the metals and improve the phytoextraction process [55]. The root of the plants displays citrate and oxalate (organic acids) which affects the availability of the metals. In induced phytoremediation, NTA and EDTA (synthetic chelating agents) are applied to increase the phytoextraction process of heavy metal removal. Ligands usually affects the heavy metal uptake by forming a complex with the metals and changes to leach metals [56].

5. CONCLUSION

Phytoremediation is a novel and unusual approach that employs the use of higher plants for the clean-up of contaminated environments. Conventional methods utilized before for reclaiming the contaminated soil, disrupt the soil and eliminates its quality. While phytoextraction removes the contaminants in an eco-friendly way without affecting the quality of the soil and there is a possibility of having access to the metals by recycling the harvested plant biomass. This method is less costly and just requires the use of plants. The only factor that is needed to be considered is the choice of the plant species, which must be an 'hyper accumulators' that could accumulate heavily contaminated sites. However, the remediation method is a unique alternative to cleaning up a polluted site, but it comes with some limitations. Prolong research needs to be conducted to minimize this limitation in order to apply this technique effectively.

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