Heavy Metal Removal from Petroleum Oily Sludge Using Lemon Scented Geraniums

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ABSTRACT

Heavy Metal Removal from Petroleum Oily Sludge Using Lemon Scented Geraniums

Ammar Badawieh

One major problem facing the petroleum industry today is to find an acceptable approach to manage oily sludge generated during the petroleum processes. As new legislations restrict land disposal of hazardous materials, implying modifications for the available disposal methods becomes increasingly important. Petroleum oily sludge has previously been disposed at landfills, landfarms or dumped in the ponds. All these methods carry a high risk of water and groundwater contamination through heavy metal leaching. In this study a response of plants to heavy metals removal from oily sludge was investigated. Lab analyses showed the presence of heavy metals such as Cd, Ni, and V in variable amounts (12 mg Cd/kg, 33mg Ni/kg and 200mg V/kg) in oily sludge samples taken from the bottom of a crude oil storage tank. Scented Geraniums (*Pelargonium sp.* "Frensham") have demonstrated a great ability to survive rough conditions (poor soil, high/low temperatures, high heavy metals concentrations, low water content, etc.). Subsequently, an investigation using Scented Geraniums was performed in a series of pots containing oily sludge where heavy metal concentrations were artificially increased up to 2000 ppm. In a period of 50 days, plants were grown in two systems: 1) oily sludge-soil, and 2) oily sludge-soil-compost. The study took place in greenhouse facilities under the following parameters: 12 h light, 28-34/ 20 °C temperature day/night, and around 30 to 40 % relative humidity. During the investigation period, soil was sampled periodically and subjected to physico-chemical analyses. The results showed differences related to the sludge system and type of heavy metal. The variation of pH values ranged between 5 and 8. Scented Geraniums were able to accumulate up to 1600 mg, 1000mg, and 1200 mg, of Cd, Ni, and V respectively per kg dry weight of the plant. The result of this research reveals the possibility of applying phytoremediation technology in the field as a successful treatment or pretreatment method for oily sludge.

Keywords: oily sludge, Scented Geraniums, metal uptake, cadmium, nickel, vanadium, phytoremediation.

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GLOSSARY

AA: Atomic Absorption Spectrophotometer

API: American Petroleum Institute

ATSDR: Agency for Toxic Substances and Disease Registry

BOD: Biological Oxygen Demand

Cd: Cadmium

CEPA: Canadian Environmental Protection Act

CFR: Code of the Federal Regulations

CST: Capillary Suction Time

Cu: Copper

DAF: Dissolved air flotation

DW: dry weight

EPA: United States Environmental Protection Agency

ERT: Environmental Research and Technology

ITRC: Interstate Technology and Regulatory Cooperation

Ni: Nickel

PACE: Petroleum Association for Conservation of the Canadian Environment

Pb: Lead

PCBs: Polychlorinated Biphenyls

RCRA: Resource Conservation and Recovery Act

TPH's: Total Petroleum Hydrocarbons

UNIDO: United Nations Industrial Development Organization

V: Vanadium

Zn: Zinc

CHAPTER ONE

INTRODUCTION

Petroleum solid wastes, specifically oily sludge, are being produced in massive and increasing quantities. These wastes have been recently classified as hazardous wastes, according to European and North American regulations. Consequently, handling the large quantities of oily sludge has become a very complicated and expensive process.

Oil sludge toxic classification comes from the fact that many constituents of the oily sludge are carcinogenic and potential immunotoxicants. These constituents contain mixture of toxic heavy metals, hydrocarbonic compounds (e.g. benzene, benzo(a)pyrene, and toluene), PCBs (polychlorinated biphenyls), and other toxic substances depending on the origin of the sludge (Mishra *et al.* 2001; Propst *et al.* 1999). Such toxicity has a big environmental impact on soil, water, plants and animals, and eventually on humans.

In the past landfilling was the common disposal method for oily sludge. However, land disposal of oily sludge was banned in 1990, after it was listed by (EPA) as a hazardous waste under the subtitle K (Abrishamian *et al.* 1992). This ban was related to the contamination caused by the leaching of heavy metals and hydrocarbons from disposal sites to the environment around.

In the past several years, new technologies have emerged in the domain of oily sludge treatment and disposal. Despite the fact that some of these technologies proved to be effective in oily sludge handling, they were not considered 100% adequate. For example, applying incineration on oily sludge would result in the conversion of most of the hydrocarbon-based wastes to carbon dioxide and water (50% to 100%) (Shleck,1990). However, combusting large amounts of toxic organic compounds results in big hazardous gas effluents, in addition to the high costs associated with this technology and most important the presence of heavy metals in the final ash product. Other technologies that are currently available are: recycling, filtration, treatment with fly ash, coking, biological treatment, and others that are still under investigations. None of these technologies proved to be entirely successful yet. Some of them have operational problems, others carry a lot of environmental risks and most of them are expensive. Therefore, it was necessary to investigate a high-quality, low cost, and environmental friendly technology for oily sludge treatment that can be applied across the world.

Phytoremediation technology is an innovative method for treatment that is considered clean, inexpensive, and effective. It is the use of plants to remove pollutants from the environment, or contain their toxic effect to render them harmless. These pollutants could be heavy metals, hydrocarbons, organic chemicals, and other contaminants that could be found in soil, and water bodies (Lasat, 2002). Different plant species were used for decontaminating soil from heavy metals, and hydrocarbons. For example, *Thlaspi caerulescens* (alpine pennycress) was shown to accumulate high amount of Zn and Cd from a sludge-amended soil without showing any major toxicity effect (Brown, *et al.*

1995). In other study, planting *Salix viminalis* in oil contaminated soil, resulted in 79% oil degradation in the root zone of the stand (Vervaeke *et al.* 2003).

The main reason for the failure of the conventional sludge treatment methods was the undegradable heavy metals in the sludge. Some of the most common metals in the sludge are cadmium, nickel, and vanadium. The objective of this research is to investigate the possibility of heavy metals (Cd, Ni, and V) removal from oily sludge using phytoremediation concept. This will be done by choosing the right plant that could survive and accumulate large amounts of heavy metals, while living in oily sludge contaminated conditions.

CHAPTER TWO

LITERATURE REVIEW

2.1 Petroleum Oily Sludge

Petroleum oily sludge is the viscous oily residues produced in almost every process in the oil industry, starting from digging for the oil, transporting it, refining, and finally storing it in the storage tanks. Sludge it self is referred to as an oxidized product resulted from the oxidation of the hydrocarbons in the oil, forming insoluble materials, mostly organic in nature, such as dirt, grit, tank rust-scale, etc (E-Oil, 2002). Combining this product with other inorganic sediments and water yields what is known in general as petroleum oily sludge. Other sources for oily sludge include the cleanup operations for the facilities, and after spell accidents. The Resource Conservation and Recovery Act (US RCRA), which is issued by the Environmental Protection Agency (US EPA), identified the main sources of oily sludge and residues under subtitle K. Table 1 shows the main sources of petroleum oily sludge (Abrishamian *et al.* 1992).

Storage tanks are not only used for crude oil, it is also used for storing refined oil products through the various steps of refining, and for storing the final refined products. The bottoms of these tanks accumulate large percentages of refinery solid wastes and pose difficult disposal problem due to the presence of heavy metals, and toxic organic hydrocarbons (US EPA, 1995).

Table 1: Sources of Oily Sludge

RCRA Code	Sludge Source
K048	Dissolved air flotation (DAF) float
K049	Slop oil emulsion solids
K050	Heat exchange bundle cleaning sludge
K051	API separator residue
K052	Leaded tank bottoms
K169	Crude oil storage tanks from refining processes
K170	Clarified slurry oil tank sediments

After (US EPA1998, Abrishamian et al. 1992)

One of the problems concerning the quantities of waste, and sludge produced, is that most of the oil companies do not give exact numbers of the wastes they are generating, but one of the most trusted sources of information about quantities of waste produced was a survey conducted by the American Petroleum Institute (API 1988). They surveyed number of companies about their oil drilling, production, and the associated wastes produced, by the responds, API found that their answers were proportional to their productions, and that allowed API to estimate the amounts of waste produced (US EPA, 2000). The result of the survey pointed out the size of the problem (Table 2), illustrated in 12 millions tank sludge wastes associated with oil production per year.

According to API, tank bottoms are defined as the liquid and residues, such as hydrocarbons, solids, sand and heavy metals collected in treating facilities, or what is accumulated in the bottom of the storage tanks (API 1989).

Table 2: Total Oil and Tanks' Sludge Produced in the U.S per Year

Oil Production (Thousand barrel)	Associated wastes (Barrels)	Tank Bottoms (Barrels)	Tank Bottoms % of All wastes
2,818,450	11,759,000	1,231,863	10.73%

(API, June 1988)

Away from North America and into the land of oil, Saudi Arabia produces about 8 million barrels of crude oil everyday, and it has the largest reserves in the world. A survey conducted by Saudi Aramco in 1994, showed that, the amounts of oily sludge produced by the Saudi refineries, bulk plants, and the tank farms exceed 30,000 m^3 per year (Hejazi *et al.* 2003).

2.2 Petroleum Oily Sludge Components

The composition of the petroleum oily sludge varies depending on the origin of the crude oil, and the material used through the refining processes. However the basic components include: oil, water, sand, and heavy metals (Ni, Cu, Cd, V, Pb, and others) in different ratios. Oil component consists of a mix of hydrocarbon and non-hydrocarbon organic compounds with some traces of inorganic compounds, which include not negligible amounts of heavy metals.

According to a survey conducted by the Petroleum Association for Conservation of the Canadian Environment (PACE), a composition of oily sludge produced from about thirty-eight refineries varied with the refinery and sludge source, but in general had the following characteristics (Table 3).

Table 3: Average Content of Oil, Water, and Solids in Sludge Wastes

Sludge Source	**Oil %**	**Water %**	**Solids %**
Desalter bottoms	25.5	53	21.5
Neutralization pit sludge	0.5	66.5	33
Lub. & grease production wastes	85 to 100	4 to 50	0 to 15
API sludge	7.5	62	30.5
Biological sludge	0.5	94.5	5
Basin settling	3	75	22
Unleaded sludge	43	12	45

(Geadah, 1987)

2.3 Problems Associated with Oily Sludge

Oily sludge has become a major problem in the oil industry. This problem is a result of the nature of this sludge that causes environmental and operational concerns.

2.3.1 Environmental Concerns

Petroleum solid wastes, specifically oily sludge, are being produced in massive and increasing quantities, and the variation of the sludge components makes it very difficult to deal with.

All petroleum-containing wastes such as slop oil-emulsion solids, sludge from the bottom of the storage tanks, API separator sludge and other wastes that contain aromatic, polycyclic aromatic hydrocarbons, and heavy metals, according to EPA are identified and listed under hazardous-waste category in the Code of the Federal Regulations (CFR) title 40, paragraph 261.3 (Atlas, 1984).

The environmental concerns come from the fact that many constituents of the oily sludge are carcinogenic and potential immunotoxicants. These constituents contain mixture of toxic heavy metals, hydrocarbonic compounds (e.g. benzene, benzo(a)pyrene, and toluene), PCBs (polychlorinated biphenyls), and other toxic substances depending on the origin of the sludge (Mishra *et al.* 2001; Propst *et al.*1999). Such toxicity has a great environmental impact on soil, water, plants and animals, and eventually on humans.

The effect of petroleum sludge on plants could be: direct toxicity effect or indirect but related to the microbial component of the soil. Direct effect is usually associated with the tender parts of the plants' shoots and roots, where toxicity occurs when the low-boiling hydrocarbons acts as a solvent on the lipid membrane of the cells. While the indirect effect includes oxygen loss of plant roots, because of an excessive consumption of soil oxygen by the hydrocarbon degrading microorganisms (Atlas, 1984).

All the environmental concerns in this manner are associated with the oily sludge disposal methods, for example if the oily sludge would undergo landfarming, the biggest concern here is related to soil, plants, and groundwater through contamination by heavy metals' leaching. If incineration is the method of treatment then we are more concerned about air pollution and heavy metal containing ash disposal.

The environmental concerns were recognized as early as 1920's, just one year after the American Petroleum Institute was established. Their first contribution to solve the problem was a survey conducted in the 1920's regarding the petroleum pollution in general, and in their 1928 report the announced that the petroleum industry is becoming one major source of pollution. Right away API established a waste-disposal committee that took control of the disposal monitoring and treatment processes since then (Davis, 1967).

2.3.2 Operational Concerns

As it was mentioned in section 2.1, oily sludge generation is associated with almost every step of the oil production and refining industry. The build-up of sludge in pipelines, bottoms of storage tanks, and any other place in the refineries, power plants, and fuel oil users, causes important operational problems.

Accumulation of the sludge residues at the storage tanks, results in a big loss of valuable space in these tanks, and sludge build-up in the pipe lines during oil pumping, results in blocking these lines partially or completely, which leads to lower production, extra costs for cleaning these facilities. Considering the fact that there is no reliable disposal technique regulated yet, this issue becomes more difficult to deal with.

2.4 Disposal and Treatment Procedures

Oily sludge is rapidly becoming one of the big environmental problems in the world; managing it is an expensive, time consuming, and not fully guaranteed process. While the toxic varied constituent this oily sludge is made of control the disposal process, the fact that sludge wastes are commonly inconsistent, thick and viscous, complicate their treatment, especially as they influence equipment performance.

In the last decade, US EPA came up with legislations that could provide some secure methods of disposal and treatment of the refinery wastes, especially oily sludge. In 1990, the Pollution Prevention Act, Congress established new policy of "pollution prevention" that aims to reduce hazardous wastes or limit its discharge. US EPA responded in 1992 with a plan "statement of definition" that contains group of approaches that should be followed while dealing with hazardous wastes, including refinery wastes and especially oily sludge (US EPA, 2000). These approaches in general are; a) pollution prevention; b) recycling; c) treatment prior to disposal; and d) disposal.

In the past, landfilling was the common disposal method for oily sludge, but US EPA through its Resource Conservation and Recovery Act (RCRA), listed oily sludge from different sources under subtitle K as a hazardous waste, that are prohibited from land disposal (Abrishamian *et al.* 1992).

Because of that, and the increase of environmental awareness, new disposal and treating techniques were developed through the years. The major disposal and treatment methods that are used in U.S include: i) recycling through oil reclaimers, ii) landspreading or landfarming, iii) incineration, and iv) other under- research techniques (US EPA, 2000).

2.4.1 Recycling

New legislations demand that, oily sludge shouldn't be disposed unless its oil content is reduced to a certain limit (Jean, and Lee 1999). Different methods could be used to achieve this purpose, including on-site treatment, and oil reclaimers. These processes will result in minimizing the waste generated, and the recovery of the valuable oil that could be used or sold. RCRA defined recycled oil as "any used oil which is reused following its original use, for any purpose, including the purpose for which the oil was originally used; thus, recycled oil includes oil which is re-refined, reclaimed, burned, or reprocessed" (Atlas, 1984).

Refineries could use on-site oil reclaimers, which follow different methods for oil, water and solids separation. Jean and Lee (1999) described the mechanical separation of oil and water from oily sludge by the deliquoring process of oily sludge, which still needs a lot of research. Habibi and Elektorowicz (2004) used electrokinetic phenomena for an effective separation of oily sludge into phases including water, hydrocarbons, and solid phase. They suggested that this method allows for recycling of hydrocarbon residue from a waste product to a usable refinery product by reducing water content by 63%.

2.4.2 Filtration

It could be considered a method of dewatering oily sludge; usually this process yields reduced amount of oily cake, and little oil in the liquid phase. Applying filtration before sending the sludge into a disposal or incineration site will reduce the cost of these processes considerably, depending on the sludge volume, and oil or water content. It is preferable that the oily sludge introduced to the filters would contain low oil concentrations, since it was found that sometimes this oil block the filter cloth, but adding calcium carbonate to the sludge could prevent it (Dando, 2003).

2.4.3 Treatment with Fly Ash

Dewatering is a very important process to reduce sludge volume; however the presence of oil in the sludge causes operational problems. It was found that adding fly ash to the oily sludge, decreases the specific resistance to filtration, and capillary suction time C.S.T (dewaterability) of the sludge (Hwa and Jeyaseelan, 1997).

Hwa and Jeyaseelan (1997) added in their experiment different dosages of fly ash to multiple samples of oily sludge, after each dosage, the sludge characteristics (capillary suction time (CST), filtration resistance, solid content in the sludge cake, and the particle size distribution in the sludge after conditioning) were measured. The optimum dosage that yielded in the least CST, and the lowest specific resistance to filtration was 3%. However, this value would vary depending on the original characteristics of the sludge.

As a result, solid content increased in the sludge cake, and there were less suspended solids of filtrates. But the volume of toxic waste increased. On the other hand, fly ash might contain heavy metals, which means more toxicity in the final mix.

2.4.4 Incineration

One of the most common methods for oily sludge disposal is incineration. Rotary kiln and fluidized bed incinerators are most known incinerators; they are either integrated with the refinery or placed off-site, where the process could be carried by a contractor.

A rotary kilns usually 8-12 m long, 1-5 m in diameter, and the average combustion temperature inside is between 800 to 1400°C for duration of 60 minutes. While the fluidized bed incinerator consists of vertically cylindrical brick-lined combusting chamber. Sludge or wastes in general are introduced into the chamber from the sides into the fluidized bed where it gets incinerated on a relatively low temperature 800-950°C (UNIDO, 1993).

In the process, the contaminated oily sludge is fed into the incinerator that contains gas or oil burners that provide operating temperature of 800 to 1400 °C. Waste material is combusted in the presence of a relatively large excess of oxygen (air), which will result in the conversion of most of the hydrocarbon-based wastes to carbon dioxide and water vapor (50% to 100%) (Shleck, 1990). Despite the fact that incineration is a very effective method, it is considered to a big extent not environmental friendly, and the following shows some concerns associated with incineration (Szente *et al.* 2003):

1. The combusting of toxic organic compounds results in a big hazardous gas effluents that need to be treated before being released into the atmosphere;
2. In the case of off-site incinerators (which is the case in most refineries), transportation costs are high due to environmental risks;
3. Incineration processes are usually very expensive, and it is more expensive in case of oily sludge incineration, because typical oily sludge from most refineries could contain up to 60% water, which implies great energy to burn;
4. Fly ash resulted from the incineration process, contains heavy metals, and since this ash is usually sent to landfills, heavy metal leaching becomes another problem to be solved.

2.4.5 Coking

EPA explained that the main purpose of cokers, is to thermally convert longer-chain hydrocarbons to recover more light hydrocarbons, that are used to produce fuels. The typical coker yield about 30% petroleum coke and 70% light hydrocarbons that will be refined to get the high-grade fuels (Orr and Maxwell, 2000).

Coking operations are used to dispose undesirable residues by converting them into valuable products. Coker plants produces coke from oily sludge that is collected from different sources in the refinery. In the operation, while most of the oily sludge fed into the coker vaporizes in the hot coking process, the lighter fractions are returned through the upper lines back to the refinery fractionation process. The final coke product will combine solids and non-volatiles from the original oily sludge which include heavy metals (Shah, 2004).

2.4.6 Biological Treatment

BOD reduction in the refineries' effluent could be achieved by a complete oxidation of the organic matter into inorganic matter and microbial cells. Biological treatment goal is reducing organic wastes and its toxic effects to very low levels. In biological treatment some factors must be controlled like: pH, sulfides, nutrients, and temperature. For example the presence of sulfides increase the oxygen demand to assure effective aerobic processes, also the availability of nutrients is essential for microorganisms (Davis, 1967).

Oxidation ponds, activated sludge treatment, and biological contactors are considered the major units of the biological treatment facility (Atlas, 1984).

2.4.6.1 Biodegradation of Oily Sludge

Biodegradation is carried out by soil bacteria and fungi as a natural process. Recently and after an extended research, many microbial communities demonstrated their ability of breaking down certain hydrocarbons, or transforming some chemical substances in the petroleum wastes into non hazardous products (Korda *et al.* 1997).

Bioremediation in comparison to other technologies, such as incineration, is considered a cost-effective technology that rarely yields undesirable side compounds in specific biodegradable compounds treatment. In this technique, organic sludge is mixed with active microbial seeds and appropriate nutrients in an engineering reactor. This treatment is that; it increases the speed of biodegradation of the organics, by providing optimal conditions (pH, temperature, nutrients, and dissolved oxygen) for these microorganisms (Korda *et al.* 1997).

Some microbial strains, are available commercially for bioremediation, each is responsible for degrading specific compounds. Soriano and Pereira (2002) grew microorganisms in a medium that contains only oily sludge as a source of carbon and energy. The two parameters that were investigated were the microbial adaptation to the environmental variables around it, and the aeration process. In 21 days, they were able to achieve high organic matter biodegradation demonstrated in the following results: consumption rate was: 89%, 99%, and 93% for oil and grease, n-paraffins, and total polyaromatics respectively.

Usually hydrocarbons in oily sludge are found as a mixture; thus, and because none of the organisms could degrade all the different kind of hydrocarbons, the more variety of cultures mixed, the better remediation will be achieved. Said *et al.* (2004), applied fungal strain (*Paecilomyces variotii*) and a bacterial strain (*Bacillus cereus*) as a co-culture to an oily sludge that was taken of a crude oil storage tanks. About 35% of the non-volatile total petroleum hydrocarbons and 81% of the aliphatic hydrocarbons were degraded.

It is obvious that the biological treatment is only concerned with the organic hydrocarbon part of the oily sludge, other major toxicant, such as heavy metals are ignored, which indicate, that these methods are solving part of the problem only.

2.4.6.2 Composting

EPA defined composting as "the use of a biological system of micro-organisms in a mature, cured compost to sequester or break down contaminants in water or soil" (US EPA, 1997). Oily sludge composting techniques, are very similar to the open and closed composting systems, already used in treating organic wastes such as municipal sewage solids, agricultural crops, manure and others. In the other hand, some adaptation is necessary, due to the fact that the behavior of soil is different from that of organic wastes. Aeration of the soil is forced to take place in the composting process which allows microorganisms to use contaminants in the soil transforming them into carbon dioxide, water, and salts (Dando, 2003).

In the case of having oily sludge as the contaminant, the ultimate goal will be to reduce the hazardous organic compounds concentrations in the sludge in order to stabilize it. Giles *et al.* (2001) examined the feasibility of using composting as an effective bioremediation method. They found that nine bacteria from the twenty strains that were isolated from the sludge used the sludge as the carbon and energy source. These strains were used in their experiment which resulted in the following: the total petroleum hydrocarbons (TPH's) at 46 μg/g were reduced in the sludge by 97.4% in 10 weeks.

2.4.7 Landfarming

Landfarming (called also landtreatment) is a technique that depends on the soil microbial communities to degrade and stabilize hydrocarbon wastes. Landfarming involves spreading excavated contaminated soils or sludge in a thin layer on the ground surface and stimulating aerobic microbial activity within the soils through aeration and the addition of minerals, nutrients, and moisture. The enhanced microbial activity results in degradation of adsorbed petroleum product constituents through microbial respiration (US EPA, 1994). Unlike land filling, land treatment was an accepted land-disposal technique under RCRA (with some conditions applied), and it does not use any physical barriers to isolate hazardous waste from leaching or migrating, instead, soil processes (precipitation, cation exchange reactions, and complexations) guarantee, to a some extent the immobility of these constituents. EPA defined land farming as "an open system that relies on dynamic physical, chemical, and biological processes to degrade, transform, or immobilize hazardous organics in the soil" (Atlas, 1984).

General report evaluating land treatment was conducted by the Environmental Research and Technology association (ERT) in 1984 and handed in to API. In the report ERT indicated that land treatment, could successfully result in degrading the organic matter, immobilizing hazardous heavy metals and any other inorganic matters, if the appropriate environmental and operational conditions exist (US EPA, 2000). Such operational conditions according to EPA and under RCRA directions include that:

a. Landfarming location should be outside of a 10-year flood zone;
b. The depth of the waste should not exceed 1.5 m;
c. Continued monitoring of the groundwater must be repeated for 90 days from the last waste application.

Despite the fact that land farming is a cheap, effective, and natural technique for oily sludge treatment, there are still operational and environmental concerns associated with it. One problem is the very long time needed to achieve complete degradation, and although it is a natural process in every mean there are still some environmental risks associated with it that involves all media: surface and ground water, soil, and atmosphere. Recent study by Hejazi *et al.* (2003) indicated that the high volatile organic compounds that are associated with the degradation processes on the land farming sites impose high environmental health risks to workers on the site. Other disadvantage is associated with the heavy metals permanent presence in land used for landfarming, since these metals might migrate into groundwater if the appropriate plant cover is not provided to protect soil from erosion or any extreme weather conditions. Plus the facts that, despite metals are immobilized they are still there, which means problem is not solved yet.

On 1992, US EPA published a final rule for various hazardous wastes disposal that include hydrocarbons. This LDR prohibited the land disposal of untreated hazardous waste. As a result, most of the traditional landfarming areas in North America were closed (Hejazi *et al*, 2003).

2.4.8 Phytoremediation

In simple terms, phytoremediation is the use of green plants to remove pollutants from the environment, or contain their toxic effect to render them harmless. These pollutants could be heavy metals, hydrocarbons, organic chemicals, and other contaminants that could be found in soil, and water bodies (Lasat, 2002).

Using plants for environmental remediation is a very old idea. However recent studies and field applications yielded group of very interesting results, which in many cases, confirmed the feasibility of phytoremediation as a trusted remediation option.

Plants usually depend on their roots as their contact to the contaminants; therefore, bigger plants could treat larger areas with their extended and deep root systems. In the process of phytoremediation, pollutants could be treated as follows:

a. Stored in the roots, stems, or leaves. For example *Brassica juncea* (Indian Mustard) is a high-biomass plant that could transport lead to the shoots, accumulating >1.8% lead in the shoots (dry weight) (Kumar *et al.* 1995);
b. Transformed into less hazardous materials in the plant (Lasat, 2002);
c. Volatilized into gases that are released into the air during the transpiration process in the plants. According to Burken *et al* 2001, introducing live hybrid poplar plants into benzene contaminated soil enhanced the volatilization process of the benzene without observing any toxicity effect on the plant itself;
d. Changed into less harmful chemicals by microorganisms that live in plant's rhizosphere, which also enhance the degradation process. For example, growing Willow stand (*Salix viminalis*) in oil contaminated sediment, resulted in 79% oil degradation in the root zone of the stand (Vervaeke *et al.* 2003);
e. Stabilized in a way that guarantees their immobilization (Matso, 1995).

After the uptake or sorption process; the plants either will be harvested and destroyed, or kept for recycling, for example some metals could be extracted from the plants and reused (US EPA, 2001).

One very important parameter in land treatment is time. The time needed to clean up a contaminated site using phytoremediation depends on the following:

1. Nature and characteristics of the contaminants;
2. Size of the polluted site;

3. Type and characteristics of the soil;
4. Kind and number of plants to be used.

Although the time issue does not fall in favor of this technique, there are a lot of contaminated sites that has been left out without any kind of treatment for many years, like the case of petroleum oily sludge, which contains considerable amounts of non degradable heavy metals, in such cases applying this technique could be very useful.

According to Glass (1998), the phytoremediation market in the United States is expected to expanded from \$16.5-\$29.5 million in 1998 to \$214-\$370 million by 2005. In comparison to other soil treatment methods, phytoremediation costs are the cheapest, and Table 4 shows a cost comparison between phytoremediation and other conventional methods.

Table 4: Cost Comparison of Soil Treatment Methods

Treatment	**Cost(\$/ton)**	**Additional factors/expenses**
Landfilling	100-500	Transport/excavation/monitoring
Chemical treatment	100-500	Recycling of contaminants
Electrokinetics	20- 200	Monitoring
Phytoremediation	5-40	Monitoring

(Lasat, 2000)

Phytoremediation strategies diverge depending on variety of parameters. It includes the following techniques: phytoextraction, phytodegradation, phytovolatilization, and phytostabilization.

2.4.8.1 Phytoextraction

Phytoextraction is the extraction of pollutants from the contaminated zones by plants that accumulate these contaminants in their tissues. In some cases, the contaminant could be restored and reused again, like the case of some heavy metals. This process requires specific plants that have the ability to accumulate particular contaminant to a very high concentration. These species are known as hyperaccumulators (Prasad and Freitas, 2003).

Zavoda *et al.* (2001) described hyperaccumulators as the plants whose tissues may contain >100 mg Cd, >1,000 mg Ni and Cu, or >10,000 mg Zn and Mn per kg of its dry weight when grown in metal-rich media. Some of the known plant families in this manner include *Zea mays, Brassica juncea, Alyssum bertolonii, Berkheya coddii, Helianthus annuus,* and *Pelargonium* sp. 'Frenshman'. Table 5 introduces eight hyperaccumulator plants with the potential to be used in the phytoremediation treatment (Zavoda *et al.* 2001).

While it is obvious that the ideal hyperaccumulators are the ones with larger biomass (bigger storage and larger root system), most of the discovered hyperaccumulators have low biomass, but they have the ability to accumulate large amounts of metal in their tissues without showing any major toxicity effects (Lasat, 2000).

To hyperaccumulate metals, soil metals should also be bioavailable, or subject to absorption by plant roots. Bioavailability of contaminants is a starting point in phytoextraction, and to be bioavilable, is to be ready for uptake. This situation depends on metal solubility in soil solutions. Metals can be bioavailable in the following two situations: (a) when they have the form of free ions and soluble metal complexes in the soil solution, and (b) when the metals are adsorbed to inorganic soil constituents at ion exchange sites, however in case of having metals that are not bioavailable in the soil or not adequate for sufficient plant uptake, chelates or acidifying agents could be applied to release them into the soil solution (Lasat, 2000).

In the process hyperaccumulors usually transplanted or seeded into metal-polluted soil then after sufficient plant growth and metal accumulation, the plants are harvested and removed, and consequently removing metals from the site.

Using hyperaccumulators to remove toxic heavy metals from soil has big group of advantages such as: lower associated costs, generation of a recyclable metal-rich plant residue, applicability to a range of toxic metals, minimal environmental disturbance, and has great public acceptance. On the other hand, there are still some minor limitations that could be associated with phytoextraction, for example, most hyperaccumulators grow slowly, have small biomass, and little is known about their characteristics (Cunningham *et al.* 1995).

2.4.8.2 Phytodegradation or Phytotransformation

Phytodegradation (or phytotransformation) is a process that includes the uptake of organic contaminants from soil, and transforming it to non hazardous forms, by any plant-associated microflora (Schnoor, 1997).

Similar to phytoextraction, phytodegradation requires organic contaminants to be biologically available for absorption or uptake by plants. Bioavailability of organic matters depends on the soil characteristics (organic matter content, pH, clay or sand type and content), age of the contaminant, and the characteristics of the compound (Cunningham *et al.* 1995).

Plants could have direct or indirect effect on organic remediation in the soil. The following processes attain this effect by: (a) improving the chemical and physical characteristics of the contaminated soil; (b) releasing roots exudates and enzymes which stimulate soil microbial activity and biochemical transformations; (c) release oxygen into the root zone which encourages aeration in the soil; and (d) direct uptake of organic pollutants (Schnoor *et al.* 1995).

2.4.8.3 Phytovolatilization

Phytovolatilization is another form of phytoremediation, whereby volatile compounds are uptaken and released into the atmosphere through transpiration processes in the plants. Phytovolatilization is observed when plants take up water, organic and inorganic contaminants. Some of these contaminants could go directly through the plants to the leaves and volatilize into the atmosphere at rather low concentrations (ITRC, 1999).

One problem associated with phytovolatilization, is that by transferring contaminants from soil or groundwater into the atmosphere, toxic gases are being released into the air. As a result, phytovolatalization technology must be monitored to avoid pollution translocation.

2.4.8.4 Phytostabilization

Phytostabilization is an opposite process to phytoextraction. In this case, the goal is to make the contaminant (metals and organics) less bioavailable for plant uptake, which will protect plants from the toxic effect of these elements, and consequently prevent entering the food chain. Therefore, since metals will be insoluble and stable, lower leaching of metals into near groundwater aquifers is expected (Matso, 1995).

In phytostabilization, some additives must be mixed with soil such as: phosphates, mineral oxides, organic matters, and bio-solids along with some soil microbes, to ensure the adsorbing, precipitating, and changing of the valence state of the contaminants which makes them insoluble, or immobilize and stabilize them. Vegetation cover should be added to prevent soil erosion, reduce water infiltration, provide more detoxifying effect, and create better conditions for microbial activity in the root zones (Lasat, 2002).

2.4.8.5 Mechanism of Metals Translocation within the Plant

While it is still unclear what is the real mechanism that govern the movement of metals into the roots, their movement into the shoots and the upper parts of the plant, and role of the soil elements in that process (microorganisms, root enzymes and exudates, pH, organic matter, moisture content, temperature, etc). Metals uptake starts by transporting the contaminants into the roots across the cellular membrane, and by special proteins that have transporting role; metals are carried through the lipophilic cellular membranes of the root (Lasat, 2000). Figure 2 below illustrates the basic steps of this process.

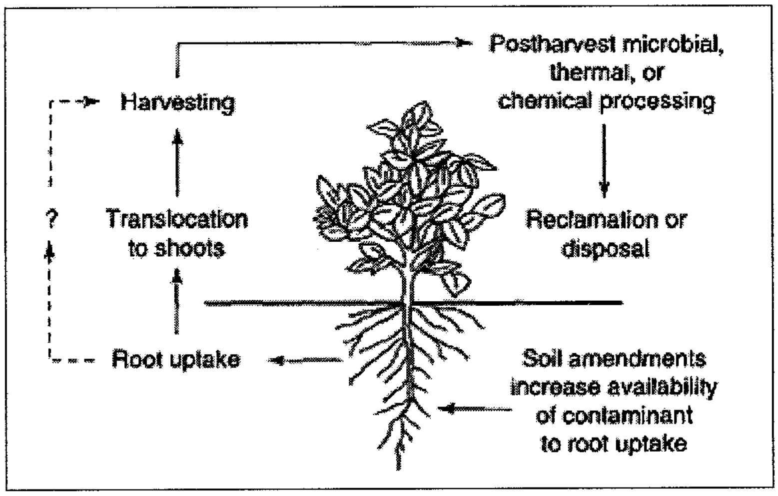


Figure 1: Phytoremediation process (Cunningham *et al.* 1995)

Table 5: Plants Used in Phytoremediation Applications

Common name	**Scientific name**	**Phytoremediation Ability**			**Growth habitat**	**Soil hardness**	**Countries**
		Hydrocarbon tolerance	**Contaminants**	**Application**			
Nodding thistle[1,2]	*Cardus nutans*	Weak tolerance for hydrocarbons	Pb	Phytoextraction	2-5 ft	6 to 8.9	Europe, Asia
Alpine Penycress[2]	*Thlasp caerulescens*	Weak tolerance for hydrocarbons	Zn,Cd,Ni	Phytoextraction	N/A	5 to 6	Germany
Scented Geranium[3,4]	*Pelargonium sp*	Strong hydrocarbon tolerant	Cd,V,Ni	Phytoextraction Phytovolatilization	1to 6 ft	7.2 to 8	Africa, N America Europe, East Asia.
Alyssum[2,5]	*Alyssum murale*	Weak tolerance for hydrocarbons	Ni,CO	Phytoextraction Phytovolatilization	1to 3 ft Forb/herb	6 to 8	Africa, South America
Canola[2,6,7]	*Brassica rapa L*	Hydrocarbon tolerant	Pb (1),Zn,Cd	Phytoextraction	Herb,up to 2.3 ft	7.3	North America

Maize[2,8]	*Zea mays L*	Hydrcarbon tolerant	Pb (2)	Phytovolatilization Phytoextraction	Herb, up to 2ft	7 to 8	Mexico, Europe, North America
Hybrid Willow[7,9]	*Salix L*	demonstrated phytoremediator for fuel oil	(in the leave tissue) (3)	Phytoextraction Phytovolatilization	Shrub 20to70 ft at maturity	N/A	North America
Indian Mustard[2,10]	*Brassica juncea*	Hydrocarbon tolerant	Zn,Cd,Ni,Pb,Cu	Phytoextraction	1 - 3 feet tall	N/A	Eastern Europe

1- Butterfield, *et al.* 1996, 2- Brook, 1998, 3- Dan, *et al.* 2001, 4- Feltwell, 2003, 4- Missouri Botanical Garden 2005, 6- Looman and Best, 1994, 7- Yong Cai, 2002, 8- Bailey, 1951, 9- Carman, *et al.* 1998, 10- Hamlin, 2002

2.4.8.6 Lemon-Scented Geraniums (*Pelargonium Crispum*) as a Phytoextractor

Lemon-Scented Geraniums (Figure 1) is a member of a big family (Geraniumns), that is well known for its' amazing odor, and for what is more important; their ability to hyper-accumulate heavy metals.

Figure 2: Lemon Scented Geranium (Pelargonium 'Frensham') used in this research

a- General Descriptions

The Greek family name for this plant (*Geraniaceae*) came from the word geranos (crane), referring to the beak-like fruit, while the kind (*Pelargonium*) is a Greek word also, that refers to the seed heads. And finally the word crispum means: with curled or wavy margins (Becker and Brawner, 1996). Lemon Scented Geraniums could be simply identified by its lime scent (IGS, 2000). Subsequently, these plants are grown for their scent (Figure.1). The original habitat of Geraniums is South Africa but in the time being they could be found all over the world due their great ability to tolerate drought, little dependency on fertilizers, and their easy growth. However, the best conditions for growing Geraniums are: 25 to 35 °C temperature range, 6.5 to 7.5 soil pH, and a good drainage system. Usually these species grow to a maximum of 45-60 cm high, and propagation methods could include stem cuttings, in addition to the normal seed spreading (Feltwell, 2001).

b- Lemon Geraniums as a Hyperaccumulator

Greenhouse experiments performed repeatedly on Lemon Scented Geraniums illustrated the ability of these plants in extracting and accumulating large amounts of heavy metals without showing major toxicity effects (Dan *et al.* 2001). Scented Geraniums that were grown in an artificial soil system were exposed to an elevated concentration levels of cadmium and nickel solutions. Results showed that in 14 days Scented Geraniums were able accumulate more than 27 g, and 0.750 g of cadmium per dry weight of roots and shoots respectively; for nickel, plants were able to accumulate 21g and 1.190g per kg of the plants roots and shoots dry weight respectively.

In another study, Scented Geraniums were also able to tolerate nearly 29,000 ppm of hydrocarbon contaminants (Saxena, 1998). This quality gives these plants further more advantages than their ability to tolerate rough conditions, which include drought, little fertilizing, and high temperatures that could reach 40°C. Those qualities, plus the fact that, the essential aromatic oils in the Lemon Scented Geraniums, can be safely extracted, and consequently extracting heavy metals; makes Geraniums, in comparison with other hyperaccumulators superior in the phytoremediation domain (Saxena, 1998).

2.5 Heavy Metals as Trace Contaminants

Heavy metals are raising a lot of environmental concerns, not only because of their toxic effects on plants, animals, humans and soil microorganisms, but also to the fact that metals can not be degraded like most of the organic matters. They can not be removed off soil in a natural way, since they are often immobilized within different soil components.

Metals mobility in the rhizosphere could be influenced by many factors, which some of them are not well documented. Basic factors include pH, temperature, redox potential, and cation exchange capacity. Researchers also included the competition between metal ions, which affect the uptake of metals by plant's root (Merian, 1991). Sorption could also affect metals mobility in the soil, given that heavy metals can be sorbed into the soil organic matter limiting the mobility of metals (Vincent *et al.* 1996).

Metals in soil can be found in various forms: (a) free ions in the soil solution; (b) soluble metal complexes; (c) bounded to carbonate, (this fraction is sensitive to changes of pH); (d) bounded to soil organic matter (result in the release of soluble trace metals during the oxidizing or degrading processes of organic matter); and (e) precipitated residuals such as oxides, hydroxides, and carbonates (Tessier *et al.* 1979).

2.5.1 Nickel

Physical and Chemical Properties

Nickel is a silver-white, hard, ductile, ferromagnetic metal, with an atomic mass of 58.78, melting point of metallic nickel is 1453° C and it reaches the boiling state 2732°C. Nickel has multiple oxidation states that include: -1, 0, +1, +2 , +3, and +4 but the prevalent valences are 0, as in nickel metal, and +2 in common water-soluble nickel compounds, such as bromide, chloride, nitrate, and sulfate salts. While nickel exists in aqueous solutions mostly as Ni $(H_2O)_6$, which is poorly absorbed by most living organisms, it could be also be found in an insoluble forms, such as, NiO, Ni_2O_3, $Ni(OH)_2$, NiAs, and $NiCrO_4$, which are all water-insoluble compounds. Other nickel compounds include $Ni(CO_4)$,which is an organic compound that could be used for nickel refining processes, and is used as a catalyst in the chemical and petroleum industries. Nickel alloys are used in vehicles, processing machinery, tools, electrical equipment, and household appliances, Nickel compounds are also used for batteries (Merian, 1991).

Sources and Distribution in Soil

Nickel makes up for almost 0.008% of the earth's crust. It is obtained primarily from sulfides ores, and to a fewer extent, from oxides ores by hydro-metallurgical refining processes.

In 1985, world wide production of nickel was approximately 67 million kg. Agricultural soil originally contains about 3 to 1000 mg nickel /kg, and the primary sources of nickel emissions into the atmosphere are the combustion of coal and oil for heat or power generation, incineration sewage sludge, and steel manufacture. Nickel compounds, generated from these processes usually include nickel sulfate, oxides, and sulfides, and to a lesser extent, metallic nickel.

In various soil types, nickel shows a high mobility within the soil layers finally reaching groundwater, rivers and lakes. Nickel could be mobilized in soil by acid rain, and by same plants, which have the ability of uptaking and accumulating metals in roots or shoots. This movement depends on a group of parameters that include: (a) type of soil, (b) soil pH and humidity, (c) the organic matter content of the soil, and (d) the concentration of extractable nickel (Hertel *et al.* 1991)

Nickel Effects

Inhalation of the nickel compounds seems to be the most dangerous method of absorption. It is confirmed that an acute inhalation of nickel to humans may produce headache, nausea, respiratory disorders, diarrhea, shortness of breath, and in some cases death (ATSDR, 2003). Other ways of exposure includes: drinking water, eating food or smoking cigarettes, even skin contact with nickel-contaminated soil or water may also result in nickel exposure. Exposure to large amounts of nickel could result in: birth defects, lung embolism, allergic reactions, heart disorder, and in the case of uptaking less soluble forms of nickel compounds such as Nickel carbonyl ($Ni(CO)_4$); higher chances of developing lung cancer, nose cancer, and prostate cancer will rise (CEPA, 1994).

Nickel is not a very mobile element in soil; since the larger part of all nickel compounds released to the environment will be adsorbed to soil particles and become immobile as a result. However, in acidic ground water, nickel becomes more mobile and it will often rinse out to the groundwater in runoff, either from natural weathering or from disturbed soil. It could also enter water bodies through atmospheric deposition (Young, 1995).

There is lack of research regarding the effects of nickel upon organisms other than humans. Nevertheless, some studies confirmed high nickel concentrations on sandy soils can clearly damage plants, but some plants react to these high concentrations in a way that reduces toxicity effects, such plants could be either excluders (do not let metals into the plant body) or hyperaccumulators. Nickel is considered an essential food substance for animals, but in small amounts. However, it could also be dangerous when the maximum tolerable amounts are exceeded, which, could cause various kinds of cancer on different sites within the bodies of animals (Young, 1995).

2.5.2 Cadmium

Physical and Chemical Properties

Cadmium is a silver-white, lustrous and ductile metal, with a density of 8.64 kg/m^3 at 20°C. It has a melting point of 320.9°C, and reaches boiling state at 767°C. The atomic number of cadmium is 48, its atomic mass is 112.4, and its oxidation state is +2 in all compounds. Cadmium is readily soluble in nitric acid, and insoluble in basic solutions. Salts of cadmium with strong acids are soluble in water; less soluble are the sulfide, carbonate, and hydroxide (Merian, 1991).

Sources and Distribution in Soil

Cadmium enters the environment naturally by the transport of soil particles, forest fires, and volcanic emissions. In agricultural soil it mostly enters through fertilizers. Cadmium is considered of greatest concern in agricultural soils since it is loosely held by soil constituents and is readily available to plants.

Cadmium slag, sludge, and solid waste land disposal accounts for most of the total cadmium wastes. Available data indicate that around 159 tones of cadmium wastes are released annually to the Canadian environment as a result of domestic activities. Approximately 340 tones of cadmium wastes from the metal smelting and refining industry are deposited into landfills. Industrial activities result in adding 3 to 10 times more cadmium via three main routes: refining and use of cadmium, copper and nickel smelting (CEPA, 1994).

The bioavailability and movement of cadmium in soil, and potential accumulation in plants is induced by low pH (under 6.0). Also, mobility of cadmium seems to be much higher in soil with low organic matter, large soil particles, higher water content, and high soil retention. However, cadmium mobility sometimes seems to be limited, because of its sorption to organic matter and clay. On the other hand sandy soil provides cadmium with greater mobility, which raises the risk of leaching into any close aquifers (CEPA, 1994).

Cadmium Effects

Cadmium could be transported into the human bodies by: (a) breathing cadmium contaminated air; (b) eating foods containing cadmium.(almost all food contain some levels of cadmium, but it may be higher in some cases because of direct accumulation, or through the food chain; for example: shellfish, liver, and kidney contain higher cadmium content than any other kind of meat); (c) cadmium intake could happen through smoking; and (d) drinking heavy metal contaminated water (CEPA, 1994).

Even a long-term exposure to low levels of cadmium in air, food, or water results in a slow buildup of cadmium in the kidneys and possible kidney disease. Studies confirmed that cadmium accumulates in the liver and kidneys more than any other body part. While acute oral exposure to 20-30 g proved to be fatal to humans, exposure to lower amounts may cause gastrointestinal irritation, vomiting, abdominal pain, and diarrhea (ATSDR, 1999). Also inhaling air that contains cadmium or any of its compounds may result in: headache, chest pains, muscular weakness, pulmonary edema, and sometimes death (Young, 1991).

Cadmium proved to have a large number of negative effects on animals. It could have an impact on the behavior, growth, and physiological state of different animal species and fish. Animals that were exposed to cadmium in food or water developed high blood pressure, iron-poor blood, liver disease, and nerve or brain damage. Cadmium is found to be the only metal that clearly known to accumulate in the kidney with increasing age of the animal (Irwin, 1997).

Cadmium has a poor effect on plants, but it is only seen when cadmium is given in solutions. When cadmium is bounded to the soil particles it is less available to plants. Cadmium uptaken by plants affects mostly leaves and roots. At high cadmium exposure, leaves started to show signs of wilting and a big reduction in the number of roots initiated (Dobson, 1992).

2.5.3 Vanadium

Physical and Chemical Properties

Vanadium is a white to gray metal, which is often found as crystals. Metallic vanadium has a density of 6.11 kg/m^3, atomic mass of 50.94, melting temperature of 1890 °C, and it reaches boiling state at 3000 °C. Vanadium exists in multiple oxidation states (+2, +3, and +4). Naturally occurring vanadium consists of around 99% ^{51}V and the rest as ^{50}V. It has no particular odor. It is usually combined with other elements in the environment such as oxygen, sodium, sulfur, or chloride (Merian, 1991).

Sources and Distribution in Soil

Vanadium compounds have an average concentration of 150 mg/kg of the earth crust. While vanadium as an element does not occur in nature, its compounds exist in over 50 different mineral ores and in association with fossil fuels. Rock weathering, and soil erosion, and in a process that involves conversion the less-soluble vanadium form to a more soluble one; all contribute in releasing vanadium to water and soil (ASTDR, 1992).

Vanadium could be also found in many petroleum products and coal, in which it occurs naturally. Subsequently, it is also a by-product of petroleum refining. Other possible source of the element is the extraction of vanadium from petroleum ash (Irwin, 1997).

One of vanadium characteristics is that it stays in the air, water, and soil for a long time, and it does not dissolve well in water. It combines with other elements and particles, and bonds to soil sediments. The transport of vanadium in water and soil is largely influenced by pH, redox potential, and soil particles presence (ASTDR, 1992).

Vanadium Effects

Humans exposure to vanadium could happen through food (olive oil, sunflower oil), or through air, which could cause bronchitis, irritation of lungs, throat, eyes and nasal cavities. The vanadium uptake has many known toxic effects, such as vascular disease, sickness and headaches, weakening, severe trembling and paralyses, skin rashes, bleeding of livers and kidneys, damage to the nervous system, and inflammation of stomach and intestines (IPCS, 1988).

It was found that small amounts of vanadium in the environment might tend to stimulate plants (Merian, 1991). However, exposure to large amounts could be toxic due to the fact that this metal is considered to be one of the 14 most harmful heavy metals. Vanadium can be found in the environment in algae, plants, invertebrates, fishes and many other species. In mussels and crabs vanadium strongly bioaccumulates, which can lead to concentrations of about 10^5 to 10^6 times greater than the concentrations that are found in seawater. Vanadium toxicity is attributed to its ability to inhibit enzyme systems in animals, which have several harmful effects. It could also cause breathing disorders, paralyses and negative effects on the liver and kidneys for the animal (Merian, 1991).

Summary

Literature review in this chapter permitted to generate the following conclusions:

1. Oily sludge is a major problem in the oil industry for operational and environmental aspects;
2. Oily sludge component consists of a mix of hydrocarbon and non-hydrocarbon organic compounds, with some traces of inorganic compounds, which include heavy metal and soil particles;

3. Oily sludge disposal and treatment is a complicated process due to the variable components of the sludge (degradable and non degradable material). For example, dumping the sludge into a landfill could result in a heavy metal leaching into any near water resources;
4. New method for oily sludge treatment is required;
5. Phytoremediation could be applied on oily sludge, because of the ability of some plants to hyperaccumulate heavy metals while tolerating elevated amounts of hydrocarbons in the soil;
6. Lemon Scented Geraniums (*Pelargonium crispum)* have the ability to tolerate very high amounts of heavy metals and hydrocarbons, which make it a potential candidate for oily sludge treatment;
7. Nickel, cadmium, and vanadium, are of the common metals that could be found in petroleum oily sludge;
8. Mobility of these metals in water and soil is basically influenced by pH, redox potential and soil organic particles;
9. Combining phytoremediation with other conventional methods could result in a very sound treatment method that could solve the problem.

CHAPTER THREE

RESEARCH OBJECTIVES AND GENERAL APPROACH

3.1 Scope of the Problem

The main problem associated with oily sludge disposal, is fact that sludge constituents, as it was shown in the literature review, vary depending on the source, transportation and storage of the petroleum it self. While incinerating hydrocarbons causes air pollution, landfilling and landfarming carry the risk of heavy metals leaching into groundwater, or any adjacent water bodies; not forgetting that the ash resulted from incineration processes contains heavy metals also which forbid us from land disposal. Thus, in order to find a sound disposal method, some modifications could be applied to the conventional methods that were mentioned in chapter 2.4.

Phytoremediation technology is an innovative method for heavy metal extraction that is considered clean, inexpensive, and effective. However, several problems associated with using plants in such conditions have to be solved.

As it was discussed earlier in section 2.4.8.1, variety of plants has an impressive capability of extracting heavy metals from soil, or water. Though, the ability of these plants to extract metals from petroleum oily sludge has not been investigated yet.

However, in an experiment that was carried out in 1994, the ability of different species to survive in a landfarming oily sludge disposal site was examined (Elnawawy et al. 1994). The plants that were used included, Ryegrass, Oats, and Barely, and by studying the effects the oily sludge had on these plants, it was found that species reacted in different ways. For some plants, oily sludge was considered a source of certain micro-nutrients, which are deficient in the sandy soil; for others, it was a source of toxic heavy metals and hydrocarbons that affected the plant growth negatively. Therefore, it was concluded that, uptake and distribution of elements in plants tissues varies according to the plants species, and the sludge characteristics.

3.2 Objectives

The main goal for this study was to investigate the possibility of heavy metal removal from oily sludge using phytoremediation concept. This objective could be attained by applying the following actions:

- Formulation of an adequate sludge-soil system for an effective metal phytoremediation;
- Determining the influence of soil pH on nickel, cadmium, and vanadium uptake and mobility in a particular sludge system, and use the results to improve the extraction capability;
- Determining other environmental parameters that may affect the metal removal processes (e.g. presence of organic matter);

- Assessing the synergetic effect of heavy metals on each other, which might affect the plant availability mechanism;
- Defining the best conditions to be provided for the plant in order to achieve higher metal removal rate.

The target metals to be studied are: cadmium, vanadium, and nickel. To fulfill the research objectives, Lemon Scented Geranium was chosen to remove these heavy metals found in the oily sludge, due to its ability to accumulate large amounts of heavy metals, and tolerate hydrocarbons without showing major toxicity effects (Chapter 2.4.8.6).

3.3 General Procedure

Sludge samples were collected from the bottom of a crude oil storage tanks at Shell® Canada refinery in Montreal. In the preliminary stages of the experiment, oily sludge samples were digested and then analyzed in order to find out the heavy metals content using flame Atomic Absorption Spectrophotometer (Perkin Elmer AAnalyst 100). In order to get more reliable results in the final stages of the experiment such as, the concentrations of the metals at the final sludge samples, roots, and shoots; oily sludge samples were enriched with higher concentrations of nickel, vanadium, and cadmium chlorides.

In this study, two major sludge systems were investigated. In the first system, oily sludge was mixed with sandy loam in a volume ratio of 1:2. The oily sludge was enriched with nickel in the first series of the experiment, cadmium in the second, vanadium in the third, and finally a mixture of the three metals (Cd, V, Ni) (Figure 3). In the second system, dried compost was introduced to each metal enriched sludge/soil combination in order to achieve 1:1:1, sludge: soil: compost ratios respectively (Figure 4).

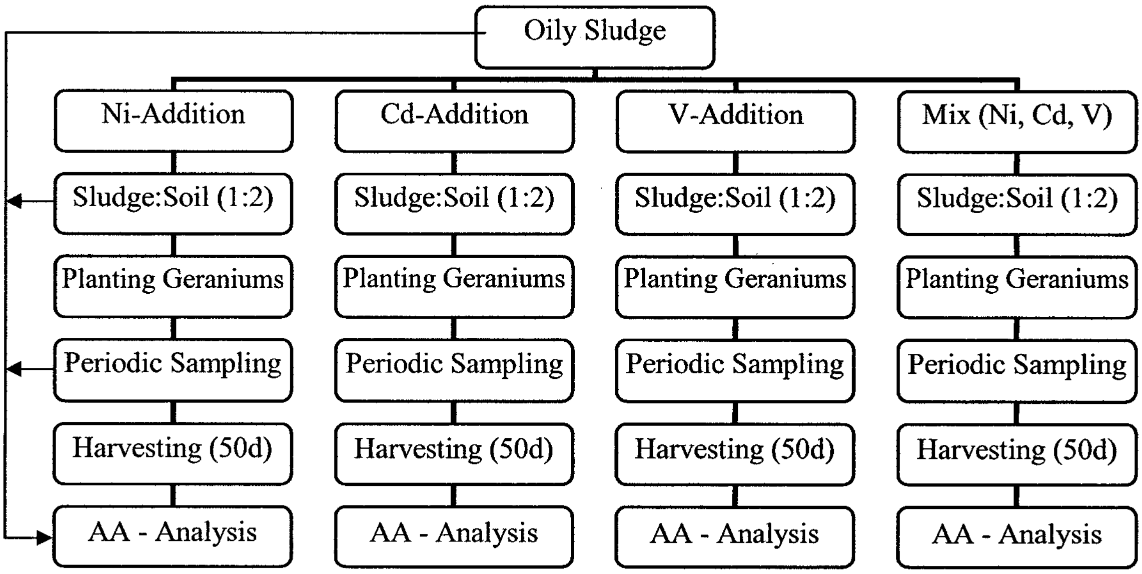


Figure 3: System 1 (sludge:soil, 1:2)

Before planting the geraniums, the mixtures were again analyzed to find out the initial metal concentrations in the systems. From each pot three samples were taken from different locations (Chapter 4), in order to ensure that the mixture is homogeneous; sludge pH values were taken before, during and after harvesting the plants in the pots using simple stir and measure method (Chapter 4.4).

The final investigation included 8 soil contamination conditions in which three month old Scented Geraniums (*Pelargonium* sp. 'Frensham') were planted in glass pots. Gravel stones were added inside serving as drainage system. The study was held in the greenhouse at Concordia University. Samples from the two systems were taken periodically, pictures of the plants, and leaf and shoot samples were taken every two weeks for a period of 50 days. At the end of this period plants were harvested, washed, dried, digested and analyzed at the lab (Chapter 4).

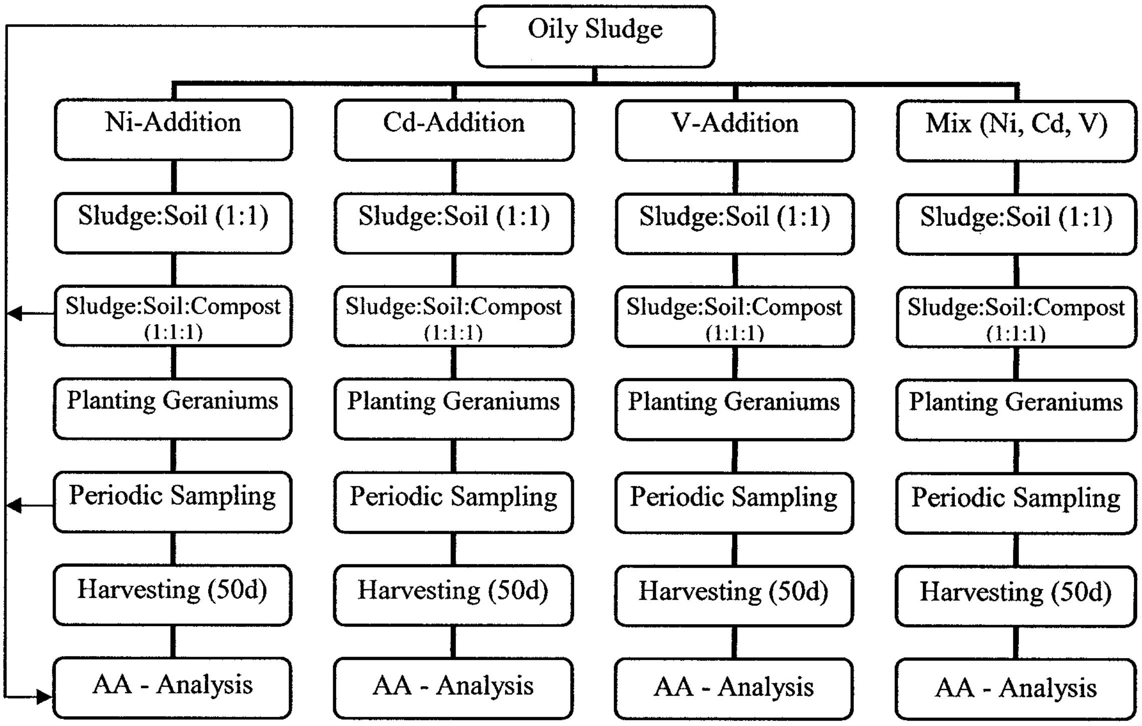


Figure 4: System 2 (sludge:soil:compost, 1:1:1)

Depending on the analysis that were performed on the sludge samples and plants, and the initial concentration values we had got previously for the three metals (Ni, Cd, V), in addition to the pH values that were taken throughout the experiment, complete evaluation of the study was introduced, and reasonable justifications for the results were presented (Chapter 4.5).

CHAPTER FOUR

MATERIAL AND EXPERIMENTAL SETUP

4.1 Material

4.1.1 Petroleum Oily Sludge

Sludge samples were collected from the bottom of a crude oil storage tanks at Shell® Canada refineries in Montreal, Canada. Liquid oil was partially separated using glass separating funnels, and the wet solid sludge left in the funnels was used in that form throughout the experiment (Figure 5). Metal analysis done in the lab under EPA Testing Methods#3051 EPA (1994) showed that oily sludge in the solid form contains much higher concentrations of metals than in the liquid form. In fact, metal analysis of the liquid oil samples showed the negligible concentrations of metals. Therefore, this study was concentrated on the solid part of the oily sludge.

The process of drying the petroleum oily sludge completely is difficult and expensive. In addition, there are not many studies that are involved in the separation and solidification of oily sludge. Habibi (2004) found out that the application of electrokinetic's phenomena to oily sludge samples has reduced the amount of water by almost 63%, and light hydrocarbon content by almost 43%. However, in all cases the remaining solid phase contains metals that should be removed.

The oily sludge was modified in order to provide the plants with adequate living conditions that would support the plant growth. Two systems were introduced: a) sludge: soil system with a ratio of (1:2); and b) sludge:soil:compost system with a ratio of (1:1:1). These systems mimic the natural conditions in the field: including landfarming and disposal ponds.

Figure 5: Petroleum oily sludge used in the experiment

4.1.2 Soil

Soil used in the mix that eventually provided the soil cover in the pots was collected from a geotechnical lab in Montreal, Canada. The soil had a density of 1900 kg/m^3 with the following components: 5% clay, 35% silt, 50% sand, and 10% gravel. It was classified according to the soil texture triangle as a sandy loam soil. The reason behind choosing a sandy soil was the fact that Lemon Scented Geraniums (Chapter 2.4.8.6) requires soil that would allow easy drainage of water.

4.1.3 Compost

The second set of samples in which the plants were grown at, contained mix of oily sludge, sandy loam, and compost. Dairy farm manure compost was brought from Macdonald Campus at McGill University, Ste. Anne de Bellevue, Quebec. Moisture and organic carbon content were 62 %, 19% respectively, these values were determined in the lab using simple weight loss methods. Compost was included in the second set for two reasons: 1) to study the effect of organic matters on the potential availability of the targeted heavy metals for plant uptake; and 2) to provide the plant with the basic nutrients (having the fact that compost is a good source for nutrients), which would insure their survival in the rough conditions of oily sludge.

4.1.4 Plant Used

Pelargonium cryspum not only has the ability to survive at high concentrations of several heavy metals and elevated amounts of hydrocarbons content, but it is also considered an excellent phytoextractor for some metals (Ch 2.4.8).

Three months old Lemon Scented Geraniums plants (*Pelargonium cryspum*) were brought from "*Frank Flouriest*" (Montreal East) in August 2004. Geraniums were placed at the greenhouse facility of Concordia University, Sir George William campus, Montreal. Generally the whole set of plants were about 5-8 inches high and were planted in a 6 cm diameter glass pots (Figure 6) for a period of 50 days. These pots were filled with a modified sludge over a 1 cm layer of well-washed Perlite. Certain conditions regarding light exposure, humidity, and watering procedure were followed, to assure the healthy survival of these plants.

Figure 6: Lemon Scented Geranium in a glass pot at initial conditions

4.2 Experimental Set-Up

4.2.1 Metal Enrichment

Initial analysis showed the presence of nickel, cadmium, and vanadium in the oily sludge with the following concentrations, 33 mg/kg, 12 mg/kg, and 200 mg/kg respectively. However, since the sludge samples were to be mixed with big amounts of soil and compost, which would affect the concentration, and the fact that some studies confirmed the ability of Geraniums to accumulate large amounts of metals, especially nickel, and cadmium (Tereza *et al.* 2001); metal enrichment deemed to be a necessary process to assure the consistency of the process, and to get a further look at the maximum ability of these species to resist and uptake the high concentrations of these metals.

The enrichment process considered the toxicity level of the plants. Previous studies showed that this level exceeded 30,000 mg of cadmium and 6,400 mg of nickel in one kilogram dry weight of the plant tissues (Dan *et al.,* 2001). The enrichment process included two kinds of contamination, and went as follows:

a) Single metal contamination: Where three sludge samples were contaminated with nickel, cadmium, and vanadium separately, and as follows: solutions containing the chloride of these metals ($NiCl_2$, $CdCl_2$, VCl_3) with a concentration of 2000 mg/L in each solution were mixed well with the wet sludge samples in covered plastic containers. Manual shaking was applied for 5 min, and then the samples were left for 24 hours before further mixing with soil or compost, to allow diffusion within the sludge to take place

b) Combined metal contamination: Sludge samples were contaminated with the three metals (Ni, Cd, V) added together in the same solution as follows: solution that contained 2000 mg/L of each metal ($NiCl_2$, $CdCl_2$, VCl_3) was mixed with sludge samples, covered, and left aside for 24h for diffusion to take place

4.2.2 Mixing Procedure

The two systems suggested for this study are directly related to the pots' filling material. This material was prepared with: metal enriched sludge, soil, and compost, mixed together using a procedure that would guarantee the homogeneity of the mix. Mixing procedure was based on dividing, mixing, and re-combining the samples, which resulted in a fairly homogeneous mix. The following sub-sections describe the preparation processes of the two systems used in the pots: a) sludge/soil system; and b) sludge/soil/compost system.

4.2.2.1 Sludge/Soil System with 1:2 Volume Ratios

In order to get homogeneous mix of metal enriched oily sludge with a sandy loam soil, in a sludge/soil volume ratio of 1:2 respectively, the following steps were applied:

1. Each oily sludge sample enriched with one of the three metals; nickel, cadmium, or vanadium, were divided into eight equivalent sections;
2. The volume of each section was determined using water displacement method;
3. The soil to be used was crushed to pass #10 sieve in order make the mixing process easier and to later simplify diffusion;
4. Sandy loam sample was divided into 8 sections. Each section has double the volume of the 8 sludge samples, in order to get sludge: soil = 1: 2 ratios;
5. Sludge samples were mixed with the soil samples in eight special plastic containers;
6. Each container was manually shaken in all directions for about 5 to 6 minutes, and big particles were crushed during the shaking process using a normal lab spatula;
7. The mixed material was left for 24 hours to allow diffusion to take place;
8. After 24 hours, each two plastic containers were combined in one plastic container, resulting in 4 containers only;

9. After repeating steps (6 to 8) on the four resulted containers, each two were recombined into 1 container and left for 24 hours, resulting in two plastic containers only. It was finally combined in one big container that would contain the final homogeneous mix used for the first scheme of the study.

4.2.2.2 Sludge/Soil/Compost System with 1:1:1 Volume Ratios

To achieve that homogeneous mix, a method similar to the previous one, but with new component introduced to the mix (compost), the following steps were followed:

1. Steps (1, 2, and 3) from the previous method were repeated for this one;
2. Resulted soil was divided into 8 sections that have the same volume the 8 sludge samples have;
3. Compost was dried in the oven for 1 day at 80 C° to make the crushing and mixing processes easier;
4. Compost was grounded, and then sieved using #10 sieves;
5. Resulted compost was divided into 8 parts, where each part had the same volume of the sludge and sand samples it would be mixed with;
6. Taking into consideration the addition of the compost samples, steps (5 to 9) from the previous method were followed in the same order;
7. The final homogeneous mix (sludge, soil, and compost, with 1: 1: 1 ratios) would be used in the second part of the study.

4.3 Plants and Pot Preparations

4.3.1 Pot Preparations

A total of 10 glass pots with a diameter of 6 cm and a height of 9 cm were filled initially with 1 cm layer of perlite stones at the bottom that would function as a drainage system (Figure 7).

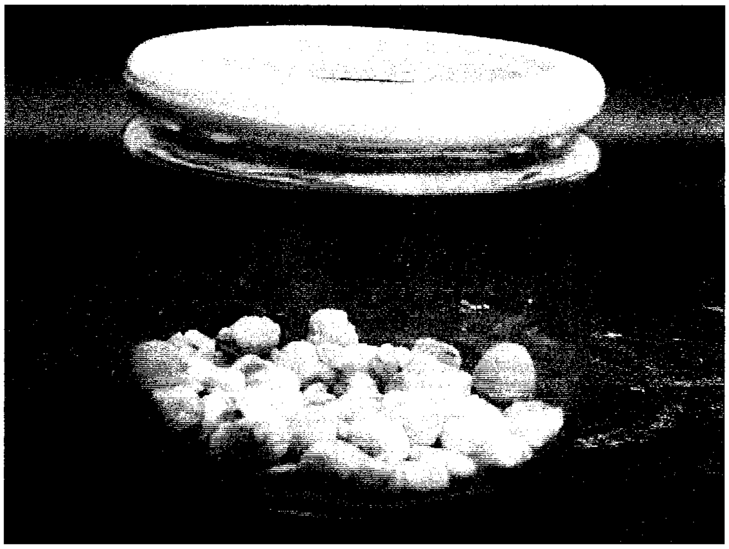


Figure 7: Glass pot filled with perlite stones at the greenhouse facility

Taking into consideration the filling material, pots (Table. 6) were distributed as follows:

1) Four pots were filled with the initial mix that is the first phase of the experiment, which included the sludge/soil combination with a volume ratio of 1:2 respectively. Each of the four pots was filled with one of the prepared fillings; nickel enriched sludge and soil in one pot, cadmium enriched sludge and soil in another, vanadium

enriched sludge and soil in the third and mix of the three metals enriched sludge and soil in the last one. The total dry weight of soil and sludge added in each pot was about 220 g.

2) Four pots were filled with the second mix that could be described as the second phase, which is shaped by the sludge/soil/compost combination with a volume ratio of 1:1:1. These pots were filled with the combination of soil, sludge enriched with one of the three metals (nickel, cadmium, vanadium), and dried compost. The total dry weight of the mix added to each pot was about 160 g (Figure 8).

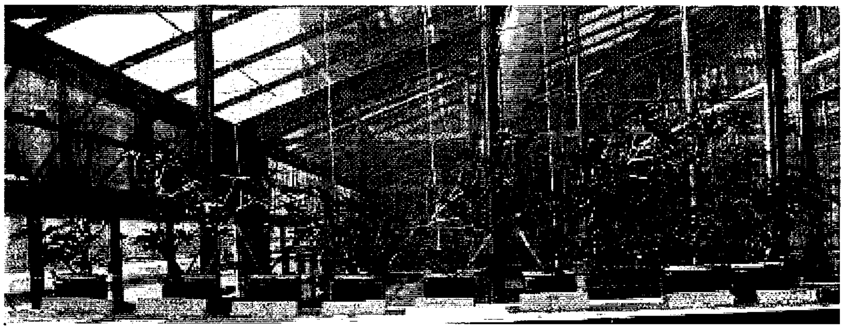


Figure 8: Setup of experiment in the greenhouse facility at Concordia University

3) Two control units included two pots: (1) first pot was filled with a mix of soil and sludge (not metal enriched) with a volume ratio of 2:1 respectively with a total dry weight of 200 g; and. (2) second pot was filled with a mix of soil, sludge, and compost with a volume ratio of 1:1:1 and a total dry weight of 130 g.

The following (Table 6) explains these systems:

Table 6: Different Systems Used in the Experiment.

Pot #	**Content**	**Metal added***	**Dry weight**
1	Soil, Sludge	Nickel	**220g**
2	Soil, Sludge	Cadmium	**220g**
3	Soil, Sludge	Vanadium	**220g**
4	Soil, Sludge	Mix (Ni, Cd, V)	**220g**
5	Soil, Sludge, Compost	Nickel	**160g**
6	Soil, Sludge, Compost	Cadmium	**160g**
7	Soil, Sludge, Compost	Vanadium	**160g**
8	Soil, Sludge, Compost	Mix (Ni, Cd, V)	**160g**
9	Soil, Sludge	No metals added	**200g**
10	Soil, Sludge, Compost	No metals added	**130g**

4.3.2 Plants and Greenhouse Preparations

Ten three months-old Lemon Scented Geraniums plants (*Pelargonium Cryspum*) similar in their physical parameters 5-8 inches high, were used in this study. The steps followed in preparing and planting these species in the pots were as follows:

1. The plants were pulled out from their original pots gently, without disturbing the roots, or the plants body;
2. Washed thoroughly, especially the roots with deionized water in order to get red of any stuck soil particles;
3. A 5 cm hole was dug in each pot using a hollow plastic pipe, and soil extracted was kept a side;

4. Plants were inserted in the pots all the way to the bottom, and then the roots and part of the stem were covered with the extracted soil, and compacted well.

The greenhouse conditions were not entirely stable due to some problems in the facility itself but generally the following conditions were provided: a) light 12 h; and b) temperature day/night: 28-34/ 20 °C. Watering was applied twice to three times a week depending on the dryness of the pot content, and was done by a 50 ml tube filled completely with deionized water. During the watering process, it was necessary to add the same amount of water to each pot. This amount of water did not exceed the field capacity in the system; consequently, water did not drain out of the system.

4.4 Analytical Methods and Sampling

Each sampling step in this study was followed by a separate analyzing process, where samples were taken, digested and detected for heavy metal presence. The following two sub-sections will describe the sampling and analysis applied throughout the experiment, starting with the original sludge and finishing with the plant body analysis.

4.4.1 Sampling Procedure

Samples were taken from: (a) the original petroleum oily sludge; (b) the final mixture of sludge/soil, and sludge/soil/compost; (c) the pots during and after the greenhouse experiment; and (d) the plants themselves, (body and roots separately) at the end of the experiment.

a. Samples from the original sludge was taken in order to prepare them for metal detection analysis as follows: three 2g samples of the sludge were taken from three different positions using a normal steel spatula and placed in 50 ml plastic test tubes (Figure 9)

b. In the final mix, three samples were taken for each system (Table 6) prior to adding them into the pots in order to get the initial concentrations of the metals. To make sure the mix is homogeneous, samples were taken from various locations (Figure 9)

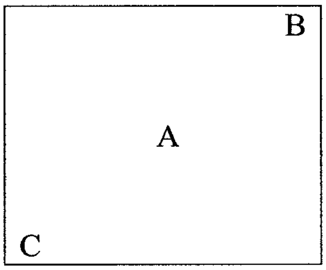


Figure 9: Sampling locations in containers
(Sample B was taken from the surface while samples C, and A were taken at 2 cm depth)

c. During the greenhouse experiment, soil samples were taken every 10th day throughout the 50 days period. Sampling was performed using a 5 ml diameter hollow plastic tube. The tube was forced into the partially wet soil (around 2 days after last watering process), 1 cm away from the plant body, and close to 5 cm in depth. Then it was spun and pulled out gently with the sample inside

Concerns that were followed in the sampling process:

a. Not to disturb or affect the root system while injecting, spinning or taking the tube out. Everything had to be done gently;
b. After pulling out the tube, the space that was left behind had to be covered and compacted immediately so as not to disturb the roots;
c. It was important to take the samples from the same spot that was taken from the previous time; in order to be able to build an accurate comparison between the results.

4.4.2 Analytical Methods

4.4.2.1 Sludge and Soil Metal Analysis

Original wet sludge samples were digested using EPA Microwave Assisted Acid Digestion method of sludge and soil (EPA, 1994). Samples of 2 g were digested in 20 ml concentrated nitric acid and left for 24h. The samples in acid were placed in a microwave vessel, capped and placed in the microwave unit. The microwave was operated on a three stages with a maximum pressure of 1386 KN/m^2 (200 psi). When temperatures and pressure went back to normal, and the process was completed, the vessel contents were filtered, and analyzed by Atomic Adsorption Spectrometer, Perkin-Elmer AAnalyst 100 (Figure 10).

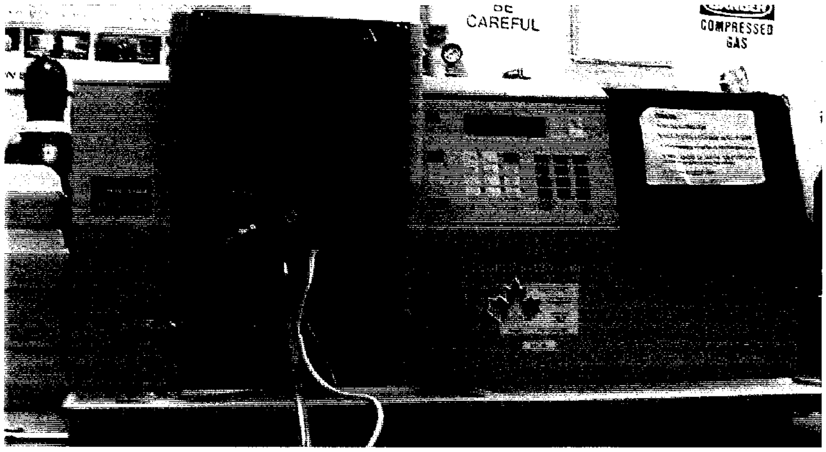


Figure 10: Perkin-Elmer AAnalyst 100 (Atomic Adsorption Spectrometer)

After mixing sludge with soil and compost (section 4.2.2), digestion was necessary to provide the metal initial concentrations values in the pots. EPA Microwave Assisted Acid Digestion method was applied with the addition of one step that included grounding the dried mix before digesting and analyzing it.

Depending on samples collected from the pots throughout the 50 day period from the rizosphere area around the roots; results regarding metal concentrations variation in the mix were calculated by averaging the three replicate values obtained from atomic absorption (AA) analysis for each experimental set.

4.4.2.2 pH and Redox Readings

Values of pH and redox were measured in samples throughout the experiment in order to: a) check the initial alkalinity of the mix; b) give an overlook of how appropriate it is for plant's survival; and c) have an indication about the changes in the availability of metals for geraniums uptake.

The method used for pH measurements was developed at Concordia Environmental Lab, and based on taking the readings while stirring processes are under going. The following steps summarize this technique:

a. 25ml distilled water was added to a 2 g of any sample analyzed, and placed in a 50 ml glass beaker;
b. The beaker was placed on a stirrer for 5 minutes;
c. pH probe was installed while the stirring process took place;
d. After the pH readings were taken, the probe was taken out and rinsed with distilled water, and then redox values were measured following the same steps;
e. Steps were repeated for all samples.

4.4.2.3 Plant Digestion and Analysis

Plants were taken out of their pots, dried, digested, and analyzed for metals at the end of the 50 day period. The following procedure was followed:

1. Large volume of the pot content was taken away to reduce the pressure on the roots while taking it out;
2. Plants were pulled smoothly from the soil, to minimize roots loss as much as possible;
3. Roots were washed thoroughly with distilled water, in order to get red of the stuck soil particles;
4. Plants were separated into two major parts (roots and shoots);

5. The separated parts were left to air dry for a week, with an average temperature of 35 to 40 °C, then it was oven dried for 24 h under 80°C degrees;
6. Dry weight was taken for roots and shoots separately, for the purpose of finding the total accumulation of metals;
7. Roots and shoots were grounded using a simple manual mortar and pestle;
8. Metal extraction was done by digesting 1 to 2 g of the plant dried matter, roots or shoots, in a 20 ml concentrated nitric acid. And microwave digestion was introduced to complete the process;
9. After digestion was completed, samples were filtered using normal filter papers;
10. To check for extracted metals; solutions were finally analyzed via atomic adsorption spectrophotometer (Perkin Elmer AAnalyst 100);
11. Metal concentration in the samples was then calculated using the following formula, after each (AA) analysis.

$$\mathbf{C' = ((CV_n) / Ms)\ 1000 g/kg}$$

Where:

C': Targeted Metal concentration in the sample, mg/kg
C: Measured metal concentration in the solution, mg/L
V_n: HNO_3 Volume that was initially used for digestion, L
M_s: Mass of the original sample digested, g.

CHAPTER FIVE

RESULTS AND DISCUSSION

The results showed that Geraniums were successful in: a) uptaking the heavy metals; and b) surviving oily sludge conditions. However, the ability of these plants to remove particular metal depended on: a) oily sludge system in the pot; b) the initial concentration of each metal; and c) the contamination with a sole metal and mix of metals. In addition, pH analyses were performed on each sample in order find out how does soil pH affect metal bioavailability in the various sludge systems: sludge/soil, and sludge/soil/compost systems.

5.1 Results for Sludge/Soil System

In the sludge/soil system, and as it was illustrated in the experimental analysis, sludge was mixed with sandy loam to form a mix of a volume ratio of 1:2 (sludge: soil) respectively. Sludge used was initially enriched with nickel, cadmium, vanadium, and mix of the three metals.

Through the 50 days experiment, concentration of metals in soil, and plants' uptake varied from one metal to another. But in all cases, Geraniums were able to accumulate relatively high amount of each metal, and survived the contaminated living conditions.

5.1.1 Results for Nickel Removal

Figures 11 and 12, shows the variation of nickel concentration in the sludge/soil system around the roots throughout the period of the experiment. Figure 11 presents conditions where nickel was added as sole contaminant to the sludge at the beginning of the experiment, while Figure 12 describes the nickel concentration behavior in the presence of cadmium and vanadium in the mix.

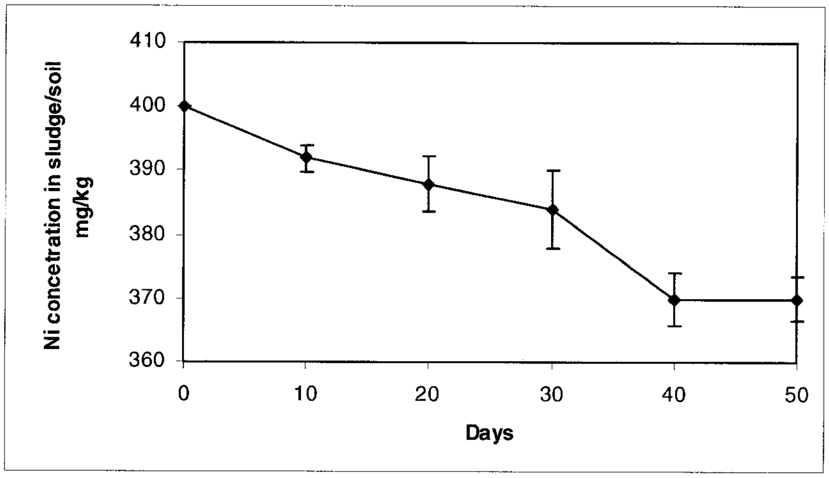


Figure 11: Nickel removal from sludge/soil system, case 1 (Sludge contains nickel only)

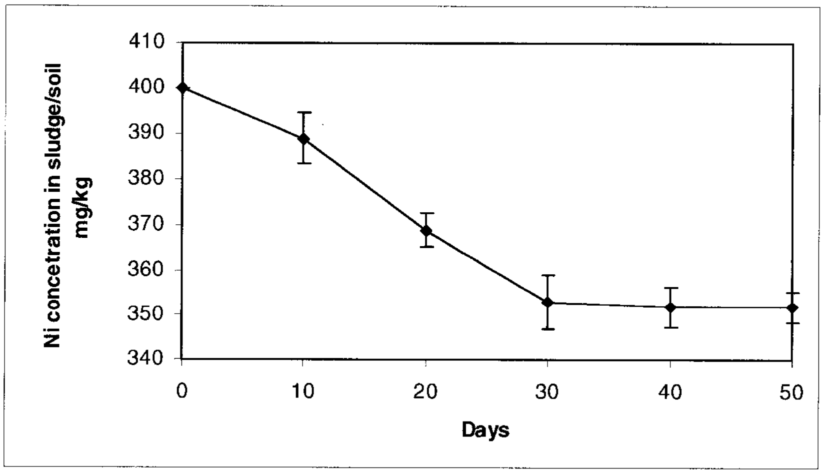


Figure 12: Nickel removal from sludge/soil system, case 2 (Sludge contains nickel, cadmium, and vanadium)

Figure 11 shows the reduction of the nickel concentration from 400 to 370 mg/kg, in a period of 50 days. The general behavior of the nickel removal from sludge was characterized by a gradual drop of the concentration in the first 30 days followed by a bigger drop (from 384 to 370 mg/kg) in a 10 days period, and stabilized until the end of the experiment. On the other hand, Figure 12 describes the behavior of nickel concentration with the presence of cadmium and vanadium in the original sludge. In this Figure, the gradual reduction in the nickel concentration was bigger until day 30, where the concentration stabilized at 350 mg/kg.

The error bars that appear on the diagrams throughout Chapter 5 were created using the three sets of samples taken in each sampling from two systems. The mean and standard deviation were calculated from these sets using spread sheets and accordingly, these bars were formed.

Values of pH related to the samples are demonstrated in Figure 13. It is clear that there was a relatively important decrease in the sludge/soil pH, starting from day 10 until day 30, where pH reached its lowest values (around 7.06). However, pH values started to increase again until it reached 7.3 on the last sampling day.

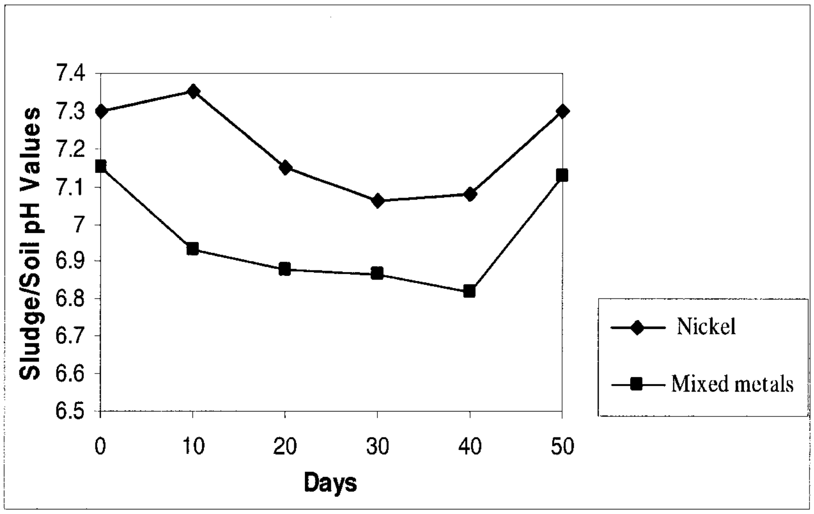


Figure 13: Sludge/Soil pH variation in two different contamination scenarios

In the case where other metals were present in the system, pH value had its highest drop on the first 10 days, followed by a gradual decrease until day 40, where the value was 6.8 (lowest pH value). After day 40 pH values started to increase again to reach finally 7.1.

It could be concluded that due to pH increase at the end of the experiment, the availability of nickel for uptake; might be affected. It could be seen in Figures 11 and 12, nickel reduction in the system seemed to be stabilized 10 days before the experiment was completed.

Figure 14 illustrates the accumulation of nickel in the Geraniums roots and shoots.

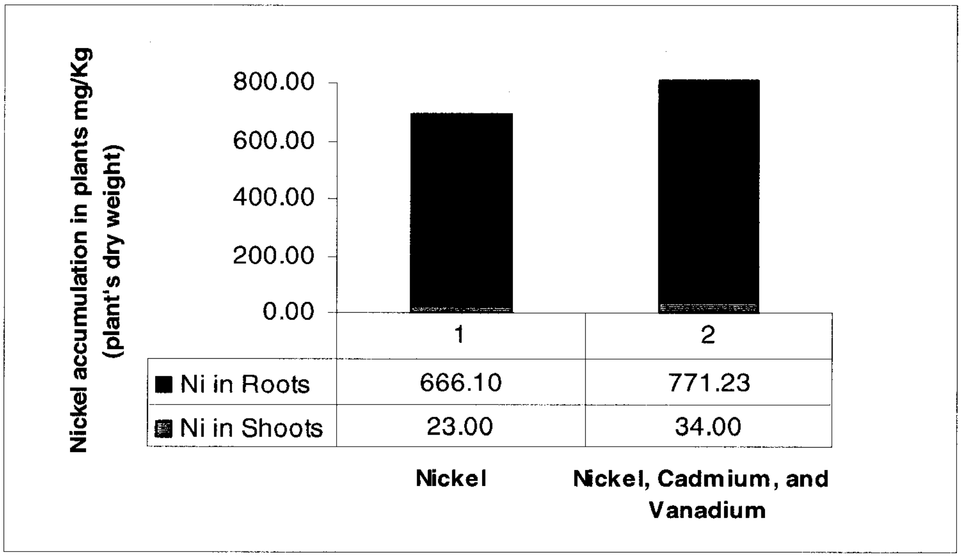


Figure 14: Nickel accumulation in Geraniums, system 1
(1) Nickel is present only; and (2) a mix of Cd, Ni, and V are present in the sludge

Scented Geraniums accumulated up to 680 mg/kg-plants dry weight of nickel, mostly in the roots, which suggests the plant was not effective in transporting the metals into the shoots. In the case were other metals were added, the nickel accumulation was higher by around 100 mg/kg-plant's roots dry weight, which demonstrate a synergetic effect of cadmium and vanadium on nickel mobility and uptake into the plants.

5.1.2 Results for Cadmium Removal

Figures 15 and 16 describe the behavior of cadmium in the sludge/soil system where two cases of contamination were applied: cadmium was present alone (Figure. 15); and b) nickel, cadmium, and vanadium were added together to the sludge (Figure. 16).

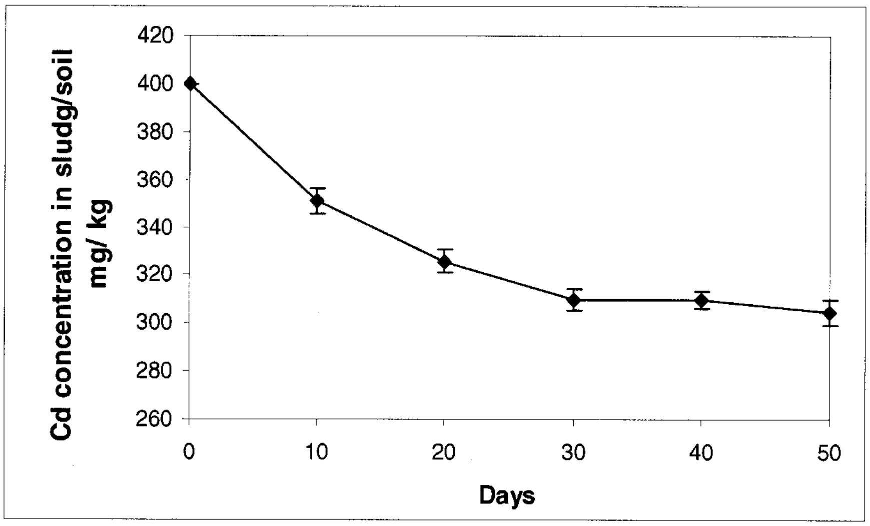


Figure 15: Cadmium removal from sludge/soil system, case 1
(Sludge contains cadmium only)

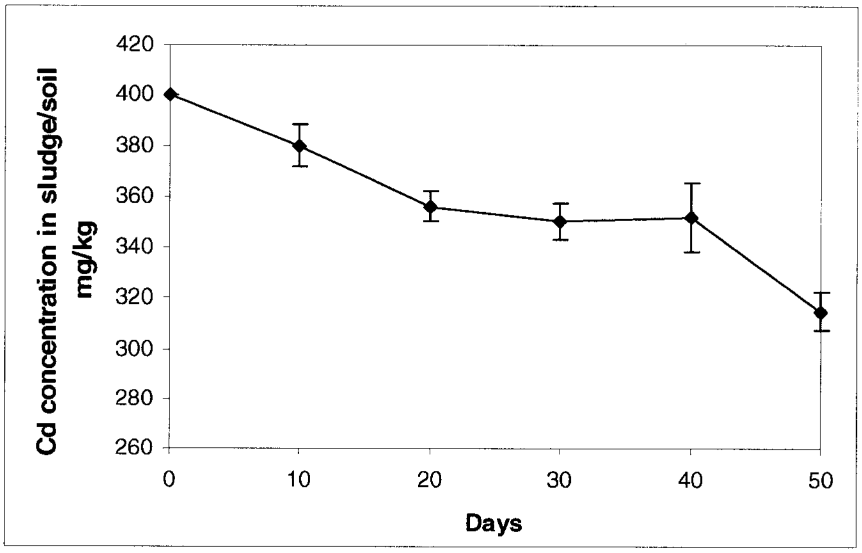


Figure 16: Cadmium removal from sludge/soil system, case 2
(Sludge contains nickel, cadmium, and vanadium)

The value of pH did not vary much in the test with cadmium available alone in the sludge. However, in the case where nickel, cadmium, and vanadium were added together into the original sludge, pH dropped to lower values and by the end of the study it reached the neutral value. It was observed that the highest metal uptake period was initiated on day 40, which is associated with the lowest pH value recorded (around 6.8).

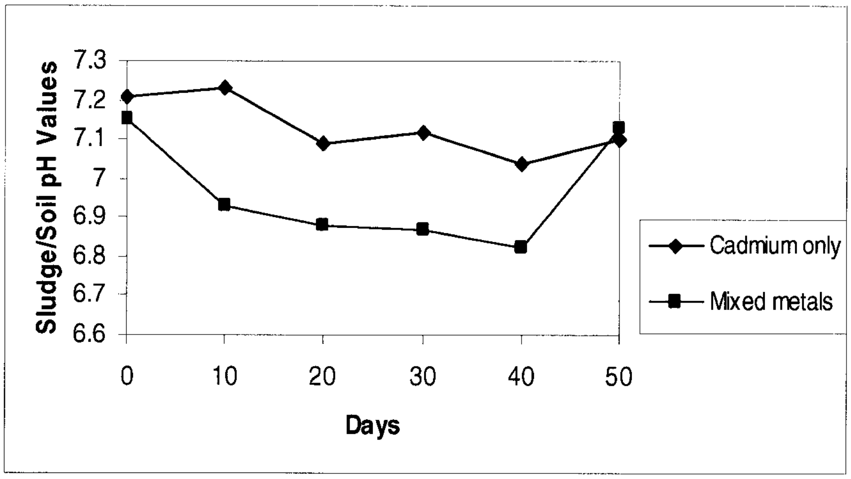


Figure 17: Sludge/Soil pH variation for two different contamination scenarios

This could emphasis the fact that decreasing pH of the soil would increase cadmium bioavailability, which would usually increase plant uptake of cadmium unless Cd initiates toxic response in the plant, as it was also mentioned by Salisbury (1992).

The total uptake of cadmium by the plant was similar in two cases of contamination, where in both cases the plant was able to extract around 870 mg of Cd/kg-plant dry weight (Figure 18). However, in the case of mixed metals, the shoots were able to accumulate around 50 mg of Cd/kg-plant dry weight, which indicate higher transfer mobility of cadmium within the plant. Although cadmium accumulation was higher than nickel accumulation, yet in both cases plants didn't show major toxicity effects (Figure 36), which reveals an impressive potential in the Geraniums species for cadmium uptake.

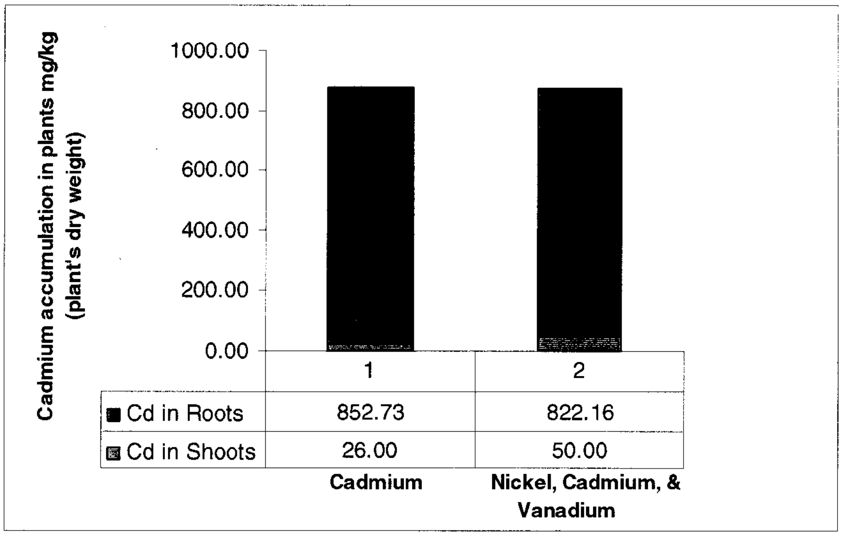


Figure 18: Cadmium accumulation in Geraniums, system 1
(1) Cadmium is present only, and (2) a mix of Cd, Ni, and V are present in the sludge

5.1.3 Results for Vanadium Removal

Similar to the case of nickel, and cadmium, Geraniums demonstrated fairly good ability in uptaking vanadium from the sludge/soil mixture and storing it in its tissues. Figures 19 and 20 illustrate the decrease of vanadium concentration in the sludge/soil system in two different cases: (a) vanadium is present alone (Figure 19); and (b) nickel, cadmium, and vanadium are added together to the sludge (Figure 20).

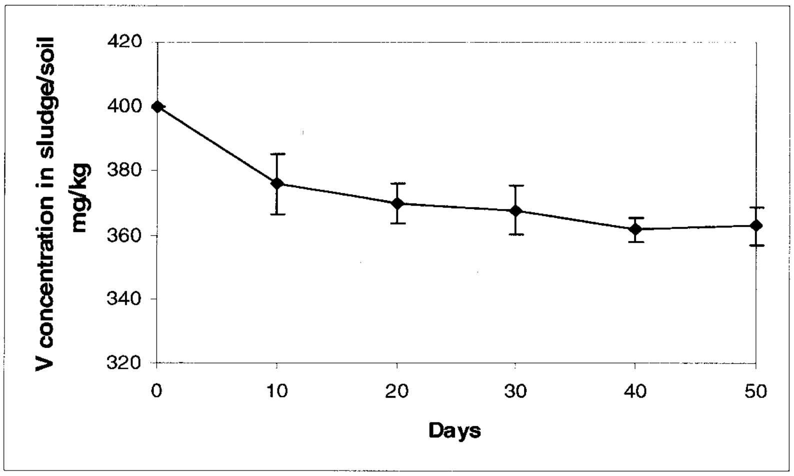


Figure 19: Vanadium removal from sludge/soil system, case 1 (Sludge contains vanadium only)

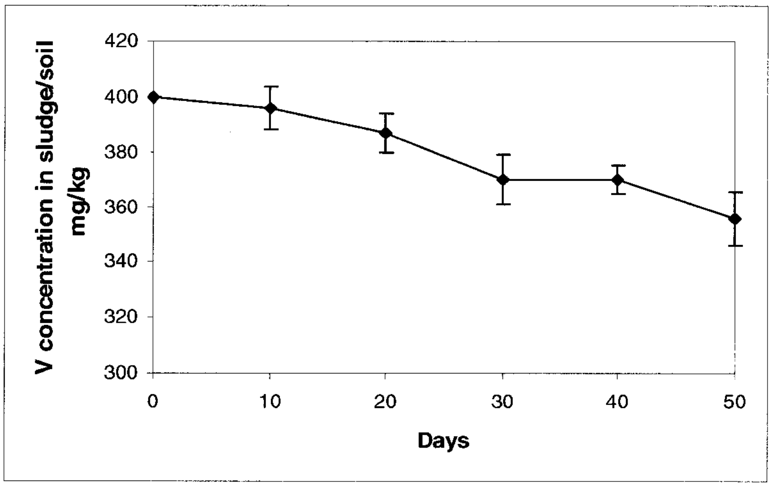


Figure 20: Vanadium removal from sludge/soil system, case 2 (Sludge contains nickel, cadmium, and vanadium)

The decrease of the vanadium concentration around the roots in the sludge/soil system was around 40 mg/kg, and almost 50 mg/kg in the case of mixed metals. In the fist case, the biggest drop (21 mg/kg) in the concentration was noticed during the first 10 days, followed by a gradual decrease in the concentration. A steady drop in concentration characterizes the behavior of vanadium concentration until day 30, where it was stabilized for 10 days, then dropped again in the last 10 days.

Values of pH associated with previous diagrams are shown in Figure 21. It could be noticed that pH readings were behaving similarly in both systems, except on day 40, where sample analysis indicated relatively lower pH value in the system with the mixed metals. Decreasing pH of the soil would increase vanadium bioavailability, which would usually increase plant uptake of vanadium.

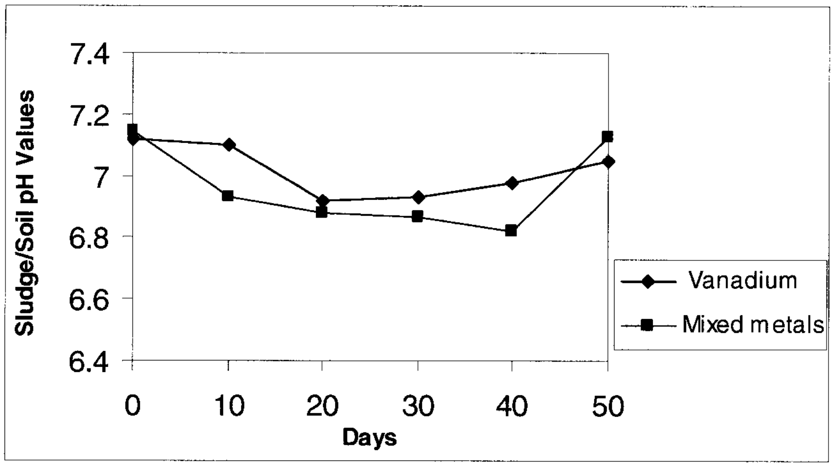


Figure 21: Sludge/Soil pH variation, in two different contamination scenarios

Scented Geraniums demonstrated good ability to remove vanadium from sludge, and were able to accumulate up to 960 mg vanadium/kg-plant dry weight. Although there was a relatively bigger amount of vanadium (in comparison to nickel and cadmium) transported into the shoots, it is still considered very little by looking at the roots' accumulation. But yet again this result demonstrates geraniums ability to extract vanadium from different contaminated systems (Figure 22).

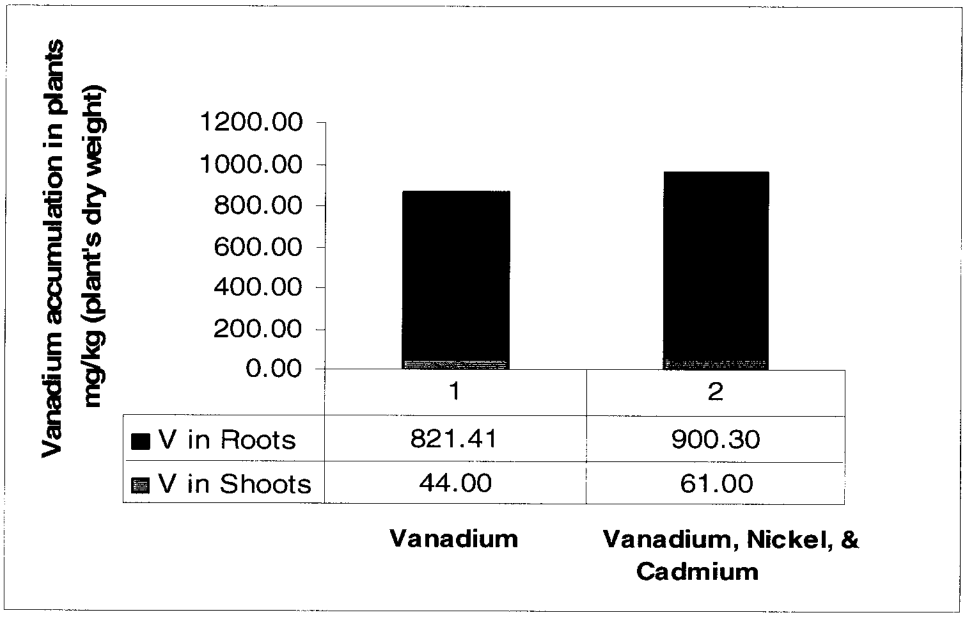


Figure 22: Vanadium accumulation in Geraniums, system 1
(1) Vanadium is present only, and (2) a mix of Cd, Ni, and V are present in the sludge

5.2 Results for Sludge/Soil/Compost System

In this system, original petroleum oily sludge was modified by adding sandy loam soil and compost in a 1:1:1 sludge/soil/compost volume ratio. The sludge was initially enriched with nickel, cadmium, and vanadium (Chapter 4). Each metal was added alone in one case, and a mix of the three metals was added in the other case. Same analyses that were applied on the sludge/soil system were used in this system. However, higher metal uptakes, and more obvious toxicity symptoms, were visible in this system.

5.2.1 Results for Nickel Removal

Figure 23 shows that the reduction of nickel concentration was relatively big in the first 10 days of the experiment. This could justify the obvious toxicity effects that started to show on the plant after short period after the planting period (Figure 35). The nickel concentration maintained its gradual decrease after day 10, to reach a 650 mg /kg on the last set of samples that were taken on the 50th day of the experiment. On the other hand, Figure 24 shows a relatively big drop in nickel concentration in the early stages of the study for the sludge/soil/compost system that contains mixed metals. However, this drop was almost half the one observed in the sludge/soil/compost system that contained nickel only. Similar to the previous system, there was gradual decrease in the nickel concentration in the following 40 days.

The compost addition resulted in a lower initial pH values (Figure 25). As the experiment proceeded, pH values started to increase again, and despite the fact that the initial and final pH values of the system were close in both cases (nickel alone and mixed metals), general behavior of the pH curve was different throughout the experiment. In the case of the nickel alone, pH curve was relatively steady, but in the case of mixed metals, pH curve was variable during the experiment.

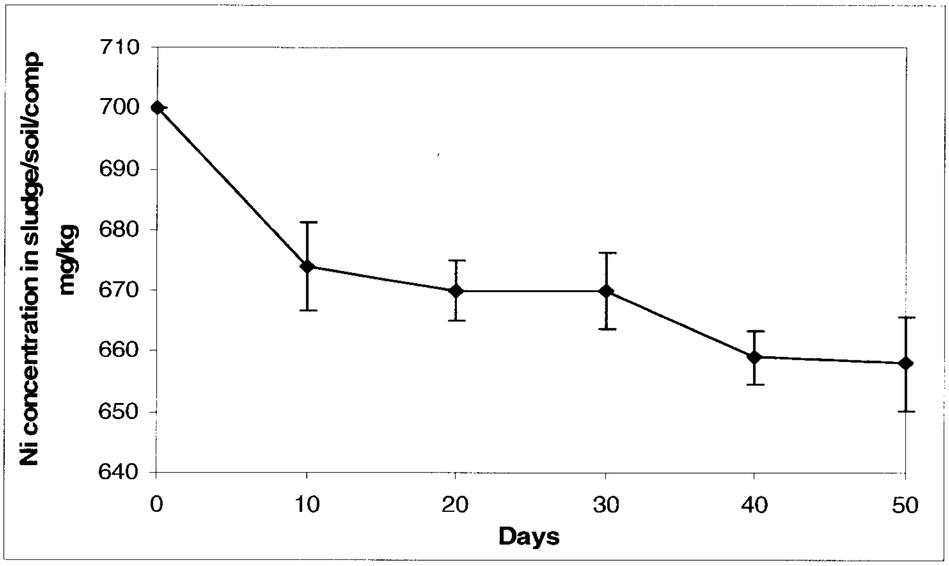


Figure 23: Nickel removal from sludge/soil/compost system, case1
(Sludge contains nickel only)

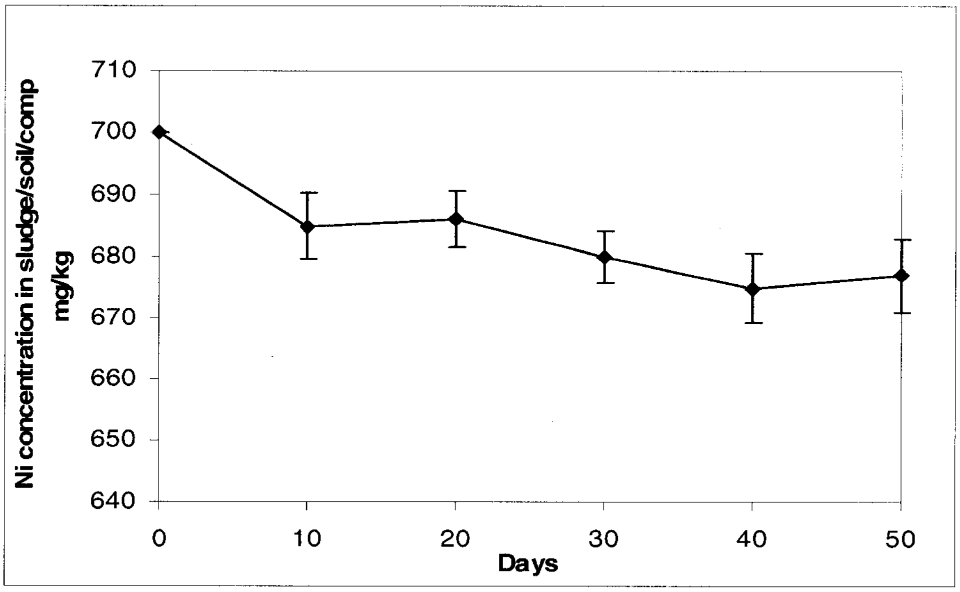


Figure 24: Nickel removals from sludge/soil/compost system, case 2
(Sludge contains nickel, cadmium, and vanadium)

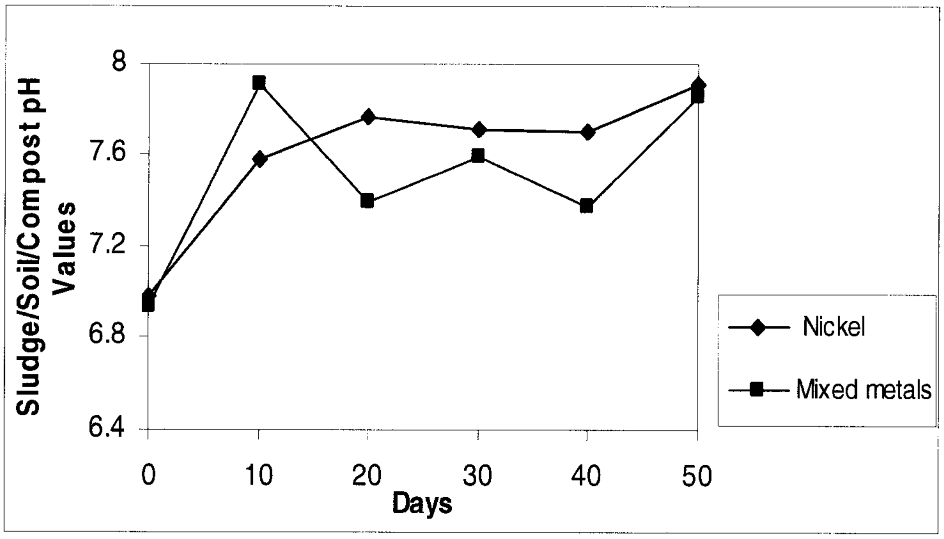


Figure 25: Sludge/Soil/Compost pH variation, in two different contamination scenarios

Figure 26 demonstrates accumulation of nickel in Geraniums planted in a sludge/soil/compost system. The first series, with nickel alone in the sludge, shows large accumulation of nickel, especially in the roots of the Geraniums. The plant was able to accumulate a total of almost 1000 mg/kg-plant's dry weight. Pictures from the greenhouse (Figure 35) illustrate how this accumulation affected the plant later in the experiment. The compost addition did not only increase the uptake of nickel, but it also enhanced the internal translocation of nickel into the shoots of the geraniums. On the other hand, the second diagram in (Figure 26) shows that there was no remarkable changes in the accumulation of nickel, when mixed metals were added to the sludge/soil/compost system. In this case the total accumulation didn't exceed 680 mg/kg-plant's dry weight. The presence of other metals, namely cadmium and vanadium, could affect the mobility of nickel into the roots and consequently affect its bioavailability for plant's uptake.

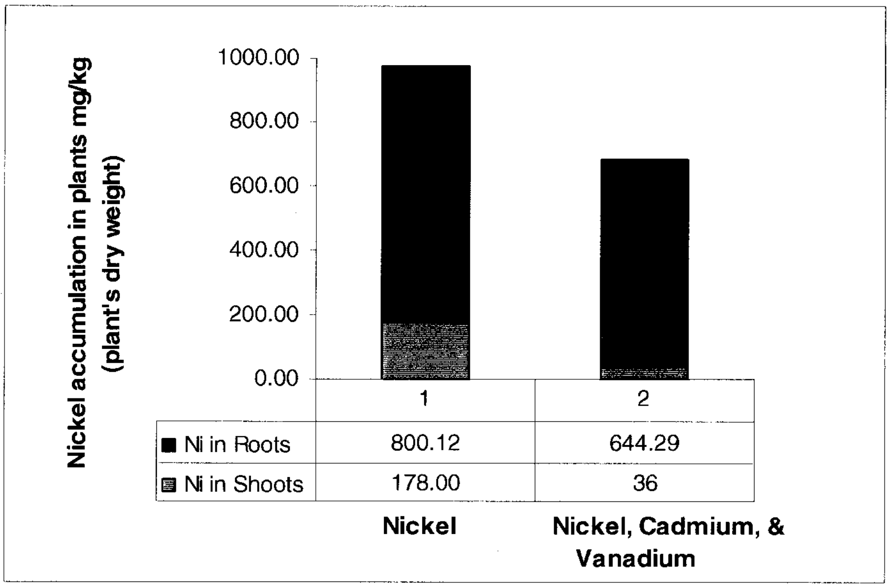


Figure 26: Nickel accumulation in Geraniums, system 2
(1) Nickel is present only, and (2) a mix of Cd, Ni, and V are in sludge

5.2.2 Results for Cadmium Removal

Similar to the previous case of nickel, we could see from Figure 27, the early drop in cadmium level in the sludge-soil-compost system, where this drop reached 100 mg/kg in 10 days period, followed by a gradual decrease in concentration in the following 40 days, where the final concentration of cadmium in the system was close to 560 mg/kg on day 50 of the study. In the case of mixed metals contaminated sludge, Figure 28, the final concentration of cadmium in the system was around 620 mg/kg, and concentration behavior was characterized by a gradual decrease for most of the study period. However, this decrease was relatively smaller compared to the previous one. The later could indicate that; with the presence of high amounts of organic matters, cadmium was less available for uptake when other metals were present, than it is usually when it is present as a sole contaminant.

The diagrams of pH values (Figure 29) related to the cadmium enriched sludge/soil/compost systems, showed fluctuation from one sample to the other in each 10 days sampling set. In spite the fact that both set of samples taken from each case (cadmium alone, and mixed metals) had almost same pH initial values, these values varied largely during the experiment. Yet both systems ended with a higher pH values.

The overall behavior indicates a general increase in the pH value, which may suggest a decrease in the bioavailability of cadmium for uptake with time, especially in the mixed metal case, where the final pH value was around 7.9.

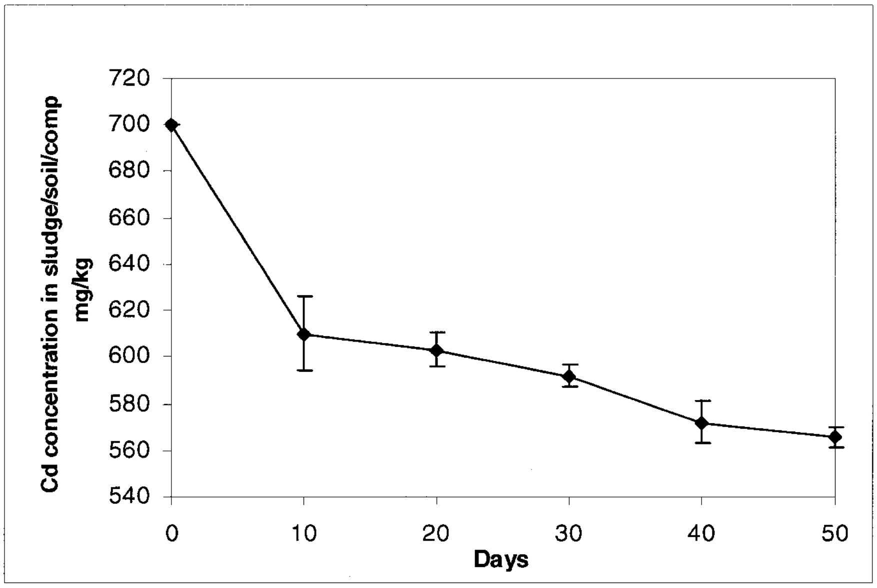


Figure 27: Cadmium removal from sludge/soil/compost system, case1 (Sludge contains cadmium only)

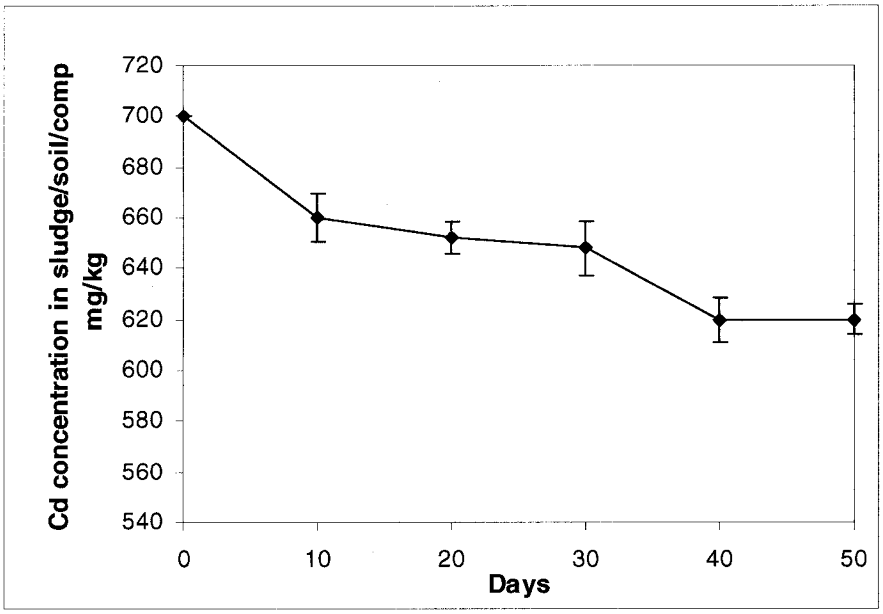


Figure 28: Cadmium removal from sludge/soil/compost system, case 2 (Sludge contains nickel, cadmium, and vanadium)

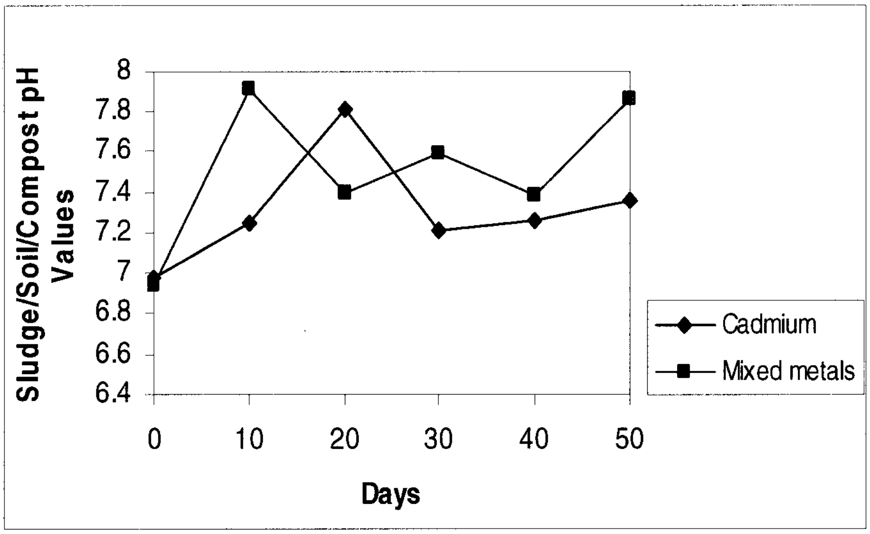


Figure 29: Sludge/Soil/Compost pH variation, in two different contamination scenarios

Scented Geraniums demonstrated a very good capability in removing cadmium from the sludge/soil/compost system. The species that were planted in the cadmium enriched sludge were able to accumulate up to 1600 mg/kg-plants dry weight of cadmium. This uptake compared to other metal accumulation is considered to be the highest that point out the ability of these plants to uptake high amounts of cadmium in short period of time. Figures 27 and 28 show a big drop in the cadmium concentration in the system, which justify the higher accumulation of cadmium in the plant where cadmium was the only metal present in the original sludge.

The accumulation of around 185 mg/kg-plants dry weight of cadmium in the shoots of the Geraniums was observed. However, this accumulation was associated with a clear toxicity effect on the plant that resulted in a general weakness in the plant (Figure 36). It was observed that the plants were in a very poor condition shortly after the planting process.

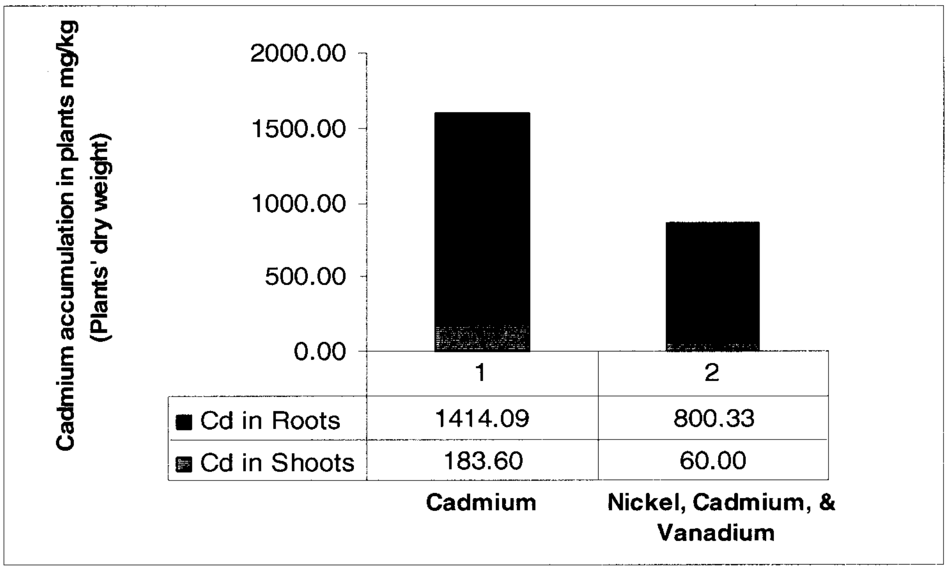


Figure 30: Cadmium accumulation in Geraniums, system 2
(1) Cadmium is present only, and (2) a mix of Cd, Ni, and V are in the sludge

5.2.3 Results for Vanadium Removal

The reduction of vanadium concentration was relatively big but yet gradual during the 50 days experiment (Figure 31). In the first 20 days of the planting period, the decrease in concentration was around 70 mg/kg (from 700 mg/kg to 630 mg/kg). However, in the case of mixed metals, there was much lower decrease in vanadium concentration in the 50 days period (Figure 32). This indicates a relatively slower uptake of vanadium by the geraniums while other metals are available. However, and in contrast to cadmium and nickel cases; plants managed to maintain good living conditions throughout all stages of the study.

Figure 33, shows that by adding compost, the system resulted in lower initial pH values, and as the experiment proceeded, pH values started to increase again. In both cases (vanadium alone, and mixed metals), the general behavior of the pH curve was similar to a certain extent throughout the experiment, and it featured a variable results from one set of samples to another.

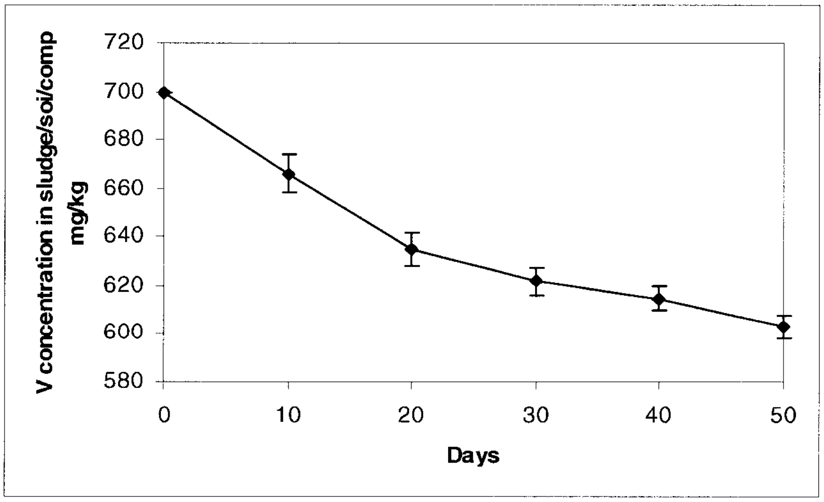


Figure 31: Vanadium removal from sludge/soil/compost system, case 1 (Sludge contains vanadium only)

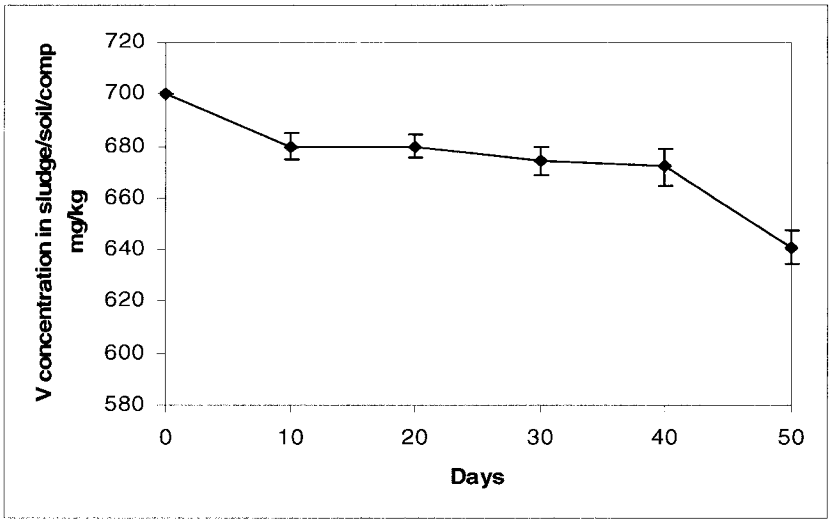


Figure 32: Vanadium removal from sludge/soil/compost system, case 2 (Sludge contains nickel, cadmium, and vanadium)

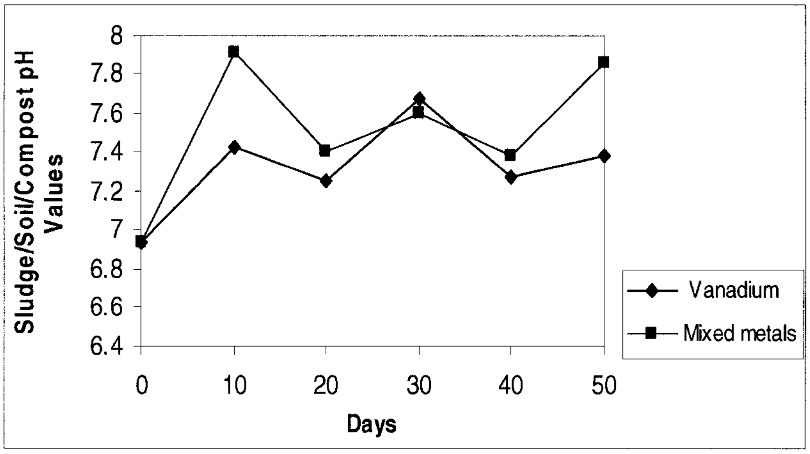
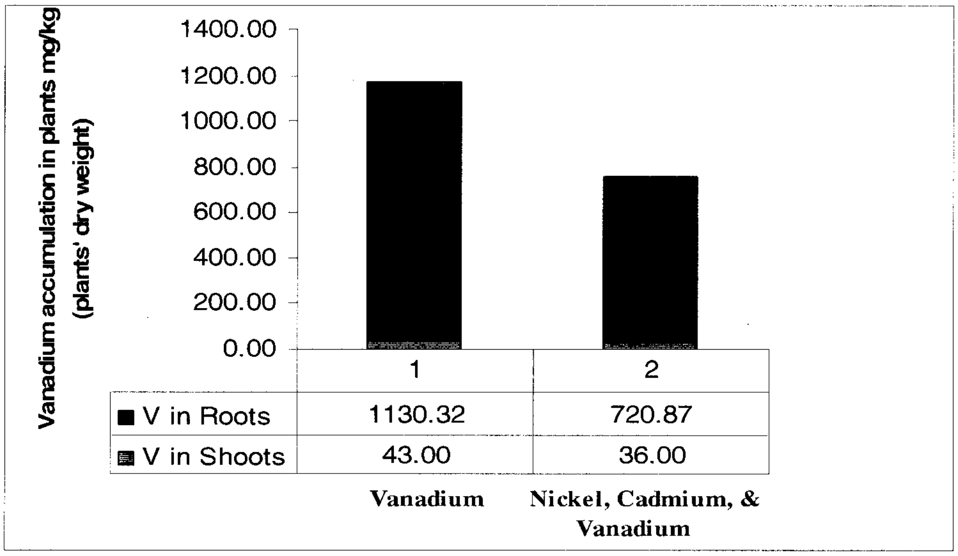


Figure 33: Sludge-Soil-Compost pH variation in two different contamination scenarios

Again, the addition of compost to the sludge/soil system proved to be useful in increasing heavy metal uptake by plants. In the case of vanadium, Geraniums accumulated up to 1200 mg of vanadium/kg-plants dry weight in no more than 50 days. In comparison to the poor conditions of Geraniums in cases of cadmium and nickel contaminations, plants in this system maintained good conditions throughout the whole experiment (Figure 37).

One possible justification for the less toxicity effect on the Geraniums is that unlike cadmium and nickel, the translocation of vanadium into the shoots was much lower, and didn't exceed 43 mg/kg-plants dry weight.



	1	2
■ V in Roots	1130.32	720.87
▨ V in Shoots	43.00	36.00

Figure 34: Vanadium accumulation in Geraniums; system 2
(1) Vanadium is present only, and (2) a mix of Cd, Ni, and V are in the sludge

5.3 Comparison of Metal Uptake from Sludge/Soil system and Sludge/Soil/Compost System

Lemon Scented Geraniums demonstrated more ability to survive heavy metals contaminated oily sludge conditions in the pots that did not contain any compost (the first system). Nevertheless, adding compost resulted in a higher metal uptake in a relatively short period of time. The presence of humic acids in compost helped to increase the translocation of metals into the shoots, especially in the case of cadmium. The following compare both systems for each metal.

5.3.1 Case of Nickel

5.3.1.1 Nickel is the Only Metal Present in the Sludge

Comparing the two systems (sludge/soil, and sludge/soil/compost) where nickel was the only metal added to the original sludge, it is clear in the presence of compost (Figure 26), Geraniums were able to accumulate a total of 1000 mg nickel/kg-plants dry weight (DW), while in the case of sludge/soil system (Figure 14), plants accumulated a total of 700 mg/kg. However, in the system where Geraniums accumulated 1000 mg/kg-DW, major toxicity symptoms started to appear on the plants (Figure 35). The plant accumulated around 180 mg nickel/kg-shoots dry weight, which is seven times more than its accumulation in the sludge/soil system (33 mg/kg). One possible explanation for the higher accumulation of nickel in plants was the addition of compost. The effective phytoremediation of soils contaminated by heavy metals depends on these metals' availability for plant. It seems that metal availability increased with the addition of compost. This increase could be resulted from the following two processes: (a) humic substances could form metal-humic complexes with the metals, which could insure a temporary bioavailability of metals, and prevent their rapid transformation into insoluble species; and (b) addition of organic matter to the soil could reduce vertical mobility of metal species in soil, which makes it available for roots uptake (Halim *et al.* 2003).

The development of the Geraniums in the greenhouse in the 50 days span is shown in Figure 35. Major toxicity effects were observed on day 30 of the experiment within the system of sludge/soil/compost, where big loss of leaves was noticed, in addition to a general reduction in the plants total biomass.

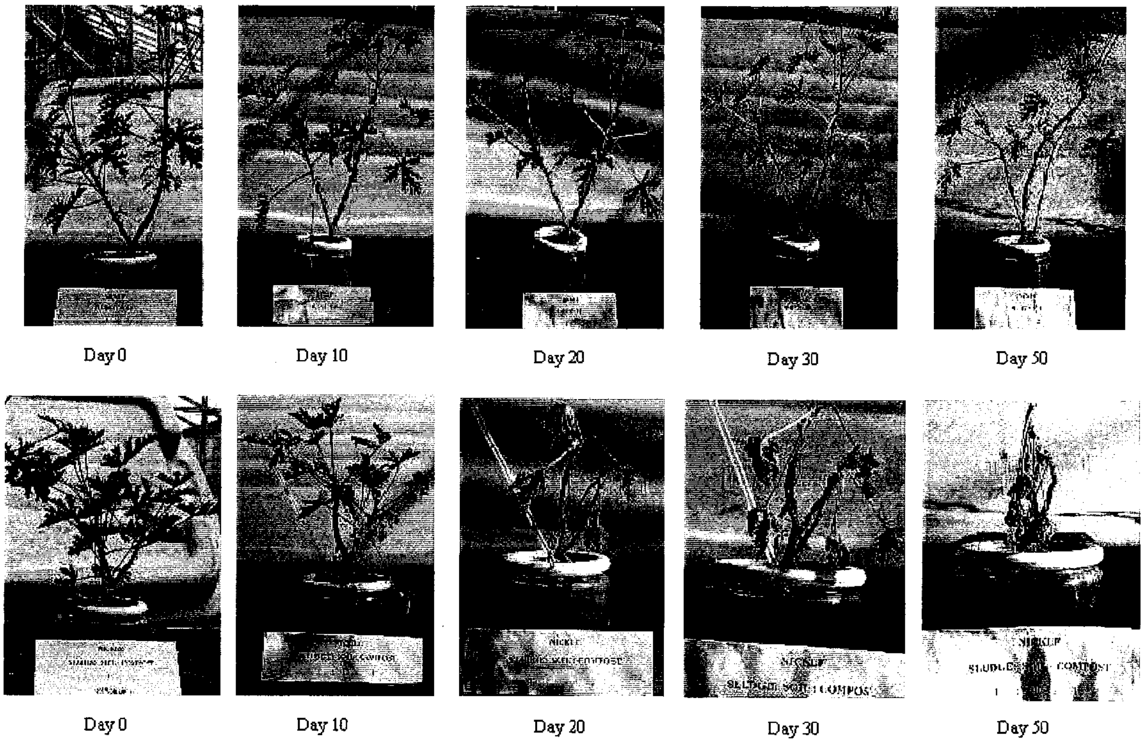


Figure 35: Geraniums development in the greenhouse for the two systems (nickel)
a) nickel enriched sludge/soil system, and b) nickel enriched sludge/soil/compost system
This Figure demonstrates the toxicity effects that appeared in the sludge/soil/compost system

5.3.1.2 Case of Mixed Metals Presence in Sludge

In the case were mixed metals were added to the original oily sludge, nickel accumulation in plants did not vary much in two systems. Contrary to the case where nickel was the only metal added, Geraniums accumulated relatively low amounts of nickel when compost was added. This situation might be explained by a formation of favorable metal-humic complexes with other metals, namely cadmium, and vanadium, which subsequently decreased the availability of nickel for uptake.

5.3.2 Case of Cadmium

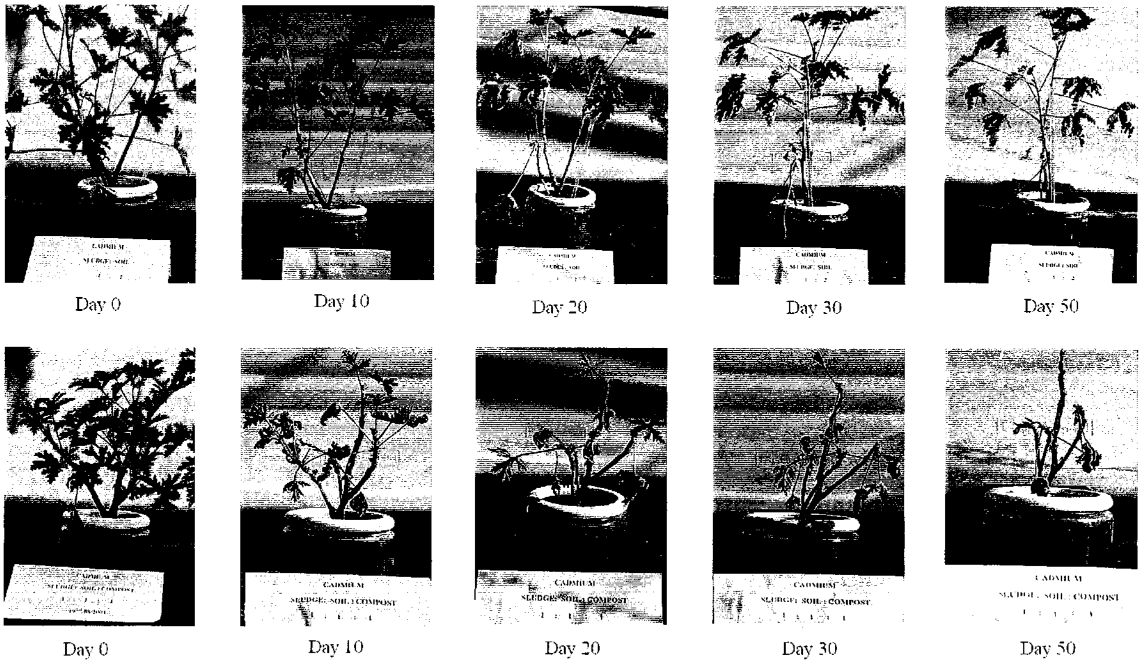
5.3.2.1 Cadmium is the Only Metal Present in the Sludge

Geraniums applied to the sludge/soil/compost system were able to uptake large amounts of cadmium that reached in total around 1600 mg/kg-per plants dry weight (Figure 30). This value is almost double the accumulation that occurred in the sludge/soil system, where the total accumulation reached 880 mg cadmium/kg-plants dry weight (Figure 18).

Figure 36 illustrates the plant development in the two systems. It is clear that the relatively big uptake of cadmium negatively affected the plant. The toxicity symptoms were obvious in the early stages of the experiment. Similar to the case of nickel, the compost addition could insure a temporal bioavailability of cadmium for uptake, and prevent its rapid transformation into insoluble species. In addition, compost results in decreasing the initial pH of the system, and increasing the Cd bioavailability, as it was also confirmed by Salisbury and Ross (1992), a decrease of soil pH will usually increase plant uptake of Cd because at lower pH values, exchange and bioavailability might be influenced. But as the experiment continued, it was noticed that the uptake decreased after 10 days, which could be related to the fact that cadmium with time binds to organic matter with high affinity, which could actually decrease Cd bioavailability. This theory was also introduced by Street *et al.* (1977) in their research about solubility and uptake of cadmium in soils amended with cadmium and sewage sludge.

5.3.2.2 Case of Mixed Metals Presence in Sludge

In the case where mixed metals were added to the original sludge, there was no big difference in cadmium uptake in both sludge/soil and sludge/soil/compost systems. The total accumulation for both cases was around 870 mg/kg-plant dry weight, this result could be associated with the presence of the other two metals in the mix, which would create competition for adsorption.



Day 0 Day 10 Day 20 Day 30 Day 50

Day 0 Day 10 Day 20 Day 30 Day 50

Figure 36: Geraniums development in the greenhouse for the two systems (cadmium) a) cadmium enriched sludge/soil system; and b) cadmium enriched sludge/ soil/compost system. This Figure demonstrates the toxicity effects that appeared in the sludge/soil/compost system

5.3.3 Case of Vanadium

5.3.3.1 Vanadium is the Only Metal Present in the Sludge

Similar to cases of nickel and cadmium, the accumulation of vanadium was higher in Geraniums planted in a sludge/soil/compost system. Total accumulation was close to 1200 mg/kg-plants dry weight (Figure 34), compared to around 860 mg/kg-plant dry weight in the sludge/soil system (Figure 22). Justifications of the latest results could be related again to the same speculations introduced earlier. However, Figure 37 shows that despite the high accumulation of vanadium in the plants, especially in the case where compost was added, relatively minor toxicity effects were observed on the plants. This indicates the particular ability of Geraniums to hyperaccumulate excessive amounts of vanadium.

5.3.3.2 Case of Mixed Metals Presence in Sludge

The case where mixed metals were introduced to the original sludge, the compost addition resulted in a higher accumulation of vanadium in the plant, and the total accumulation increased by around 200 mg/kg-plants dry weight. This outcome is different than the ones in case of nickel and cadmium, where the concentration did not vary much between the mixed metal in sludge/soil/compost and mixed metals in sludge/soil systems. The higher bioavailability of vanadium in the presence of the cadmium and nickel in the soil mixture seems to indicate that vanadium successfully compete for adsorption place with cadmium and nickel.

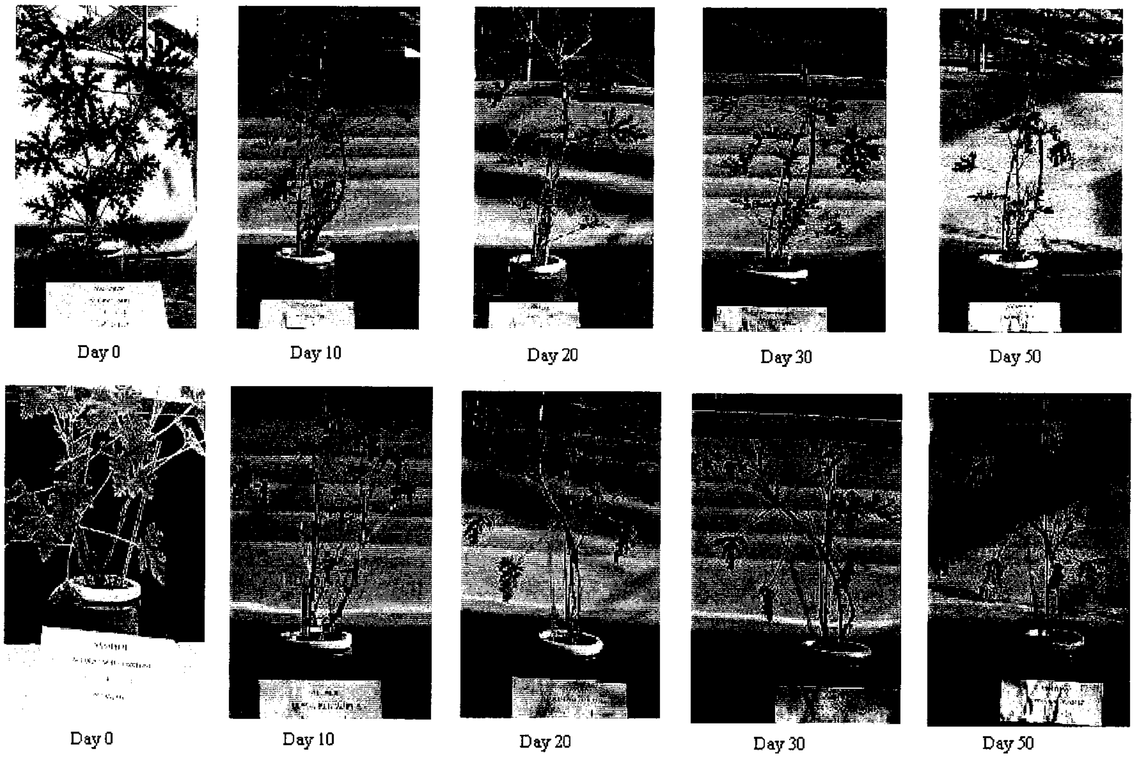
CHAPTER SIX

CONCLUSION AND RECOMMENDATIONS

The present study developed a successful method that could be used for petroleum oily sludge treatment. For the fist time, phytoremediation technology applied to oily sludge as a major treatment method proved to be efficient.

Lemon Scented Geraniums were able to survive in metal contaminated sludge systems. In the first system, which included sludge and soil mixed together in a 1:2 ratio respectively, Geraniums were able to accumulate up to 1000mg/kg of vanadium, per plants dry weight. In the case of cadmium and nickel, the accumulation was around 900 mg/kg, and 750 mg/kg of the plants dry weight respectively. Over 95% of the accumulation of the three metals was in the roots, which indicated the low mobility of Ni, Cd, and V in the plant it self. This low ability of translocation of the metals within the plant could be one of the reasons behind the Geraniums survival in the sludge/soil system.

Aadding compost to the system increased the bioavailability of the metals. This increase resulted in a higher accumulation of the metals in the plants roots and shoots. For example, Geraniums were able to accumulate up to 1600 mg/kg of Cd per dry weight of the plant. However, especially in the case of cadmium where the accumulation was the highest, some toxicity effects appeared on the plants by day 20 of the experiment. This



Day 0 Day 10 Day 20 Day 30 Day 50

Day 0 Day 10 Day 20 Day 30 Day 50

Figure 37: Geraniums development in the greenhouse for the two systems (vanadium)
a) vanadium enriched sludge/soil system, and b) vanadium enriched sludge/soil/compost system
This Figure demonstrates the toxicity effects that appeared in the sludge/soil/compost system

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Compost also resulted in decreasing the initial pH of the system; then, decrease of soil pH usually increases the uptake of metals, because at lower pH values, metals exchange and bioavailability might be enhanced. However, as the experiment progressed, it was noticed that pH values increased again, which could be related to metal binding to organic matter with a high affinity.

The synergetic effect of Ni, Cd, and V was obvious in this study. However, this effect was different from system to system. In the sludge/soil system, adding the three metals together resulted in a higher uptake of metals, which means that the presence of other metals in the sludge enhanced the metal mobility. In the second system (sludge/soil/compost) the effect was the opposite, as the metals showed more availability when they were added alone to the sludge in the presence of compost.

Considering the fact that various Geranium plants can express genetic differences, the amounts of metals absorbed by the plants could slightly vary.

The result of this research reveals the possibility of applying phytoremediation technology in the field as a successful treatment or pretreatment method. This application could take several forms:

a. Lemon Scented Geraniums could be directly applied to a pond of sludge modified by soil and compost, which would result in the uptake of heavy metals of the sludge, and make it ready for other conventional treatment methods;

b. Phytoremediation through Geraniums could be applied on sludge after applying an effective pretreatment technology. For example, applying Electrokinetics as a pretreatment method would result in the separation of the oily sludge into solid and liquid phase (Habibi and Elektorowicz 2004), and since the oil could be reused, the Geraniums could applied on the solid parts that contains most of the metals;

c. This technology could be applied on landfarms for the purpose of remediation. Planting the geraniums directly on the site used for oily sludge disposal would result in the uptake of the metals minimizing the leaching process of these metals;

d. Technology can also be applied to the soil contaminated due to accidental spills of hydrocarbons.

Recent studies proved the possibility of re-extracting some of the metals from the plants bodies, which could be of great economical value. This could be applied on the Lemon Geraniums, especially when it is grown on sludge/soil/compost system, since the accumulation is much higher than the normal sludge/soil system. Since the accumulation of the metals was shown to be proportional to the toxicity effect, Geraniums must be harvested in less than a month, and new plantings should be added and so on, and because Geraniums accumulate the metals in the roots, the harvested flowers can be still used for other transformation, for example for the production of scented oils.

Overall the result of this research introduces a new technology that is effective, clean, and economically tolerable. The development of this innovative method may change the management of petroleum wastes. It can also solve waste disposal problems created by land disposal bans.

Recommendations

There is a need to optimize this method to maximize the cleanup potential of the remediative plant; this could be achieved by applying the following actions:

- To investigate the possibility of using chemical amendments to induce metal bioavailability in the system;
- More information is needed to optimize the time of harvest. Plants should be harvested when the rate of metal accumulation in plants start to decrease. This would allow more crops to be harvested in the growing season, which would result in higher metal accumulation;
- This research should be applied in the field rather than a greenhouse in order to get more practical results of the plants behavior;
- Concentrating on the new technology of extracting metals from the plants is of a great importance for economical and environmental values;

- Research is needed regarding soil parameters in the rizosphere to better understand the behavior of metals mobility in the soil;
- Due to restrictions of the use of the facilities, the test was performed for 50 days. However, it was observed that plants in some cases were still capable of uptaking metals for a longer period, which suggest extending the growing period.

CHAPTER SEVEN

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