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Abstract

Contaminated soils and their associated problems have increasingly become a matter of concern. The most common contaminants generated by industrial urban emissions and agricultural practices are trace metals. Remediation of trace metals is mostly conducted using physico-chemical processes and this causes soils to become polluted. Nevertheless, these techniques damage the soil's biological activity and require highly sophisticated expensive equipment. Phytoremediation is a relatively low-cost technology based on the use of selected plants to remove, degrades or contains soil pollutants. The potential of Kenaf for phytoremediation on soils contaminated with heavy metals and other contaminants have been investigated and of course reported in several literatures to be very effective. In view of that, this paper would therefore underscore the phytoremediation potentials of *Hibiscus cannabinus* (Kenaf), the possible utilization of the contaminated biomass and its prospects in the field of bioremediation.

Keywords: *Phytoremediation, Hibiscus cannabinus (Kenaf), contaminants, mechanisms, prospects*

Introduction

A major environmental concern due to dispersal of industrial and urban wastes generated by human activities is the contamination of soil (Gosh & Singh, 2005). This continued industrialization of countries has led to extensive environmental problems (Abou-Shanab *et al*. 2007). Subsequently, oil and gas has become a major source of energy in the world over, thus, has so much impact on our lives in various ways and also generates revenue that is of immense benefits (Apugo-Nwosu *et al*. 2016). The vast gains accrued from the oil and gas industry through its exploration and exploitation brings along with it significant negative effect to the ecological and human environments (Oyegun, 1993), thereby impacting negatively on the socio-economic stratum of a nation.

Controlled and uncontrolled disposal of waste, accidental and process oil spillage, mining and smelting of metalliferous ores, sewage sludge application to agricultural soils are responsible for the migration of contaminants into non-contaminated sites as dust or leachate and contribute towards contamination of our ecosystem (Gosh & Singh, 2005). A wide range of inorganic and organic compounds cause contamination. These include heavy metals, combustible and putrescible substances, hazardous wastes, explosives and petroleum products. Major component of inorganic contaminates are heavy metals (Alloway, 1990; Adriano, 1986) and present a difficult problem than organic contaminants.

A wide variety of chemicals have been detected in soil, water, and air (Cheng, 2003; Turgut, 2003). Heavy metals pose a critical concern to human health and the environment due to their common occurrence as contaminant, low solubility in biota, and the classification of several heavy metals as carcinogenic and mutagenic (Diels *et al*. 2002).

A relatively promising new technology for heavy metal contaminated sites is phytoremediation (Abou-Shanab *et al.* 2007; Apugo-Nwosu *et al*. 2016; Gosh and Singh, 2005; Suresh and Ravishankar, 2004). Phytoremediation is the use of plants to remove organic and/ or inorganic contaminants from soil (phyto-extraction), uptake and conversion into non-toxic forms (phyto-volatilization), or stabilization of an inorganic into a less soluble form (phyto-stabilization) (Abou-Shanab *et al.* 2007). These technologies have attracted attention in recent years due to low cost of implementation and ecofriendly environmental benefits. Moreover, the technology is likely to be more acceptable to the public than other traditional methods (Baker, McGrath, Sidoli & Reeves, 1994; Chaney, 1938 & Suresh & Ravishankar, 2004).

This emerging technology called 'Phytoremediation' which uses plants to remove pollutants from the environment (Alkorta, and Garbisu, 2001; Salt, Smith & Raskin 1998) is preferred over traditional methods (Ansari and Sharma, 2017) because it offers site restoration, partial decontamination, and maintenance of biological activity and physical structure whilst being potentially cheap, visually unobtrusive and with a possibility of bio-recovery of metals (Baker *et al*. 1994). Because of these advantages, phytoremediation is considered as a 'green', sustainable pollution removal process. Advances in science and technology have created growth of industries leading to the unprecedented disturbances in ecological cycles (Duggal, 2008). Therefore, the objective of this paper is to underscores the efficacy of *Hibiscus cannabinus* in management and restoration of contaminated soils thereby highlighting its ecofriendly environmental benefits.

The Concept of Phytoremediation

Phytoremediation is a technology that utilizes plants and associated rhizosphere micro-organisms to remove or transform toxic chemicals located in water, soils, sediments and even the atmosphere (Ansari and Sharma, 2017). Phytoremediation is currently used for treating contaminants such as heavy metals including petroleum hydrocarbons, chlorinated solvents, pesticides, explosives, radio-nuclides, and landfill leachates. It is reported that approximately 80% polluted groundwater is within initial 20 metres of ground level. This suggests water pollution removal can be carried out using low cost phytoremediation applications (Best *et al*. 1994). The research in the field of plant technology as applied to remediation has increased recently (Paterson *et al*. 1990; Shimp *et al*. 1993; Simonich & Hites, 1995; Watanabe, 1997).

Phytoremediation, also called green remediation, botano-remediation, agro-remediation, or vegetative remediation(Wuana and Okieimen, 2010) is considered a publicly appealing (green) remediation technology that uses vegetation and associated microbiota, soil amendments and agronomic techniques to remove, contain, or render the heavy metals harmless in the soil (Cunningham and Ow, 1996; Vysloužilová *et al*, 2003; Helmisaari *et al*, 2007). It is frequently listed among the best demonstrated available technologies (BDAT) for remediation of heavy metal-contaminated sites (GWRTAC, 1997). Phytoremediation is an environmentally friendly, safe and cheap technique used to eliminate pollutants from an environment (Waziri *et al.* 2016). It is a technology which uses plants and microbes for their mediation of contaminated soils. It is a cost effective, long term, environmentally and aesthetically friendly method of immobilizing/stabilizing and transferring contaminants such as metals, pesticides and chlorinated hydrocarbon without causing any disturbance to an area (Sadowsky, 1999; Susarta *et al*. 2008; Jadia and Fulekar 2009; Zhang *et al*. 2010).

A few plant species are able to survive and reproduce on soils heavily contaminated with Zn, Cu, Pb, Cd, Ni, Cr, and As (Baker, 1987). Such species are divided into two main groups: the so-called pseudo-metallophytes that grow on both contaminated and non-contaminated soils, and the absolute metallophytes that grow only on metal-contaminated and naturally metal-rich soil (Baker, 1987).

Depending on plant species, metal tolerance may result from two basic strategies: metal exclusion and metal accumulation (Baker 1981 and Baker and Walker, 1990). The exclusion strategy, comprising avoidance of metal uptake and restriction of metal transport to the shoots (Devos *et al*. 1991), is usually used by pseudo metallophytes. The accumulation strategy caused high uptake of metal and storage in vacuoles to prevent metal toxicity. The extreme level of metal tolerance in vascular plants is called hyper-accumulation. Hyper-accumulators are defined as those plants that can contain metal concentrations 10 to 500 times higher than concentrations found in the same plant species in a non-polluted environment (Yanqun *et al*., 2005).

Processes and mechanisms of Phytoremediation by Kenaf

Phytoremediation is a set of processes that utilizes plants to remove, transfer, stabilize and destroy organic/inorganic contamination in ground water, surface water or soil. Likewise as other number of plants, Kenaf can also be used for the phytoremediation. These mechanisms include enhanced rhizosphere biodegradation, hydraulic control, phyto-degradation, phyto-stabilization and phyto-volatilization as well. Each of these mechanisms have an effect on the volume, mobility, or toxicity of contaminants, as the application of phytoremediation is intended to do (EPA, 2000) and can be discussed concisely below:

i. Phyto-extraction

This is also called phyto-accumulation. It refers to the uptake and translocation of metal contaminants in the soil by plant roots into the above ground portions of the plants. (Gosh and Singh, 2005). It is the best approach to remove the contamination primarily from soil and isolate it without destroying the soil structure and fertility. Phyto-extraction is primarily used for the treatment of contaminated soils (USEPA, 200). To remove contamination from the soil, this approach uses plants to absorb, concentrate, and precipitate toxic metals from contaminated soils into the above ground biomass (shoots, leaves, etc.). Discovery of metal hyper-accumulator species demonstrates that plants have the potential to remove metals from contaminated soils (Raskin and Ensley, 2000).

Discovery of hyper-accumulator species has further boosted this technology. In order to make this technology feasible, the plants must extract large concentrations of heavy metals into their roots, translocate the heavy metals to surface biomass, and produce a large quantity of plant biomass. (Etim, 2012). The removed heavy metal can be recycled from the contaminated plant biomass (Brooks *et al.* 1998) for further utilization. Factors such as growth rate, element selectivity, resistance to disease, method of harvesting, are also important to the effectiveness of any plant species capable of phytoremediation (Cunningham and Ow, 1996 and Baker *et al.* 1994). However slow growth, shallow root system, small biomass production, final disposal limit the use of hyper-accumulator species (Brooks, 1994).

ii. Phyto-degradation

During this process, the plant takes up the contaminant through its roots from where the contaminant is trans-located to the aerial portions of the plant. The difference between phyto-extraction and phyto-degradation is that in the latter the contaminant is converted to a less toxic form during translocation to the aerial portions of the plant (Ansari & Sharma, 2017).

Phyto-degradation is also known as phyto-transformation, and is a contaminant destruction process. Plant produced enzymes that metabolize contaminants which may be released into the rhizosphere where they can remain active (Dietz & Schnoor, 2000). Plant-formed enzymes have been discovered in plant sediments and soils. These enzymes include dehalogenase, nitroreductase, peroxidase, laccase, and nitrilase (Prasad and Freitas, 2003). Phyto-degradation has been observed to remediate some organic contaminants, such as chlorinated solvents, herbicides, and munitions, and it can address contaminants in soil, sediment, or groundwater (EPA, 2000).

iii. Rhizo-degradation

This is also known as phyto-stimulation. It is the breaking down of organics in the soil through microbial activity of the root zone (rhizosphere) and is a much slower process than phyto-degradation (Gosh and Singh, 2005). Yeast, fungi, bacteria and other microorganisms consume and digest organic substances like fuels and solvents. It is believed to be carried out by bacteria or other microorganisms whose numbers typically flourish in the rhizosphere. Studies have documented up to 100 times as many microorganisms in rhizosphere soil as in soil outside the rhizosphere (USEPA, 2000). Microorganisms may be so prevalent in the rhizosphere because the plant exudes sugars, amino acids, enzymes, and other compounds that can stimulate bacterial growth. The roots also provide additional surface area for microbes to grow on and a pathway for oxygen transfer from the environment (Etim, 2012). It can also be seen as plant-assisted bioremediation, as it involves stimulation of microbial and fungal degradation by release of exudates/enzymes into the plant root zone (rhizosphere) (Zhang *et al.* 2005).

iv. Phyto-volatilization

Phyto-volatilization involves the use of plants to take up contaminants from the soil, transforming them into volatile form and transpiring them into the atmosphere. Phyto-volatilization occurs as growing trees and other plants take up water as well as organic and inorganic contaminants. Some of these contaminants can pass through the plant leaves and volatilize/vaporize into the atmosphere at comparatively low concentrations (Mueller *et al.* 1999). Examples include the reduction of highly toxic mercury species to less toxic elemental mercury, or transformation of toxic selenium (as selenate) to the less toxic dimethyl selenide gas by *Brassica juncea* (Suszcynsky and Shann, 1995 and Mc Grath, 1998).

The advantage of this method is that the contaminant, mercuric ion, may be transformed into a less toxic substance (i.e. elemental Hg). The disadvantage to this is that the mercury released into the atmosphere is likely to be recycled by precipitation and then return into lakes and oceans, repeating the production of methyl-mercury by anaerobic bacteria (USEPA, 2000). Gary Banuelos of USDS's Agricultural Research Service have found that some plants that grow in high Selenium media produce volatile selenium in the form of dimethylselenide and dimethyldiselenide (Bañuelos, 2000).

v. Phyto-stabilization

It is mostly used for the remediation of soil, sediment and sludges (USPAR, 2000 and Mueller *et al*. 1999) and depends on roots ability to limit contaminant mobility and bio-availability in the soil. Phyto-stabilization can occur through the sorption, precipitation, complex action, or metal valence reduction. The plants primary purpose is to decrease the amount of water percolating through the soil matrix which may result in the formation of hazardous leachate and prevent soil erosion and distribution of the toxic metal to other areas. A dense root system also stabilizes the soil and prevents erosion (Berti and Cunningham, 2000). It is very effective when rapid immobilization is needed to preserve ground and surface water and disposal of biomass is not required. However the major disadvantage is that, the contaminant remains in soil as it is, and therefore requires regular monitoring (Gosh and Singh, 2005).

vi. Phyto-filtration

Phytofiltration (also known as rhizofiltration), is a phyto-remediation technique designed for the removal of metal contaminants from aquatic environments. The process involves the growth of plants in metal polluted waters where the plant absorbs and concentrates the metals in roots and shoots (Dushenkov *et al.* 1995 and Cluis and Green, 2004). This technique can be employed on both terrestrial and aquatic environment to absorb, concentrate, and precipitate contaminants from polluted aqueous sources with low contaminant concentration in their roots. Rhizofiltration can partially treat industrial discharge, agricultural runoff, or acid mine drainage. It can be used for lead, cadmium, copper, nickel, zinc and chromium, which are primarily retained with in the roots (Chaudry *et al*. 1998 and USPAR, 2000).

The advantages of rhizofiltration include its ability to be used as in-situ or ex-situ applications. Another advantage is that contaminants do not have to be translocated to the shoots. Thus, species other than hyper-accumulators can also be used. Terrestrial plants are preferred because they have a fibrous and much longer root system, increasing the amount of root area (Raskin and Ensley, 2000). Disadvantages and limitations include the constant need to adjust pH, and plants may first need to be grown in a greenhouse or nursery; there is periodic harvesting and plant disposal; tank design must be well engineered; and a good understanding of the chemical speciation/interactions is needed. The cost of remediation by rhizofiltration has been estimated to be around \$2-\$6 per 1000 gallons of water (USEPA, 2000).

Table 1: Processes and Mechanisms of Phytoremediation

S/N	Process Mechanism	Mechanism	Contaminant
1.	Rhizofiltratio	Rhizosphere accumulation	Organics/inorganics
2.	Phytostabilisation	Complexation	Inorganics
3.	Phytoextraction	Hyper-accumulation	Inorganics
4.	Phytovolatilization	Volatilisation by leaves	Organics/inorganics
5.	Phytotransformation	Degradation in plant	Organics

Source: (Gosh and Singh, 2005)

The Botany of *Hibiscus cannabinus* Linn. (Kenaf)

Kenaf is an annual or biennial shrubby herbaceous plant with reddish or greenish stem. Stem height ranges from 1.5-4m (Siepe *et al.*, 1997). The stems are 1-2cm diameter, often but not always branched. Leaves are simple and compound, depending on the variety and considered as varietal character (Singh, 2010), they are 10-15cm long, variable in shape, with leaves near the base of the stems being deeply lobed with 3-7 lobes, while leaves near the top of the stem are shallowly lobed or unlobed lanceolate. The flowers are 8-15cm diameter, white, yellow or purple; when white or yellow, the center is still dark purple. The fruit is a capsule and 2cm diameter containing several seeds (Paridah *et al.* 2011).

Hibiscus cannabinus is among the promising candidate for phytoremediation of soil contaminated with heavy metals such as Pb, Zn, Cu, Cd (Bada, 2015; Meera & Agamuthu, 2015).

Case Studies on Phytoremediation Activities of Kenaf: An Overview

Phytoremediation is one of the promising strategies to remove metals from contaminated soil with plants and it is a simple, low-cost, and environmentally friendly procedure. Among the species tested, *Hibiscus cannibinus* was found capable of Boron phyto-extraction in soils containing from

1 to 10 mg kg–1 of B (water extracts) and were able to reduce up to 24 % of B content in the soil in sixty months (Banuelos *et al.*,1993).

The studies of Pais and Jones (2000) and Kabata-Pendias and Pendiais (2001) have also indicated that *H. cannabinus* is a potential candidate for phytoremediation of lead (Pb). Ho *et al*. (2008) found that lead was totally absent in the leaves but 85 % of the total plant lead is accumulated in the roots. Munusamy and Agamuthu (2010) recently observed sequestration of 0.06 to 0.58 mg Arsenic and 66.92 to 461.72 mg iron per g plant weight in Kenaf roots and indicated that due to such high ability to tolerate these metals and avoid phytotoxicity. Takahashi *et al*. (2008) showed that an ambient concentration of NO_2 in Kenaf avoids Cd. *Hibiscus cannabinus* was labeled with NO_2 and fumigated for 8hours while the uptake and assimilation was determined by mass spectrometry and Kjeldahl-nitrogen based mass spectrometry (Takahashi *et al.*, 2005). It was found that the plant performed a high uptake and assimilation during day time as compared to night (Day 1100 to 2700 ng N mg-1 DW). Kenaf showed night uptake and assimilation as high as 1500 ng N mg-1 DW comparable with CAM plant *Aloe*. This experiment indicated that Kenaf is a potent phytoremediator of NO_2 both during day time and at night.

The study of Meera and Agamuthu (2012) on phyto-extraction of As and Fe using *H. cannabinus* from soil polluted with landfill leachate indicated that sequestration of 0.06-0.58mg As and 66.82-461.71mg Fe per gram plant dry weight in Kenaf root, which implies that Kenaf root can be a bioavailable sink for toxic metals. Insignificant amount of Fe and As was observed in the aerial plant parts (< 12% of total bioavailable metals). They further posit that, the ability of Kenaf to tolerate these metals and avoid phyto-toxicity could be attributed to the stabilization of the metals in the roots and hence reduction of toxic metal mobility (TF<1). With the application of leachate, Kenaf was also found to have higher biomass and subsequently recorded 11% higher bioaccumulation capacity, indicating its suitability for phyto-extraction of leachate contaminated sites.

Hibiscus cannabinus was also investigated for its potential to remove hydrocarbon and heavy metals from soil contaminated with 2.5% and 1% used lubricating oil and amended with organic waste; banana skin brewery spent grain and spent mushroom compost for period of 90 days. Loss of 86.4% and 91.8% used lubricating oil was recorded in the treated soil at the end of the experiment. However, 52.5% and 58.9% oil loss was recorded in un amended soil contaminated with 2.5% and 1% oil respectively. The plant did not effectively accumulate hydrocarbon from the soil but shows appreciable accumulation of Fe and Zn in the root and stem. 47.0mg/kg and 2.37mg/kg of Zn accumulated in the root and stem while 1.5mg/kg and 1.64mg/kg of Zn was accumulated in roots and stems of Kenaf respectively at the end of the experiment (Abioye *et al*. 2010).

Recently, the study of Nizam *et al*. (2016) also supported *H. cannabinus* as a promising candidate for phytoextraction of Arsenic (As) contaminated soil. During the experiment, seeds of Kenaf, Mesta, and Jute varieties were germinated in As-contaminated soil. It was found that uptake of As by shoot was significantly higher than that by root in the contaminated soil. In As-contaminated soil, Menaf and Mesta varieties accumulated more Arsenic than did Jute varieties. Also, in the plant parts above ground, mainly the shoots, the highest As absorption was recorded in Kenaf cv. HC-3, followed by Kenaf cv. HC-95. Kenaf varieties produced more biomass in terms of higher plant biomass production, and As absorption, thus, Kenaf varieties showed higher considerable potential to remediate As-contaminated soil.

A research has been done on the phytoremediation of Cu (Bada and Umunnakwe, 2011) using Kenaf and inorganic fertilizer. Bada (2015) also reported that higher leaf, stem and root yields were observed at 100 kg N ha-1 of composted market waste. The result is in conformity with previous finding of Bada and Fagbola (2014), who posited that application of composted market waste increase the Kenaf performance in the nutrient degraded soil. The higher the level of composted market waste applied, the higher the concentrations of heavy metals in the stem, leaf and root of Kenaf (Bada, 2015). However, highest concentration of Pb was observed in the stem and this is not in agreement with the finding of Wozny *et al*. (1995) who reported that Pb is more accumulated in the roots of greening barley leaves. Highest concentration of Cr was observed in the root of Kenaf. Contrary to this, Gafoori *et al.* (2011) reported highest concentration of chromium in the leaf. Kenaf had potential to accumulate Pb, Cr, Cd and Zn at every level of soil amendments (Bada, 2015). Kenaf amendment with 100 kg N ha-1 of composted market waste had the highest bioavailability index (39.76). This might be due to the ability of composted market waste to enhance the growth of Kenaf. For plant species to be suitable for phytoremediation, it must produce enough yields and accumulate high content of heavy metal (Chaney *et al.* 1997).

Possible Utilization of Kenaf Biomass after Phytoextraction

A serious challenge for the commercialization of phyto-extraction has been the disposal of contaminated plant biomass especially in the case of repeated cropping where large tonnages of biomass may be produced. The biomass has to be stored, disposed or utilized in an appropriate manner so as not to pose any environmental risk. The major constituents of biomass material are lignin, hemicellulose, cellulose, minerals and ash. It possesses high moisture and volatile matter, low bulk density and calorific value (Ghosh and Singh, 2005). Biomass is solar energy fixed in plants in form of carbon, hydrogen and oxygen (oxygenated hydrocarbons) capable of generating biofuel and has a possible general chemical formula of $CH_{1.44}O_{0.66}$. Controlled combustion and gasification of biomass can yield a mixture of producer gas and or pyro-gas which leads to the generation of thermal and electrical energy (Iyer *et al*, 2002).

Bridgewater *et al*. (1999) reported that pyrolysis is a novel method of municipal waste treatment that might also be used for contaminated plant material. Pyrolysis decomposes material under anaerobic conditions without emission to the atmosphere. The final products are pyrolytic fluid oil and coke while heavy metals that remain in the coke could be utilized in smelter.

Composting and compacting can be employed as volume reduction approaches to biomass reuse (Hetland *et al*, 2001). Ashing of biomass can produce bio-ores especially after the phyto-mining of precious metals. Heavy metals such as Co, Cu, Fe, Mn, Mo, Ni, and Zn are plant essential metals and most plants have the ability to accumulate them (Jadia and Fulekar, 2009). The high concentrations of these metals in the harvested biomass can be diluted to acceptable concentrations by combining the biomass with clean biomass in formulations of fertilizer and fodder.

The Prospects of Phytoremediation

So far, most of the phytoremediation experiments have taken place in the laboratory scale, where plants grown in hydroponic setting are fed with heavy metal diets. While these results are promising, scientists are ready to admit that solution culture is quite different from that of soil. In real soil, many metals are tied up in insoluble forms, and they are less available and that is the biggest problem as opined by Kochian (1996).

One of the key aspects of the acceptance of phyto-extraction is connected to its performance, ultimate utilization of by-products and its overall economic viability. Commercialization of phyto-extraction has been challenged by the expectation that site remediation should be achieved in a time comparable to other clean-up technologies (Garbisu and Alkorta, 2001). There are two main approaches to this problem: (i) domestication and breeding of improved hyper-accumulator species and (ii) application of genetic engineering to develop fast growing high biomass plants with improved metal uptake, translocation and tolerance (Barceló and Poschenrieder, 2003). Genetic engineering has a great role to play in supplementing the list of plants available for phytoremediation by the use of engineering tools to insert into plants those genes of interest that will enable the plant to metabolize a particular pollutant (Newmann, 1997).

The future of phytoremediation is still in research and development phase, as there are many technical barriers which need to be addressed. Both agronomic management practices and plant genetic abilities need to be optimized to develop commercially useful practices. Many hyper-accumulator plants are yet to be discovered, and there is a need to know more about their physiology (Rashin *et al*. 1994). Optimization of the process, proper understanding of plant heavy metal uptake and proper disposal of biomass produced is still needed.

Conclusion

Phytoremediation is a low-cost technology which takes advantage of the unique, selective and naturally occurring uptake capabilities of plant root systems, together with the translocation, bioaccumulation and pollutant storage/degradation abilities of the entire plant body. Phytoremediation of contaminated water and soil by hyper-accumulator plants would be a good option in long term. A large number of hyper-accumulative plant species have been tested for the remediation of toxic elements from fresh water systems and soil. Kenaf is an annual or biennial shrubby herbaceous plant with reddish or greenish stem. The plant have shown the ability to accumulate high level of heavy metals from water and thus established itself as a promising candidate in the field of phytoremediation. Several numbers of studies revealed that phytoremediation of heavy metals like Cadmium, Copper, Chromium, Zinc, Lead etc. using hyper-accumulative plants like *Hibiscus cannabinus* would be a good option to clean polluted water and soil.

Recommendations

Although there are over 400 taxa of identified hyper-accumulators plant species of heavy metals which are mostly exotic and low biomass producers. Sequel to that, there is a need to supplement the list of local plants available for phytoremediation process as well. As a general rule, native species are in most cases preferred to exotic plants, because, the latter can be invasive and endanger the balance of the ecological system. Therefore, the application of Kenaf and other related local cultivars in phyto-extraction technology and possible utilization of the by-product is advocated especially in developing countries with scarce availability of funds for environmental cleanup and restoration.

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