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Phytoremediation Studies on Arsenic Contaminated Soils in Malaysia

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ABSTRACT

Arsenic is a heavy metal that can exhibit both metallic and nonmetallic properties; concentrations in uncontaminated soil are generally in the ranges of 0.2 to 40 ppm while contaminated soils have been recorded to reach concentrations of up to 2500 ppm. Although arsenic can exist naturally, arsenic contamination occurs due to anthropogenic activities like the smelting of metals, vehicular emissions and the application of pesticides. Inorganic compounds of As can be very harmful to animals and human beings, effecting the nervous and cardiovascular system which eventually leads to death. As Malaysia faces increasing contamination problems, phytoremediation could prove to be savior as it is not only cheap, but also efficient. *Cyperus rotundus*, *Imperata cylindrica*, *Ludwiga octovalvis*, *Lycpodium cernuum*, *Melastoma malabathricum*, *Mimosa pudica* and *Nelumbo nucifera* are few plant species planted on soil contaminated with As.

1. Introduction

Rapid urbanization and growing industrialization have resulted in widespread contamination of lands. Among contaminants, heavy metals are considered to be a major threat to both the environment and to human health [1]. Heavy metals can cause environmental contamination due to anthropogenic activities. Mining, fuel production, agriculture fertilizers and vehicular emissions are just some common contributors of heavy metal contamination [2]. The past decades have seen the annual release of heavy metals reaching up to 22000 metric ton for Cd, 939000 metric ton for Cu, 1350000 metric ton for Zn and 738000 metric ton for Pb [3].

Arsenic is a heavy metal that can exhibit both metallic and nonmetallic properties; concentrations in uncontaminated soil are generally in the ranges of 0.2 to 40 ppm while contaminated soils have been recorded to reach concentrations of up to 2500 ppm [4]. Although arsenic can exist naturally, arsenic contamination occurs due to anthropogenic activities like the smelting of metals, vehicular emissions and the application of pesticides [4]. Inorganic compounds of As can be very harmful to animals and human beings, effecting the nervous and cardiovascular system which eventually leads to death [5]. Arsenic can be transferred to human beings from the ecosystem via our food or water, be seeping into our food chain and groundwater [5]. In other words, arsenic that contaminates soil will eventually end up in our bodies; thus should be remediated effectively and efficiently before widespread harm has occurred.

There are many existing methods of decontaminating contaminated soils; complete removal of soil, isolating the contaminated site, incineration, thermal treatment, solvent extraction, chemical oxidation, microbes decomposition, and others [6]. All these methods have major disadvantages, either being too costly or even increasing the risks of secondary contamination [7]. Hence, a more cost effective method of decontamination is required to address this growing concern. One such option is phytoremediation.

Phytoremediation can be best described as the usage of plants to remove, degrade or isolate contaminants from the environment [6]. The term itself is derived from the Greek word “phyton”, meaning plant, and the Latin word “remedium” which means to remedy. Phytoremediation is an *in situ*, environmentally friendly and economical approach to decontamination [1].

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2. Experimental Methods

2.1 Arsenic Contamination in Soils

Sources of soil contamination of heavy metals can be categorized into two separate groups, which are natural and anthropogenic. Natural sources of heavy metal contamination are usually the product of the weathering process of various parent materials that are inherently rich in heavy metals. Anthropogenic activities that cause heavy metal contamination of soil comprise of mining, smelting, improper municipal waste disposal, excessive usage of pesticides and herbicides and automobile usage [6]. Besides that, using sewage sludge as a soil amendment has also been found to cause heavy metal contamination. The most harmful effects of heavy metal contamination to living organisms, especially humans are usually caused by anthropogenic contamination [3]. Heavy metal contamination of agricultural soils will not only affect plant productivity, but also affect human health negatively.

Arsenic appears naturally in soils in the forms of sulfides, usually in the sulfides of ores of silver, lead, copper, nickel, cobalt and iron; which is why arsenic poisoning is more prevalent in these regions [14]. Trace amounts of arsenic can also be found in some natural soils, but rarely in toxic levels [8]. Arsenic concentrations in uncontaminated soils are in the ranges of 0.2 to 40 ppm while contaminated soils are in the ranges of 100 to 2500 ppm [4]. The most common cause of arsenic pollution is soils is caused by arsenical pesticides being used widely in the past, resulting in arsenic concentrations in these areas to be in the ranges of 200 to 2500 ppm [6]. Arsenic is mainly transported in the environment water, meaning that arsenic contamination in soils can be easily transferred via groundwater [8]. When soil arsenic contamination occurs, it will eventually lead to the poisoning of bodies of water and living organisms, hence making it a serious environmental concern [14]. Ecosystem damaged caused by arsenic, just like any heavy metals, is very damaging due to arsenic not easily being degraded, have a long perseverance in the environment and cannot be altered by microorganisms [8].

2.2 Arsenic Contamination in Malaysian Soils

Malaysia is a rapidly developing country with numerous mining and heavy industries to sustain the country’s economy, with most of the urban areas and industries situated on the west coast of Peninsular Malaysia. The various sources of heavy metals in the west coast of Peninsular Malaysia are usually from agricultural and animal management, manufacturing industries, urbanization practices, and agro-based industries [3]. Arsenic contamination in Malaysian soils is primarily due to arsenical pesticides and smelting industries. Abandoned Malaysian tin mining sites have also found to have toxic levels of arsenic in the soils [9]. Unfortunately despite the numerous existing heavy metal contaminations, Malaysia does not have definite regulations on the remediation and control of contaminated soils and ground waters [3].

Researchers and experts often used foreign or international standards to determine the pollution potential of heavy metals like arsenic in the ecosystem [7]. If the heavy metals are above the permitted levels of these standards and guidelines, it's most likely due to contamination from the improper application of fertilizers, pesticides or from atmospheric sources [10].

2.3 Plant and Heavy Metals

Plants require certain heavy metals such as Zn, Cu and Fe to maintain its wellbeing. However, in large concentrations, these metals can become toxic to plants [7]. Certain heavy metals like Cd and As can be toxic even in small concentrations. Studies on plant's relationship with heavy metals have been conducted for almost four decades; one of the most extensive research was conducted by Baker [15]. Baker [15] also stated that different plants reacted differently to heavy metal contaminations. The manner he described these plant characteristics are listed in Table 1.

Table 1 Characteristic of plants to heavy metals [15]

Plant's characteristic	Description
Accumulators	Metals are in higher concentration in above ground plant parts compared to the soil
Indicators	Uptake and transport of metals to the shoot are regulated so internal concentration reflects external levels
Excluders	Metal concentration in the shoot is constant and low even in different metal concentrations in the soil

Baker [15] also described that all plants had a critical metal concentration value in the soil; in which the plant's mechanism breaks down and unrestricted transport results, causing negative growth for the plant. Baker's work can be perceive as the foundation for phytoremediation research.

2.4 Phytoremediation

Phytoremediation is a green-technology that was developed to degrade, extract and remediate contaminants from soil and water [3]. Not only is it environmentally friendly, it is also an economical alternative to currently practiced soil remedial methods. Phytoremediation has received special attention in the last decade as this technology does not damage soil structure while preserving soil microbial consortia. The detoxification potential of the plant can be determined by examining the rate and depth of contaminant uptake from the soil, accumulation in the plant cell, and the degree of contaminant transformation to regular cell metabolites. To achieve the most desired results in the detoxification of soil, the plant that should be selected for phytoremediating purposes has to be based on multiple plants characteristic [1, 6, 7]:

- overall ability to take up and degrade contaminants in the soil
- ability to accumulate organic and inorganic contaminants in its cells and intercellular spaces
- excretion of exudates to stimulates the multiplication of soil microorganisms and secretion of enzyme participating in the initial transformations of the contaminants
- existence within the cell of contaminant degrading or conjugating enzyme
- high resistance against contaminants
- the root system(main or fibrous)
- whether the plants are endemic and non-agricultural
- tolerance to salty soil
- appropriate adaptation to warm or cold condition
- growth rate
- high biomass

Plants react differently when used as phytoremediators, depending largely on the plant species, the type of contaminant and the concentration level of the contaminant in the soil. Some plants are capable of accumulating large amounts of heavy metals without exhibiting any signs of toxicity. However, some plants accumulate metals but with negative consequences to their growth rates. This limits the total biomass and hence the total mass of accumulated metal will be lower.

Although there are many advantages in using phytoremediation as a soil remedial method, however it does have its own setbacks, namely the time required to achieve cleanup is lengthy. Furthermore, phytoremediation is limited to sites with lower contaminant concentrations [8]. Besides that, the food chain of humans could be adversely affected, due to the degradation of chemicals within the plants. Phytoremediation also poses a threat to the environment, if the plants leaves or limbs containing dangerous chemicals were to be burned, where the fumes could contaminate the air and the ashes could re-contaminate the soil. Phytoremediation on the basic of recent understanding includes the following technologies: phytoextraction, phytostabilization, rhizofiltration, phytovolatilization and phytodegradation.

2.5 Phytoextraction

Phytoextraction is a method that employs plant roots to absorb heavy metals, resulting in their translocation within the plant. This method has grown in popularity and extensively used worldwide for the last twenty years. Phytoextraction is usually used for extracting heavy metals rather than organic contaminants. Besides that, it has been used for the treatment of polluted sediment and sludge, and to a lesser extent for the cleaning of water [6]. A plant which is able to phytoextract a certain heavy metal is known as a hyperaccumulator of said heavy metal [1].

An efficient phytoextraction plant will be able to accumulate high ratios of heavy metal concentration in the plant organ like shoots and roots with relation to the heavy metal concentration in the soil. Besides that, plants with high seasonally harvestable plant biomass also make efficient phytoextraction. Furthermore, the conventional methods of cleaning up heavy metal-contaminated soil can negatively affect the soil such as changing the soil structure and nutrient content, whereas phytoextraction can clean up the soil without causing any harm to soil quality, making it an environmentally friendly process.

2.6 Phytostabilization

Certain plants have the ability to immobilize metal in the soil by absorption, precipitation and complexation. This process is known as phytostabilization. Phytostabilization depends on the roots ability to limit contaminant mobility and bioavailability in the soil and is primarily used for the remediation of soil, sediment, and sludge [8].

The primary purposes of phytostabilization plants are to (1) decrease the amount of water percolating through the soil matrix, which may result in the formation of a hazardous leachate, (2) act as a barrier to prevent direct contact with the contaminated soil and (3) prevent soil erosion and the distribution of the toxic metal to other areas [6]. Using this technology, the disposal of hazardous material/biomass is not required and it is very effective when rapid immobilization is needed to preserve ground and surface waters [8]. Phytostabilization has been used to treat contaminated land areas affected by mining activities and Superfund sites. However since the contaminant remains in the soil, it requires regular monitoring to ensure the contaminants do not become volatile or get leached out.

3. Results and Discussion

3.1 Phytoremediation Projects in Malaysia

As of 2015, there is still no government coordinate initiative to employ phytoremediation to decontaminate contaminated sites; opting for less cost-effective conventional methods such as isolation and excavation. Despite promising results from research on phytoremediation using endemic plant species in Malaysia, the actual usage of this method in Malaysia is still remote.

3.2 Determining Phytoextraction and Phytostabilization Potential of Plants Using Translocation Factor (TF) and Bioconcentration Factor (BCF)

In order to evaluate the potential phytoextraction and phytostabilization capabilities of plant species, two indicators are commonly used: BCF (metal concentration ratio of plant roots to soil) and TF (metal concentration ratio of plant shoots to roots):

$$\mathrm{BCF} = \left[\frac{\text{Metal Concentration in Roots (mg kg}^{-1}\text{)}}{\text{Metal Concentration in Soil (mg kg}^{-1}\text{)}}\right]$$

$$\mathrm{TF} = \left[\frac{\text{Metal Concentration in Shoot (mg kg}^{-1}\text{)}}{\text{Metal Concentration in Root (mg kg}^{-1}\text{)}}\right]$$

Plants with a high BCF and TF are suitable for phytoextraction; these values need to be at least above one [11]). Plants with a high BCF (BCF>1) but a low TF (TF<1) are suitable for phytostabilization [11]. Some researchers on phytoremediation in Malaysia failed to calculate the BCF and TF values; sometimes drawing conclusions solely on the total metal concentration in the plant. This is most likely due to phytoremediation research still being relatively new in Malaysia, thus still requiring time to have more standardized researches.

3.3 Researches on phytoremediation of Heavy Metals in Malaysia

Research on phytoremediation is slowly gaining prominence in Malaysia, with studies becoming more comprehensive. Most phytoremediation research in Malaysia is conducted in greenhouses, whereby potential phytoremediators are planted in soil contaminated with heavy metals. Some research has also been conducted on sewage sludge contaminated soils. Research by planting potential phytoremediators in field conditions is very rare. However, some researchers have studied on species growing naturally at contaminated sites, namely tin mining areas as they very common in Malaysia. Another aspect that needs to be considered is that there is almost no research on Phytoremediation at Sabah and Sarawak, although environmental conditions and plant species between Borneo and Peninsular Malaysia are very similar. These researchers on arsenic phytoremediation in Malaysia are shown in Table 2.

Table 2 List of plants species studied on soil with Arsenic (As)

Plant species	Soil type/site tested on	BCF / TF values	Remarks	Ref.
Cyperus rotundus L.	Old mining are abandoned for 30 years.	BCF: <1 TF: <1	Tolerant to acidic soils with high concentration of heavy metals. Not a suitable phytoremediator.	[9]
Imperata cylindrica	Old mining are abandoned for 30 years.	BCF: <1 TF: <1	Tolerant to acidic soils with high concentration of heavy metals. Potential indicator species for Cu, Pb and Zn. Not a suitable phytoremediator.	[9]
Ludwiga octovalvis	Arsenate dibasic heptahydrate (AsHNa2O4·7H2O) contaminated soils.	BCF: >1 TF: >1	NPK fertilizer addition improved As uptake. Potential hyperaccumulator of As.	[12]
Lycopodium cernuum	Old mining area abandoned for 30 years.	BCF: <1 TF: <1	Tolerant to acidic soils with high concentration of heavy metals. Not a suitable phytoremediator.	[9]
Melastomama labathricum L.	Arsenate dibasic heptahydrate (AsHNa2O4·7H2O) and Lead nitrate (Pb(NO3)2) contaminated soils.	BCF: >1 TF: >1	Tolerant to soils with high concentrations of As and Pb. Potential hyperaccumulator of As. Potential for phytostabilization of Pb.	[13]
Mimosa pudica Linn	Old mining are abandoned for 30 years.	BCF: <1 TF: <1	Tolerant to acidic soils with high concentration of heavy metals. Not a suitable phytoremediator.	[9]
Nelumbo Nucifera	Old mining are abandoned for 30 years.	BCF: <1 TF: >1	Tolerant to acidic soils with high concentration of heavy metals. Potential indicator species for As and Cu. Not a suitable phytoremediator.	[9]

3.4 Malaysian Phytoremediation Studies on Arsenic

Arsenic exists naturally, although rarely in its elemental form, due to the weathering of parent materials [5]. Arsenic has commonly used in agriculture, as pesticides and fertilizers, and also extensively in the manufacturing industry, such as the production of alloys, glass and lead-acid batteries [5]. Therefore, arsenic contamination in the soil is a very common phenomenon in countries that practice agriculture and manufacturing, such as Malaysia.

Inorganic compounds of As can be very harmful to animals and human beings, effecting the nervous and cardiovascular system which eventually leads to death. As contamination in soils has the potential to enter the food chain, eventually affecting human beings [12]. Plants are commonly first effected by environmental As contamination. Extensive research has been conducted in determining the effects of As on plants. Two forms of arsenic, arsenate (AsV) and arsenite (AsIII), are commonly taken up by plants through its roots [13]. Arsenic can affect the metabolism of plant cells, making it a toxic element to plants. Interestingly, some researchers have discovered that As in low concentrations can stimulate plant growth, although the mechanisms behind this is yet to be understood [5].

Hyperaccumulators of As are able to uptake large amounts of As without experiencing the toxicity of this element, storing this metal in the upper parts of the plant. These plants are capable of rapid uptake and translocation of As and a higher antioxidant capacity to maintain lower ROS levels [5]. Besides that, the rapid dilution in the aerial tissues allows these hyperaccumulators to neutralize the toxic effects of As. More research needs to be conducted to mechanisms behind the physical capability of these hyperaccumulators to isolate arsenite from vital metabolic targets.

Two plant species in Malaysia has been identified as potential hyperaccumulators of As. *Ludwigia octovalvis* plant is known in Malaysia for being capable to survive contaminated sites in Malaysia, making it a potential phytoremediator [16]. Titah *et al*. [12] researched on using these plants as phytoremediators of As. Arsenate was added to soils alongside nitrogen phosphate potassium (NPK) fertilizer to determine if these plants phytoremediation properties could be improved [12]. It was discovered that this *L. octovalvis* plants are natural hyperaccumulators of As, while the addition of NPK fertilizers further improved this capability [12]. A separate research conducted in a greenhouse discovered that *Melastoma malabathricum* had potential to be a hyperaccumulator of As [13]. This species were planted in soils that was added with sodium arsenate salt ($AsHNa_2O_4.7H_2O$). This research determined that *M. malabathricum* was able to live in soils with As concentrations of up to 40ppm, and also had very high TF, indicating that it was efficient in translocating As to the upper plant parts [11]. However, further field experiments needs to be conducted to confirm that this species is a potential phytoremediator.

Ashraf *et al*., [9] conducted an extensive study on determining the phytoremediator potential of endemic species that grow naturally at an abandoned tin mining area. Plants that are tolerant to contaminated soils, that is highly acidic soils or soils with higher metal concentrations, are potential phytoremediators, making plants that naturally grow in tin mining sites ideal candidates to be phytoremediators. [1]. However, in this study, it was determined that none of the species were potential phytoremediators. Two species, *Nelumbo Nucifera* and *Pterisvittata L.* were discovered to have high TF but low BCF, making them possible indicator species of As [1].

Five other species from the same research by Ashraf *et al*. [9], *Cyperusrotundus L*, *Imperata cylindrical, Lycopodium cernuum*, *Mimosa pudica Linn* and *Salvinia molesta*, were determined to be not suitable phytoremediators as they have low BCFs and TFs. However, all these species were plants that were highly tolerant to contaminated soils.

4. Conclusion

Research on phytoremediation in Malaysia is still new but shows high potential. As Malaysia faces increasing contamination problems, phytoremediation could prove to be savior as it is not only cheap, but also efficient. However, more studies need to be conducted to fully utilize the potential of these species. Besides that, studies needs to also be conducted on field conditions, as sometimes greenhouse studies can provide different results when applied on the field. Although research on this aspect in Malaysia is ever expanding, the actual usage of this method to decontaminate sites remains to be seen. There needs to be a government coordinated effort to apply phytoremediation, as the current methods being used has proven to be not cost-effective and sometimes even cause secondary contaminations.

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