Use of Surfactants to Remove Chromium (VI), Nickel (II) and Zinc (II) from a Sandy Soil

A Thesis in the Department

of

Building, Civil and Environmental Engineering

Submitted in Partial Fulfillment of the Requirements for the
Degree of Master of Applied Science (Civil Engineering) at

Concordia University, Montreal, Quebec, Canada

September, 2006

By

Mohammad Mehedi Hasan

Library and
Archives Canada

Published Heritage
Branch

395 Wellington Street
Ottawa ON K1A 0N4
Canada

Bibliothèque et
Archives Canada

Direction du
Patrimoine de l'édition

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence
ISBN: 978-0-494-28898-6
Our file Notre référence
ISBN: 978-0-494-28898-6

NOTICE:
The author has granted a non-exclusive license allowing Library and Archives Canada to reproduce, publish, archive, preserve, conserve, communicate to the public by telecommunication or on the Internet, loan, distribute and sell theses worldwide, for commercial or non-commercial purposes, in microform, paper, electronic and/or any other formats.

The author retains copyright ownership and moral rights in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission.

AVIS:
L'auteur a accordé une licence non exclusive permettant à la Bibliothèque et Archives Canada de reproduire, publier, archiver, sauvegarder, conserver, transmettre au public par télécommunication ou par l'Internet, prêter, distribuer et vendre des thèses partout dans le monde, à des fins commerciales ou autres, sur support microforme, papier, électronique et/ou autres formats.

L'auteur conserve la propriété du droit d'auteur et des droits moraux qui protège cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

In compliance with the Canadian Privacy Act some supporting forms may have been removed from this thesis.

While these forms may be included in the document page count, their removal does not represent any loss of content from the thesis.

Conformément à la loi canadienne sur la protection de la vie privée, quelques formulaires secondaires ont été enlevés de cette thèse.

Bien que ces formulaires aient inclus dans la pagination, il n'y aura aucun contenu manquant.

Canada

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

ABSTRACT

Use of Surfactants to Remove Chromium(VI), Nickel(II) and Zinc(II) from a Sandy Soil

Mohammad Mehedi Hasan

The present study focuses mainly on the efficiency of surfactants sodium dodecyl sulfate (SDS), sodium dioctyl sulfosuccinate (AOT) and Triton X-100 (Tx-100) for the extraction of heavy metals Cr (VI), Ni (II) and Zn (II) from an artificially contaminated sandy soil. In addition, it also discusses metal extraction by a complexing agent EDTA with or without the addition of surfactants. To investigate metal extraction efficiency, both batch and column studies were performed. In batch studies, all surfactants are found to be nearly 2 to 3 times more effective for Cr (VI) removal, 3.0 to 6.2 times more effective for Ni (II) removal and 1.75 to 2.88 times more effective for Zn (II) removal, compared to the metal extraction by distilled water alone. Compared to the metal extraction by distilled water alone, metal extraction by EDTA in combination with SDS was 11 times greater for Cr (VI) removal, 8.07 times greater for Ni (II) removal and 4.94 times greater for Zn (II) removal,

Column studies showed that 50 pore volumes of water alone can remove about 18 % of Cr (VI), 19 % of Ni (II) and 20 % of Zn (II). On the other hand, at 50 pore volumes, the amount of Cr (VI), Ni (II) and Zn (II) removal by SDS appears to be relatively high about 24 %, 27 % and 33 % respectively. However, injections of 50 pore volumes of SDS with EDTA were able to elute about 57 % of Cr (VI), 67 % of Ni (II) and 71 % of Zn (II). These results suggest that surfactants do improve the efficiency of soil washing by enhancing the extraction of heavy metals such as chromium, nickel and zinc.

Acknowledgements

I wish to express my appreciation to Dr. A. S. Ramamurthy for suggesting the research topic. Special thanks to Mr. H. Shalchian that provided useful suggestions during the completion of the project. The technical assistance of Mr. N. Lang Vo thankfully acknowledged.

Table of Contents

List of Figures

List of Tables

Nomenclature

AA	Atomic Adsorption Spectrophotometer
AOT	Aerosol-OT, Sodium Dioctyl Sulphosuccinate
CEC	Cation Exchange Capacity
CMC	Critical micelle Concentration
EDTA	Ethylenediaminetetraacetic Acid
EDTA salt	Disodium Ethylenediaminetetraacetate
HLB	Hydrophile-lipophile Balance
K	Hydraulic Conductivity
K_{ow}	Octanol-Water Partition Coefficient
MEUF	Micellar-Enhanced Ultrafiltration
NAPL	Non-Aqueous Phase Liquid
NPL	National Priority List
PAHs	Polynuclear Aromatic Hydrocarbon
PCBs	Polychlorinated Biphenyls
PV	Pore Volume
SDS	Sodium Dodecyl Sulphate
S/S	Solidification/Stabilization
Tx-100	Tritron X-100

Chapter 1

Introduction

1.1 Introduction

Contamination of soil environments due to widespread releases of heavy metals is a pervasive problem in industrialized areas, particularly those that have large electroplating industries. Chromium, copper, nickel and zinc are considered the EPA's list of priority toxic metals (Mulligan et al. 2001a). The U.S. EPA estimates that over 20 million cubic yards of soil at current national priority list (NPL) sites are contaminated with heavy metals (Griffiths, 1995). Uncontrolled releases of heavy metals are the growing concern of human life and environment because of their toxicity. At a low concentration they are essential for living beings. However, at elevated levels they are carcinogenic (Alloway, 1990).

Sources of heavy-metals in soils include discharges from electroplating plant, waste from mining industry, industrial bi-products, municipal solid wastes, sludge from wastewater treatment plant, and precipitation that captures heavy metals released from burning of coal, oil and incineration of municipal wastes and sewage sludge (Merian, 1991; Alloway, 1990). Leachate from landfill and runoff from heavy metal contaminated soil potentially degrade the ground water and surface water quality.

Heavy metals in the soil environment do not undergo decay with time but organic matter degrades with time following the process of biodegradation, chemical oxidation/reduction or incineration. Remediation of heavy metal contaminated soil is one of the formidable challenges at hazardous waste sites throughout the world. Several soil remediation technologies such as soil washing/flushing, solidification/stabilization, electrokinetics, phytoremediation, and bioremediation are currently using to remove metals from contaminated soil. Over the past few decades, surface-active agents (surfactants) are used as washing solvents for the remediation of organic and inorganic contaminants from soils. Surfactants reduce the surface tension to enhance the solubilization and mobilization of contaminants during the washing process, followed by desorption (Sabatini, 1995).

The present study attempts to evaluate the potential of surfactants to enhance the metal remediation from sandy soils contaminated by Cr (VI), Ni (II) and Zn (II). Both batch and column tests were conducted to observe the desorption and transport efficiency of surfactant. Two anionic surfactants sodium dodecyl sulfate (SDS) and sodium dioctyl sulfosuccinate also known as aerosol-OT (AOT), in addition to a nonionic surfactant Triton X-100 (Tx-100) and a complexing agent disodium ethylenediaminetetraacetate (EDTA salt) were used as extracting solvents in this study.

1.2 Research Objectives

The following objectives are considered in this study.

1. Determination of the efficiency of metal extraction (ratio of metal removal by surfactant to metal removal by water) from artificially contaminated sandy soil.
2. Investigation of the effects of interaction and competition among the metals [Cr (VI), Ni (II) and Zn (II).] during soil remediation.
3. Determination of the effects of aging of the contaminated soil on metal removal.
4. Study of the effects of flow rate on the desorption characteristics of the sandy soil containing a mixture of Cr (VI), Ni (II) and Zn (II).

Chapter 2

Literature Review

2.1 Soil Remediation Technologies

Organic, inorganic and radioactive contaminants of soil and ground water are the growing concern of environmental engineers. They are entering the environment directly as a result of accidents, spills during transportation, leakage from underground storage tanks or from industrials facilities. Soil washing, soil flushing, solidification/stabilization, electrokinetics, phytoremediation, bioremediation are the most common remediation methods of contaminated soils and sediments. Although many technologies are available, their selection depends on site characteristics, regulatory requirements, costs, and time constrains (Faisal et al. 2004).

2.1.1 Soil Washing

Soil washing is an ex-situ, relatively new, commercially proven water based method that relies on the traditional chemical and physical extraction and separation processes of excavated soils and dredged sediments that are contaminated with typical organic, inorganic, and radioactive hazardous materials (Anderson and Dee, 1993).

A good soil washing performance closely depends on the other parameters of the site including soil contamination level, particle size distribution, cation exchange capacity, and specific gravity (Anderson and Dee, 1993), and the soil washing process parameters include mode of extraction (example: batch or column), extractant type and concentration, pH, liquid-to-soil ration (L/S), and retention time (Lim et al.2004). The use of soil washing for the removal of toxic metals or radioactive wastes is more common than for the removal of organic materials (Roundhill, 2001).

Surface contaminant that is attached to soil through forces of adhesion and compaction is removed from the soil by abrasive scouring or scrubbing action. This soil washing action can be enhanced by introducing leaching agents, surfactants, pH adjusters, or chelating agents with the washwater (Anderson and Dee, 1993). Wastewater is to be treated to remove the contaminants prior to reuse. Figure 2.1 illustrates a continuous soil washing process.

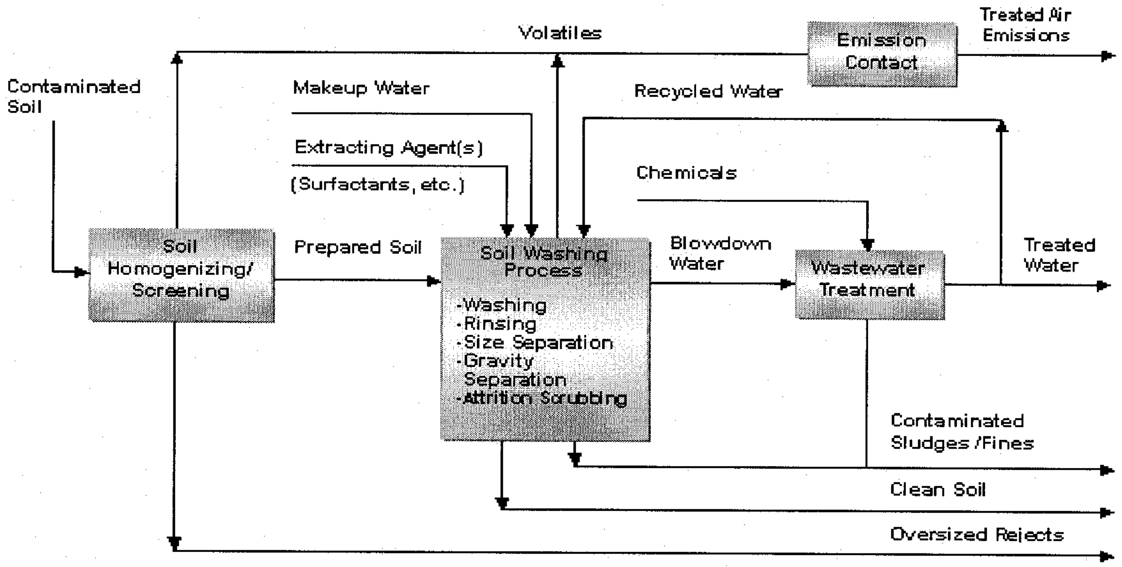

Figure 2-1. A typical soil washing diagram (Deuren et al. 2002).

2.1.2 Soil Flushing

Soil flushing is an in-situ innovative remediation technology that accelerates the transport of the contaminant. It is accomplished by injecting fluid through the in-place contaminated soils. Extracted fluids are captured and further treatment is required to meet the appropriate discharge standards. Depending on the soil matrix, organic, inorganic, and radioactive contaminants are amenable to soil flushing. The required fluids for flushing include water, surfactants, chelating agents or other solvents.

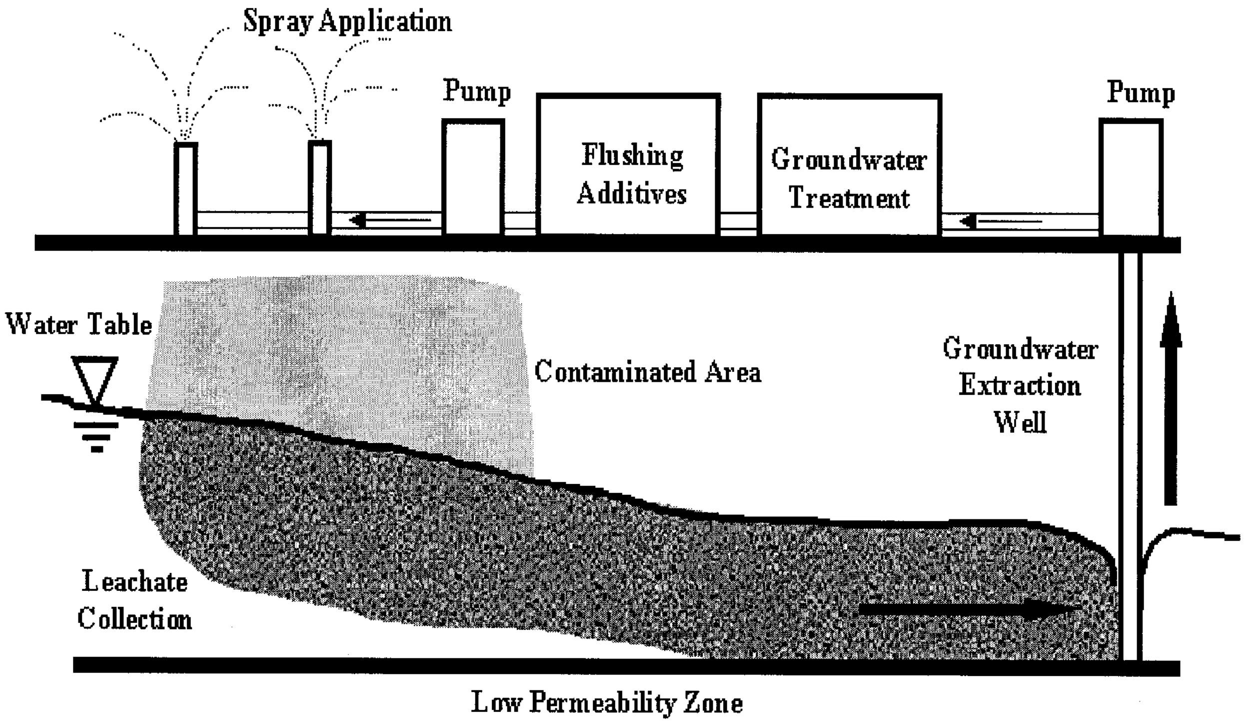

Figure 2-2. A typical soil flushing technology (Deuren et al. 2002).

Anderson and Dee (1993), have studied the transport of subsurface contaminant during the soil flashing. According to them, the following mechanisms are involved in this process.

i. Advection
ii. Dispersion
iii. Diffusion
iv. Mobilization and
v. Depletion through volatilization or solubilization

A diagram of an in-situ soil flushing process is shown in Figure 2.2. As the soil flushing is conducted in-situ, it reduces the need for excavation, handling or transportation of hazardous materials.

2.1.3 Solidification/Stabilization

Solidification/Stabilization (S/S) or fixation is an in-situ chemical transformation process, which involves conversion of metals to the original form of mineral that it was present. Another in-situ S/S method involves cementation that produces glass-like solid material by passing high level of heat to the contaminated soil. Product materials are very insoluble and immobile in water, and highly resistant to leaching (Roundhill, 2001). The S/S process can also be accomplished by treating the soil with inorganic binders such as cement, fly ash, or blast furnace slag or by organic binders such as bitumen (Smith et al. 1995).

2.1.4 Electrokinetics

Electrokinetics is an in-situ metal ion extracting process that is accomplished by passing an in-situ DC current through the soil matrix. The efficiency of the electrokinetic method depends on the electric potential and also the chemical and hydraulic gradients. Due to the electric potential, electrochemical reactions produce protons (H$^+$) and hydroxyl anions (OH$^-$) at the anode and cathode respectively. These migrate with metal ions (M$^+$) through the soil pores in the presence of water. Ionic diffusion and ionic migration are the two mechanisms involved in during the process (Roundhill, 2001).

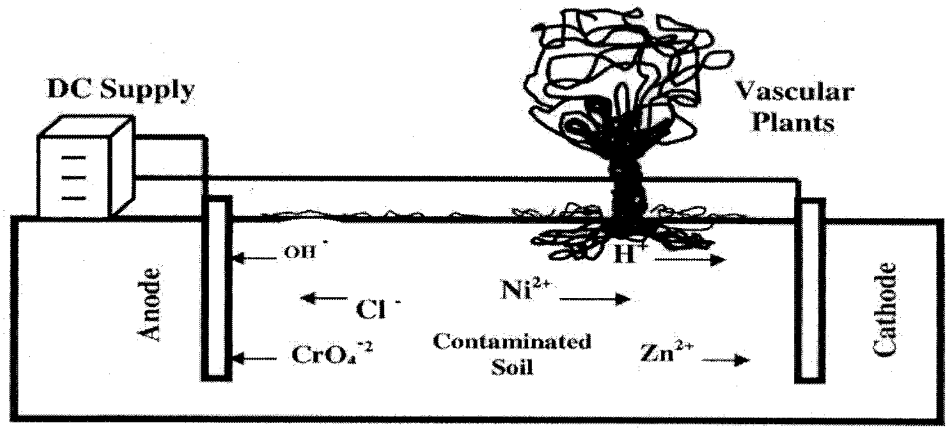

Figure 2-3. Combined uses of electrokinetic and phytoremediation technology.

2.1.5 Phytoremediation

Phytoremediation is the use of vascular plants to uptake or accumulate constituents that are present in the soil and water environment. All plants extract necessary compounds, including nutrients and heavy metals from the environments. Phytoextraction and rhizofiltration are the most common phytoremediation that are currently in use. Phytoextraction is the uptake of metals from the soil and accumulate them into the harvestable parts of plants rhizofiltration is the use of plant roots to absorb metals from the aqueous waste (Roundhill, 2001). Figure 2.3 represents combined action of electrokinetic and phytoremediation technology for metal remediation.

Alloway (1990), described that phytoremediation occur according to the following factors:

- Metal concentrations in the soil solution.
- Movement of metal from the bulk soil to the root surface of plant.
- Transport of metal from the root surface to the root.
- Its translocation from the root to the shoot.

Conner et al. (2003) states that the combination of the techniques of electrokinetic and phytoremediation represents a very promising approach to the remediation of metal contaminated soils that now requires the validation of field conditions.

2.1.6 Bioremediation

Bioremediation is the use of microorganisms to degrade contaminants. Although they are primarily used for organic contaminants, they are also focused on the remediation of heavy metals. Bioremediation falls into several categories. The two mechanisms such as bioleaching and bioextraction have gained attention. The bioleaching process involves *Thiobacillus ferrooxidans* bacteria, which oxidizes insoluble metal sulfide species into their water-soluble sulfates under aerobic and acidic conditions (pH 4) at temperatures between 15 and 55°C (Mulligan, 1998).

2.2 Uses of Chelating Agents in Remediation Technology

To enhance metal removal from the soil, chelating agents are added with the wash solution. The chelating agents react with metals and form water-soluble metal-chelate complexes (Smith et al. 1995), and they and their metal complexes have low adsorption capacity on soils (Lim et al. 2004). Ethylenediaminetetraacetic acid (EDTA), citric acid, and their salts are the chelating agents or complexing agents used to extract metals from soils. Davis et al. (1995), showed that an EDTA solution is more superior to distilled water or an anionic surfactant solution for extraction of metals from soil.

2.3 Fundamentals of Surfactants

Surface-active agents are generally called surfactants because they concentrate at interfacial regions of air-water, oil-water, and solid-liquid. They are organic chemicals and are used as wetting, cleaning and disinfecting agents (Myers, 2006).

In standard surfactant terminology, the ‘head’ refers to the solubilizing group – the lyophilic or hydrophilic group in aqueous systems and the ‘tail’ refers to the lyophobic or hydrophobic group in water (Myers, 2006).

Figure 2-4. Schematic of a surfactant (Myers, 2006).

The main desirable properties of universal surfactants include the ability to reduce surface tension, increase solubility, form critical micelle concentration, possess detergency power, wettability and foaming capacity. The properties and effectiveness of surfactants are determined by the balance between the lyophilic and lyophobic portions of the molecules (Myers, 2006). The classification of surfactants is based on the nature of the hydrophile, with the subgroup based on the nature of the hydrophobe. Myers (2006) has described the surfactants classification as follows:

1. Anionic: The hydrophile has a negatively charged group such as carboxyl ($RCOO^-M^+$), sulfonate ($RSO_3^-M^+$), sulfate ($ROSO_3^-M^+$) or phosphate ($ROPO_3^-M^+$).
2. Nonionic: The hydrophile has no charge, but derives its water solubility from highly polar groups such as polyoxyethylene (POE or R-OCH_2CHO-) or R- Polyol groups including sugars.
3. Cationic: The hydrophile bears a positive charge, as in the quaternary ammonium halides ($R_4N^+X^-$).
4. Amphoteric (Zwitterionic): The hydrophile potentially contains, both negative and positive charges, such as sulfobetaines $RN^+(CH_2)CH_2CH_2SO_3^-$.

Surfactants are also characterized by their hydrophile-lipophile balance (HLB). HLB is an experical expression for estimating the potential surface activity of a surfactant, and used primarily in emulsion technology. Surfactants with high HLB values are more water soluble, whereas surfactants with low values are more oil soluble (Sabatini, et al. 1995).

When a surfactant is added to a liquid, the surface tension or interfacial tension is reduced. For example, a good surfactant can reduce the surface tension of water from 72 to 35 mN/m and the interfacial tension (tension between polar and non-polar liquids) for water against n-hexadecane from 40 to 1 mN/m (Mulligan, 1998). The physical properties of aqueous systems include surface tension, interfacial tension, electric conductivity, or turbidity. These are functions of surfactant concentration. The surface tension and interfacial tension decreases with the surfactant concentration until the critical micelle concentration (CMC) is reached, and remains constant with the increases of surfactant concentration. Figure 2.5 shows that, above CMC, surfactant activity is constant for both types of tension (Myers, 2006).

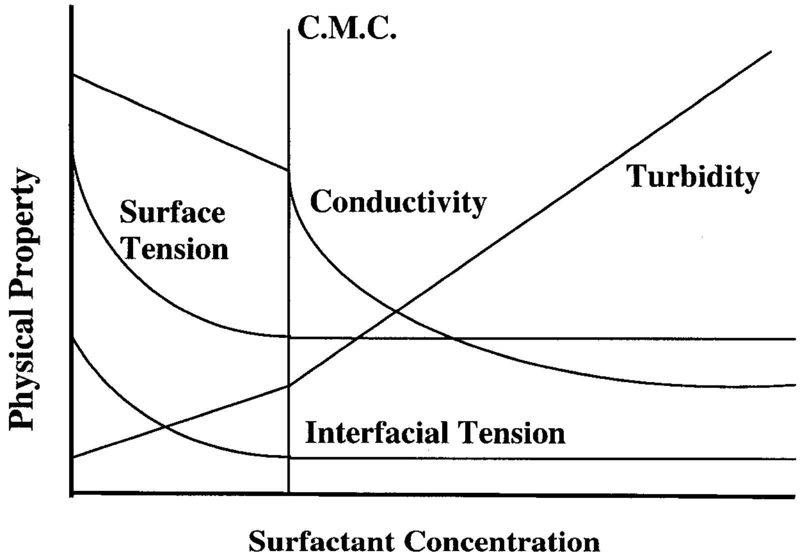

Figure 2-5. Effect of surfactant concentration on the physical properties of liquids (adapted from Myers, 2006).

The concentration of surfactant that is required inorder to form micelle, or small globule-like units that solubilize and desorb contaminants is called critical micelle concentration (CMC) (Watts, 1997). The CMC of a surfactant is influenced by the hydrocarbon chain length, pH, temperature, ionic strength and the presence of nonelectrolytes (Chu, 2003).

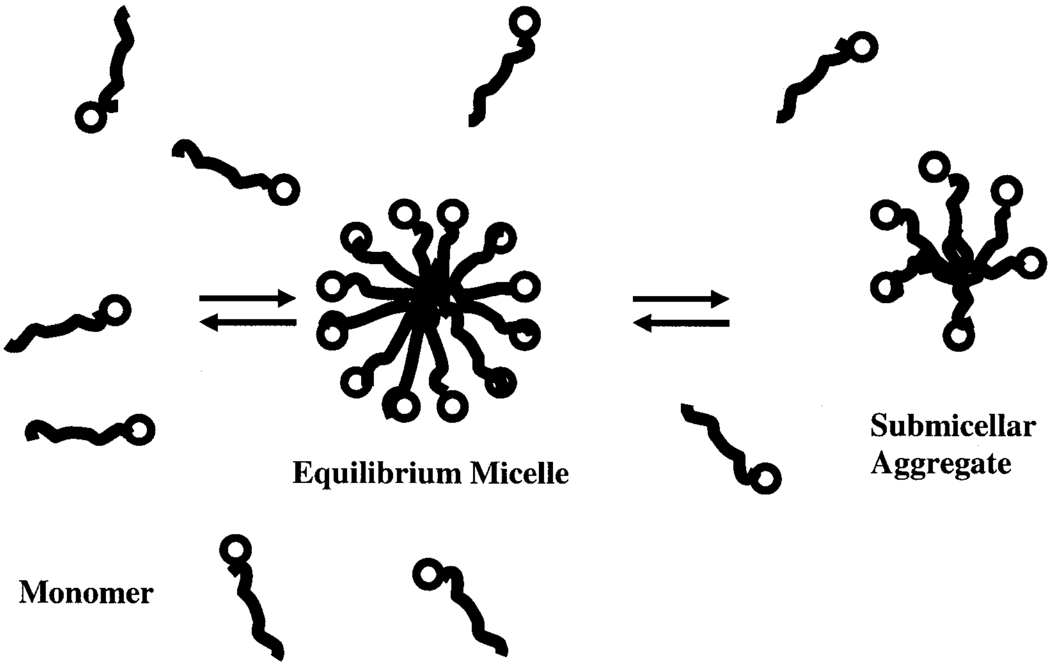

Figure 2-6. Role of surfactant micellization (Myers, 2006).

Micellar aggregates (Fig. 2-6) typically consist of 20-100 monomers and the lifetime of a single surfactant molecule within a micelle at room temperature is estimated to be in the range of 1-100 μsec (Chu, 2003).

2.4 Uses of Surfactants to Enhance Soil Remediation

Over the past few decades, surfactants have been shown to have significant potential for enhancing the remediation of soil and sediment contaminants. Because of the limitations (e.g., mass transfer, and time) of pump-and-treat technology, attention is recently focused on the use of surfactants to enhance pump-and-treat remediation of subsurface contaminations (West and Harwell, 1992; Chu, 2003).

2.4.1 Remediation of Organic Contaminants

Remediation of organic contaminants from soil and sediments is becoming a major concern and may retain these components as solid phase in the soil because of their water insoluble characteristics, and eventually impair human health through bioaccumulation, bioconcentration and food-chain system (Chu, 2003). A surfactant is often used with a co-solvent to enhance recovery of residual saturation or nonaqueous phase liquid (NAPL). Surfactants especially anionic and nonionic surfactants strongly enhance the solubility of organic compounds and assist in the remediation of contaminated soil and sediment, (Chu, 2003).

Surfactant washing and flushing technology have been successfully employed to remove sorbed heavy hydrocarbons from soils and sediments. Surfactant-modified zeolites have the potential efficiency to sorb organic materials from aqueous systems. Duffield et al. (2003), states that surfactant can promote the removal of NAPL through mobilization. As stated earlier, two mechanisms are highlighted during the soil washing and flushing processes with surfactant for the removal of organic materials, and they are solubilization and mobilization (Cheau et al, 1998).

Solubilization: Surfactants can solubilize organic contaminants by incorporating them into the interior of the hydrophobic portion of micelle [Figure 2.6]. The rate of solubilization depends on the octanol-water partition coefficient (K_{OW}). When K_{OW} is higher, the rate of solubilization is higher into the micelle (West and Harwell, 1992).

Mobilization: Mobilization is a mechanism that relies on the reduction of oil-water interfacial tension and the capillary forces that trap the residual organics. Consequently, the residual oil saturation in the presence of surfactant is appreciably lower, and more oil is mobilized that with simple water floods alone (Cheau et al, 1998). Mobilization is an efficient process for the recovery of residual saturation or NAPL.West and Harwell (1992) and Cheah et al. (1998), have found that mobilization has greater potential than solubilization to increase the rate of remediation of organic contaminants.

2.4.2 Remediation of Heavy Metal Contaminants

Surfactants are used to enhance the remediation of organic contaminants that is clearly well understood, but the role of surfactants in remediation of subsurface heavy metal contamination is less well understood. During the last decade few researchers have shown some increasing level of interest and research efforts in order to improve the performance of surfactant-based metal separation process.

Nivas et al. (1996) hypothesized that anionic and nonionic surfactants can enhance the extraction of chromate (CrO_4^{2-}) through the ion exchange and/or the precipitation-dissolution mechanisms. Further they state that extraction is further enhanced when chelating agents are used with the surfactants, however the economics of surfactant enhanced remediation is affected by surfactant losses due to the precipitation and sorption phenomena. Another treatment method for chromium-contaminated soil is immobilization. This involves the reduction of the more toxic Cr (VI) to the less toxic Cr (III) form by reducing agents such as animal manure, Fe (III)/Fe (II) salts, or organic acids, followed by precipitation of Cr (III) by NaOH (James, 1996). The studies of Puls et al. (1994) indicate that the anionic surfactant, sodium dodecyl sulfate (SDS), significantly enhances the elution of chromate (CrO_4^{2-}) in column studies.

Espositto et al. (1989) evaluated the efficiency of a surfactant, or a chelating agent for removing heavy metals (Cd, Cr, Cu, Pb, Ni, Zn) from a soil that was contaminated with various metal salts and organic pollutants.

The investigatuion of Gzara and Dhahbi (2001) show that the cationic surfactant successfully enhances the removal of chromate anions from aqueous solutions by micellar-enhanced ultrafiltration (MEUF). Ahmadi et al. (1995) successfully applied anionic surfactant in MEUF for the removal of heavy metals from wastewater. Lin and Juang (2002) showed that surfactant-modified montmorillonites have high heavy metal (Cu^{2+} and Zn^{2+}) sorption capacity from aqueous solutions. Yurlova et al. (2002) also noted that anionic and nonionic surfactants could remove Ni (II) from wastewater by MEUF.

Khodadoust et al. (2005 and 2004) investigated that nonionic surfactants are ineffective in removing Ni, Zn and Pb, and that they are effective in removing organic contaminants (PAHs). However, the combined use of nonionic surfactants and chelating agents are effective for the removal of both metals and PAHs from field contaminated silty and sandy soils. Shin and Barrington (2005) noted that surfactant (anionic or nonionic) with a ligand (NaI) can extract heavy metals from soils.

Doong et al. (1998) studied anionic and nonionic surfactants and indicated that these can enhance the desorption efficiency of Cd^{2+}, Pb^{2+} and Zn^{2+}. Addition of cationic surfactant was seen to decrease the desorption rates of heavy metals. They found that desorption efficiency increased linearly with the surfactant concentration below the critical micelle concentration (CMC) and remained constant above CMC. They also observed that desorption efficiency of heavy metals by the surfactant/EDTA mixture was of the following order: Cd^{2+}> Pb^{2+} > Zn^{2+}.

Biological surfactant or biosurfactants are surface-active agents produced by bacteria or yeast, which are potentially useful to enhance the heavy metal remediation from soils or sediments, particularly due to their attractive characteristics such as anionic nature, low toxicity, biodegradability and excellent surface active properties than synthetic ones (Mulligan et al. 2001a).

Mulligan et al. (2001b) used biosurfactants for the removal of Cu^{2+}, Cd^{2+} and Zn^{2+} from contaminated soils and sediments. They included lipopeptide called surfactin from *Bacillus subtilis*, rhamnolipid from *Pseudomonas aeruginosa* and sophorolipid from *Torulopsis bombicola*. Their study postulated that biosurfactants enhance metal removal through sorption of the surface on to the soil surface and complexation with the metal, detachment of the metal from the soil into the soil solution and hence association with surfactant micelles.

Chapter 3

Behavior and Transport of Heavy Metal in Soil

3.1 Behavior of Heavy Metals in the Soil

Soil is a complex heterogeneous medium and the key component of terrestrial ecosystems. Moisture status, pH, redox condition, organic matter, and clay mineral are the soil dynamic factors. The changes of these factors could affect the form and bioavailability of heavy metals, and are to be considered in decisions on the management of contaminated soils (Alloway, 1990).

The organic matter comprises living organisms, dead plant material and colloidal humus formed by the action of microorganisms on plant litter. These solid components have the ability to adsorb metal ions, but this differs between materials and is strongly influenced by the prevailing pH and redox conditions and the relative concentrations of the ions present in the aqueous soil solution. Plant roots modify the chemical and physical properties of the soil around them and thus influence the bioavailability of soil elements.

3.1.1 Chromium

Chromium is a d-block transition metal of group VIB of the periodic Table and has an atomic number of 24, a molar mass 51.996 and a density of 7.14 g/cm^3. It has five known radioactive isotopes. ^{51}Cr (half life 27.8 days) is the common radioisotopes mainly used in experimental work (Alloway, 1990). Presently chromium concentration in soils ranges, in general, between 5 and 1000 ppm. However sandy soils are characterized by a lower concentration (Yaron, 1996). In the soil, chromium exists either as the species of trivalent chromium [Cr (III)] or as hexavalent chromium [Cr (VI)]. Cr (III) is the more stable cationic form and exists largely in the soil by adsorption forming complexes with negatively charged inorganic or organic particles in soils. Cr (VI) is of greater concern due to its strong toxic effects on biota, and potential for ground-water contamination because of its higher mobility in the aquatic environment (Krishna. et al. 1997).

Anionic chromium [Cr (VI)] exists as chromate (CrO_4^{2-}), bichromate ($HCrO_4^-$) or dichromate ($Cr_2O_7^{2-}$). Both Cr (III) and Cr (VI) are redox and pH sensitive, with redox reactions converting them from one state to another under oxic environment (Ahmed, 2005). According to Yaron (1996), the fate of chromium in the environment is affecting by the following factors:

1. pH – increases its solubility in the aqueous phase and affecting its reduction rate;
2. Oxidation state – increases the toxicity of the compound in the hexavalent from and its mobility, due to the anionic nature of the species;
3. Electron donors or acceptors – affects the reduction process in the case of electron donors [example: soil organic matter, Fe (II)] or enhances oxidation in the case of electron acceptor [example: Mn]

Among these factors, prevailing soil pH seems to be the most important factor affecting chromium bioavailability. Thus, the adsorption of the toxic Cr (VI) in soils decreases with increasing pH, making it highly mobile above pH 8.5, whereas adsorption of Cr (III) increases under alkaline conditions (Ahmad, 2005). Again, in an anaerobic environment with a low redox potential and pH, chromium would exist only in the Cr (III) state (Yaron, 1996).

3.1.2 Nickel

Nickel is a transition metal of Group VIII of the periodic Table. Its atomic number is 28, atomic weight is 58.71, and has a density of 8.908 g/cm^3. Among the seven known radioisotopes, ^{63}Ni (half- life 92 years) is the most useful in soil-plant relations. Generally in soil environments only Ni (II) state is stable over the wide range of pH and redox conditions. Ni (II) has an ionic radius of 0.065 nm (Alloway, 1990). In literature, it is reported that 20-40 ppm is the content of Ni for normal soil, although considerable variations may occur due to anthropogenic sources (Yaron, 1996).

Soil chemistry of Ni is much simpler, because of its low oxidation states and is based on the divalent metal ion (Ni^{2+}). The solubility of Ni is inversely related to pH, and at lower pH, sulfides of Ni control the Ni concentration in soil solution, and at elevated level of pH the hydroxy-complex Ni $(OH)^+$ and Ni^{2+} ions are the most available forms in the soil environment The distribution of Ni between soil and soil solution depends on the three important factors; soil pH, clay content, and the amount of hydrous Fe and Mn (Alloway, 1990). The mobility of Ni increases in soils, if the pH of the soil solution and CEC of the soil decrease. However, Ni added to soils as a complex of EDTA results in a greater proportion of Ni in the soluble phases of the soil (Alloway, 1990).

3.1.3 Zinc

Zinc belongs to Group IIB, has an atomic number of 30, an atomic weight of 65.4, and has a density of 7.14 g/cm^3. The oxidative state of Zn is exclusively II. 10 – 300 ppm Zn contains in the normal soil (Yaron, 1996). Zinc acts as a catalytic component in the energy metabolism system for enzymes. Deficiency symptoms of zinc in humans and animals lead to poor appetite, severe growth depression, skin lesions and sexual immaturity (Alloway, 1990).

The total amount of Zn in soils is distributed over some more or less distinct fractions. Alloway (1990), distinguished the following five pools for Zn.

1. Water- soluble pool: the fraction present in the soil solution.
2. Exchangeable pool: ions bound to soil particles by electric charges.
3. Adsorbed, chelated or complexed pool: metals bound to organic ligands.
4. Pool of clayey secondary minerals and insoluble metallic oxides.
5. Pool of primary minerals.

Natural or synthetic chelating agents are important in defining Zn mobility in soil, due to the fact that chelated Zn has more solubility power than elemental Zn (Yaron, 1996).

In acidic soil environments, more zinc is available in ionic forms. Cation exchange processes influence its fate. Depending on the nature and concentrations of other mobile metals in soils, competition for the binding sites probably occurs. Zinc is mobilized in the absence of suitable binding sites. Most of the concern about excessive Zn concentrations in soils is related to its possible uptake by crops themselves and on live stock and human diet. Zn is principally phytotoxic, thus the concern about this metal is mainly directed at its effects on crop yield and soil fertility (Alloway, 1990).

In contrast to Cr, it has been suggested that Ni and Zn play an essential role in higher plants (Alloway, 1990). Gomes et al. (2001) found that heavy metal selectivity sequences varied among the soil matrix, and that the most common sequence is Cr>Pb>Cu>Cd>Zn>Ni. For some soils, Cr and Zn exchange places with Pb and Ni, respectively.

3.2 Soil Composition

The soil composition and its texture are the most important factors for the retention of contaminants in the soil. The main soil components [Figure 3.1] can be divided into organic (humic substances and polysaccharides) and inorganic (primary and secondary minerals). They are the principle components of soil that adsorb contaminants (Yong et al. 1992).

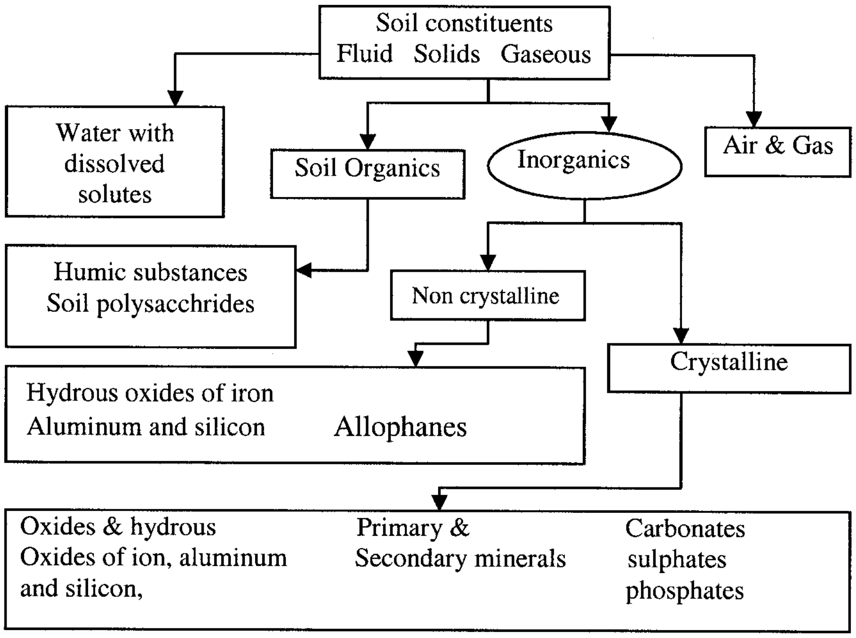

Figure 3-1. The key components of soil (Yong et al., 1992).

Retention of contaminants by the soil compounds depends on several interactions such as ionic exchange capacity, hydrogen bonding, van der Walls forces, adsorption, complexation and precipitation.

3.3 Transport Mechanisms of Metal in Soil

Soil contaminant can exist in the soil in three forms. They are solubilized contamination in the soil moisture; adsorbed contamination on the soil surface and chemically fixed contaminant as solid compounds (Evanko, 1997). The fate and transport of heavy metals in soil depends significantly on the chemical form and speciation of metal (Allen et al. 1991).

Heavy metals even at small concentrations may cause significant damage to human beings and their environment due to their mobility and their ability to contaminate ground water. The study of heavy metal transport is very important in many engineering applications. The main transport mechanisms of contaminants include advection, diffusion, dispersion, biodegradation, chemical reaction and adsorption (Nazaroff, 2001 ; Bedient et al. 1994). These mechanisms can significantly influence the ability to contaminate or decontaminate the sites. Some of this mechanisms are described below.

Advection: Advection is the transport of material caused by the net flow of the fluid in which that material is suspended. Whenever a fluid is in motion, all contaminants in the fluid, including both molecules and particles, are advected along with the fluid.

Diffusion: The random motion of fluid molecules causes a net movement of species from regions of high concentration to regions of low concentration. This phenomenon is known as diffusion. The rate of movement depends on the concentration gradient, with larger differences leading to higher rates of transport (Nazaroff, 2001) but diffusion is a slow transport process.

Dispersion: When water flows into the soil medium, another transport mechanism that occurs is dispersion. When contaminant flows with water around the solid particles of porous media, it migrates through all sides of the media, and this process repeats millions of times. And although fundamentally it occurs as a result of advection and diffusion, the rate of spreading is much faster than advection or diffusion (Nazaroff, 2001).

Advection and dispersion processes dominate the contaminant transport system in the formations of medium to high hydraulic conductivity. But in case of low hydraulic conductivity (e.g., clay), diffusion transport is the frequently controlling mechanism.

3.4 Sorption Phenomena

Sorption is an exchange and partitioning phenomenon between two-phase systems in which contaminants accumulate at the solid surface from the surrounding solution. In general, electrostatic, chemical, and physical mechanisms may contribute to the sorption phenomena. Electrostatic and chemical mechanisms are the most important mechanism for the heavy metal contaminants, and physical mechanism for the organic contaminants. They may occur simultaneously in a given soil-water system or treatment process (Watts, 1997). In soils, two sorption phenomena may be distinguished which are adsorption and absorption. Adsorption is the separation process of a contaminant from solution and its deposition to a surface or interface (e.g., solid/liquid, solid/liquid/gas). In contrast, absorption describes a process in which contaminant penetrates into the sorbent.

Adsorption is the most important sorption phenomena affecting the behaviour and bioavailability of metals in soils. This process controls the concentration of metal ions and complexes in the soil solution and thus influence their uptake by plant roots (Alloway, 1990).

3.4.1 Types of Adsorption

Adsorption in soils is more the type of concentrating material at solid-liquid interfaces. This type of adsorption can be distinguished in terms of positive and negative adsorption. Positive adsorption is the concentration of the solute on the colloidal surfaces, whereas, negative adsorption is the concentration of the solvent on the clay surface. The solute is then concentrated in the bulk solution. In this case, surface tension is increased. Surface acidity of the adsorbent may play an important role in the rate and degree of negative or positive adsorption (Tan, 1998).

3.4.2 Adsorption Characteristics

Adsorption is dependent not only on the surface charge, but also on the surface area. The amount of material adsorbed is directly proportional to the specific surface. The surface charge density is defined as the number of charges per formula weight divided by the specific surface area. Tan (1998), believes that the total charge is more important than the surface charge density in the adsorption process.

Adsorption reactions are reversible. Sometimes desorption is inhibited because of the chemical changes of adsorbed material. The positive heat of adsorption occurs characterizes when energy is released during the adsorption process. Adsorption generally decreases as temperature increases; because kinetic energy of the molecules is increased at elevated temperatures (Tan, 1998).

3.4.3 Forces of Adsorption

According to Tan (1998), several forces are responsible for adsorption reactions include physical forces, chemical forces, hydrogen bonding, hydrophobic bonding, electrostatic bonding, co-ordination reactions, and ligand exchange. Hydrogen bonding can qualify either as a chemical or as a physical process. On the other hand, electrostatic bonding, and co-ordination reactions are, in essence, chemical adsorption process. In soil-water systems all of them can significantly affect the metal adsorption process.

3.4.4 Factors Influencing Adsorption

Process kinetics describes the rate at which metal ions are transferred from solution to the pores of the soil particle. The following three steps must take place for adsorption to occur (Benefield, 1982).

1. When metal ion transferred from the bulk solution to the surface of the soil particle, it must pass through a film of solvent that surrounds the soil particle. This process is referred to as film diffusion.
2. The metal ion must be transferred to an adsorption site into the soil pore. This process is referred to as pore diffusion.
3. Finally, the metal ion must become attached to the surface of soil particle, i.e., be adsorbed.

3.4.5 Mechanisms of Adsorption

According to Alloway (1990), several different mechanisms can be involved in the adsorption of metal ions including cation exchange, specific adsorption, organic complexation and co-precipitation. Although, the adsorption of metals can be measured through isotherms but it is frequently difficult to be sure about which particular mechanism is responsible for the retention of metals in any particular soil. Adsorption processes are represented in Figure 3.2.

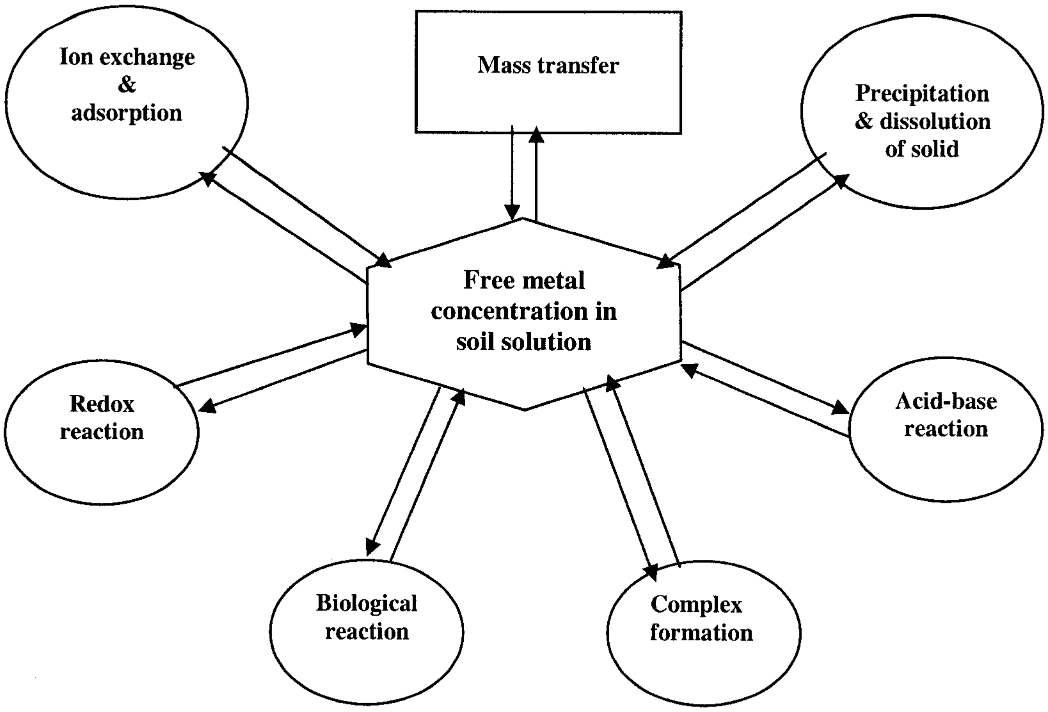

Figure 3-2. Dynamic systems of metal adsorption in soils (Watts, 1997).

Some details of these mechanisms are described below:

Cation exchange: Most heavy metal (with certain exceptions) exists mainly as cations in the soil solution. Cation exchange capacity (CEC) refers to the concentration of readily exchangeable cations and their adsorption depends on the density of negative charges on the surfaces of the soil colloids. To maintain electroneutrality, the surface negative charge is balanced by an equal quantity of oppositely charged counter ions. Cation exchange is reversible, diffusion controlled, and stochiometric and, in most cases, there is some selectivity for one ion over another by the adsorbent.

Specific adsorption: It involves the exchange of heavy metal cations and most anions with surface ligands. Adsorption of metals by mineral surface comprises there different steps: first, surface adsorption; second, diffusion into mineral particles and third, adsorption and fixation into the mineral particles. **Co-precipitation:** It is defined as the simultaneous precipitation of a chemical agent alone with other elements. **Organic complexation:** In this process humic substances adsorb metals by forming chelate complexes.

3.5 Sorption Isotherm

Graphical representation of the sorbed material data against the equilibrium concentration value of sorbate at constant temperature is termed as sorption isotherm (Watts, 1997). The mathematical expressions of sorption isotherm almost invariably involved sorption model described by Langmuir and Freundlich.

Langmuir model: A typical Langmuir model describes that the sorbate concentration on the sorbent surface is increased if the sorbate concentration increase in the aqueous phase. The standard form of Langmuir model is shown in Figure 3.3 and the equation of the model is

$$Cs = \frac{abCe}{1+bCe}$$

Where, C_s is the amount of sorbate retained by the sorbent (mg/kg), C_e is the sorbate concentration in aqueous system in equilibrium (mg/L), 'a' is empirical constant and 'b' is the saturation coefficient (L/mg).

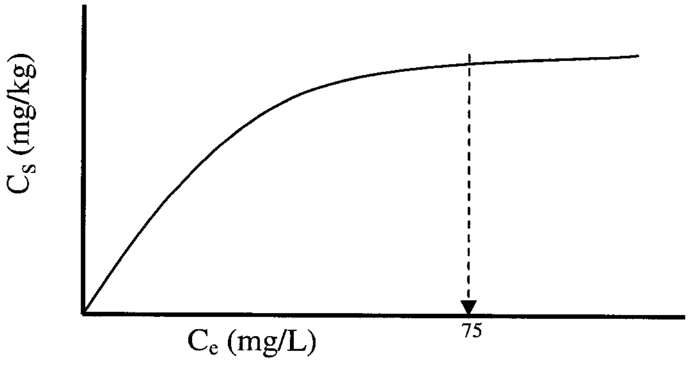

Figure 3-3. Typical Langmuir Isotherm plot (Watts, 1997).

Watts (1997) has found that single monolayer of sorbate accumulates on the sorbent surface, and if the sorbate concentration in the aqueous phase is raised above 75 mg/L, no increase in sorption occurs.

Freundlich model: The Freundlich model describes that the mass of material sorbed is proportional to the concentration of sorbate in the aqueous phase (Watts, 1997). The model is shown in the Figure 3.4, and fitted by the expression

$$C_s = KC_e^{1/n}$$

Where, 'K' is the Freundlich sortion coefficient and 'n' is the empirical coefficient.

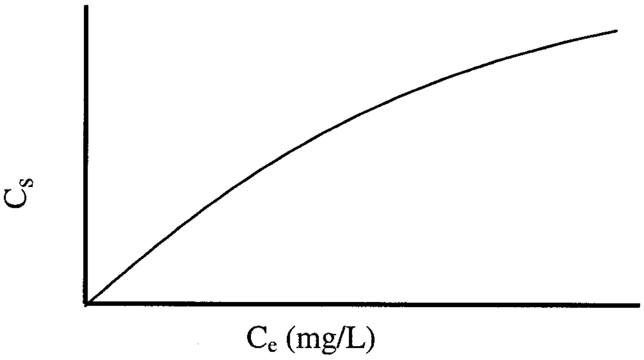

Figure 3-4. Typical Freundlich Isotherm plot (Watts, 1997).

Yaron et al. (1996), mentioned that Freundlich model does not predict a maximum adsorption capacity.

Chapter 4

Experimental Methods and Materials

4.1 Introduction

Both batch and column experiments were performed in this study to observe the effect of surfactants on the removal of Cr (VI), Ni (II) and Zn (II) from an artificially contaminated sandy soil. Sand, bentonite, surfactant, chelating agent and the target contaminants were the required materials.

4.2 Materials

4.2.1 Sand and Bentonite

All soil samples in this study were the mixture of 98 % of sand and 2 % of bentonite by weight. Sand was obtained from Geneq Inc., Canada and the bentonite was purchased from Sial Inc., Canada. Before using, sand was washed by hot water and was dried in the oven at 105^0C for 24 hours. Sand and bentonite were separately heated in the furnace at 550^0C for one hour to determine the percentage of organic matter. The measured hydraulic conductivity (K) of the soil sample (98 % sand and 2 % bentonite) was 0.2112 ± 0.0035 cm/min (See Appendix C-2). The properties of sand and bentonite are given in Table 4-1.

Table 4-1. Properties of sand and bentonite

	CEC meq/100g	pH in water	Size (Mesh)	Specific surface area	Organic matter content
Sand	0	9.4 (2)	40 (D=0.42mm) (3)	0.1 m^2/g (4)	0.07 %
Bentonite	110.5 (1)	6.7 (2)	325 (D=0.044mm) (3)	600m^2/g (5)	4.71 %

(1) Pump and Krist, 1998.
(2) 5g soil : 40mL water.
(3) U.S. standard sieve.
(4) Chiou et al. 1993.
(5) Grim, 1962.

4.2.2 Surfactants and Chelating agent

Two anionic surfactants, sodium dodecyl sulfate (SDS) and sodium dioctyl sulfosuccinate also known as aerosol-OT (AOT), in addition to a nonionic surfactant Triton X-100 (Tx-100) and a chelating agent, disodium ethylenediaminetetraacetate (EDTA salt) were used as extracting solvents. EDTA salt has the same chelating properties as EDTA acid. However, EDTA salt is more common used than EDTA acid because of its high solubility in water. In an acidic environment, the chemical transformation of EDTA salt to EDTA acid is represented in Figure 4.1. SDS, AOT, Tx-100 and EDTA salt were purchased from Fisher Scientific Company. Several physical and chemical properties of these extracting agents are mentioned in the Tables 4-2 and 4-3.

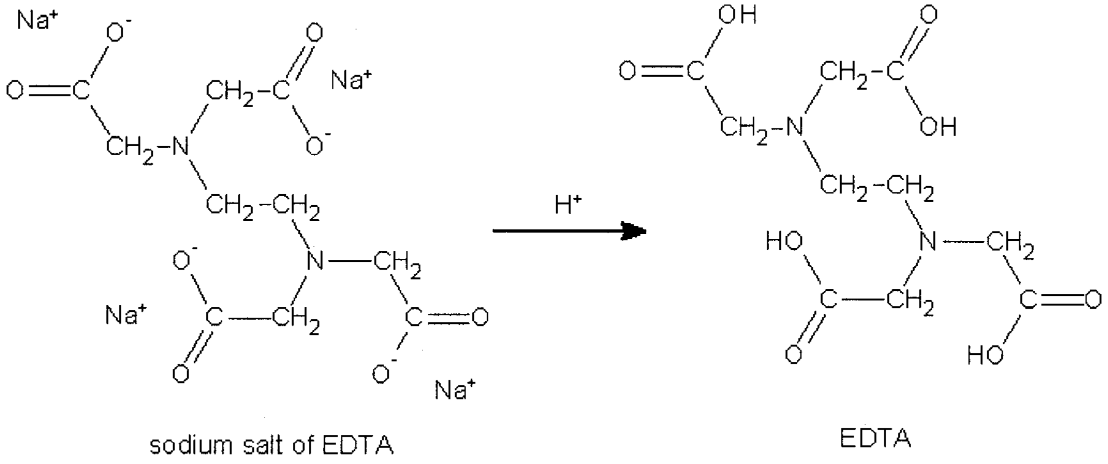

Figure 4-1. Chemical transformation of EDTA salt to EDTA acid (Sinex, 2004).

Table 4-2. Physical and chemical properties of surfactants SDS, AOT & Tx-100

Surfactant	Type	Molecular formula	Molecular weight (g)	Appearance	CMC mM
SDS (1)	Anionic	$C_{12}H_{25}OSO_3Na$	288.38	White Powder	8.20
AOT (2)	Anionic	$(C_9H_{17}O_2)_2CH_2CHSO_3Na$	444.57	White Solid	1.124
Tx-100 (3)	Nonionic	$C_8H_{17}C_6H_4(OC_2H_4O)_nOH$ (n=9-10)	628	Colorless Liquid	0.22 - 0.24

(1) & (2) Nivas et al. 1996
(3) Edwards et al. 1994

Table 4-3. Properties of EDTA acid and EDTA salt.

	Molecular formula	Molecular weight (g)	Appearance	Solubility
EDTA acid	$C_{10}H_{14}N_2H_2O_8$	292.25	White crystalline powder	0.03 % @ 25^{0}C
EDTA salt	$C_{10}H_{14}N_2Na_2O_8.2H_2O$	372.24	White crystalline powder	10 % @ 25^{0}C

A cationic surfactant was not selected in soil remediation, because of its high potential for sorption with the soil matrix (Huang et al. 1997). All the chemicals were used as received. The water used was deionized (D.I.) water.

4.2.3 Target Contaminants

Cr (VI), Ni (II) and Zn (II) were the target contaminants, they were added into the soil samples in the forms of K_2CrO_4, $NiCl_2$ and $ZnCl_2$ and were purchased from Fisher Scientific Company. Before they were added to the soil samples, they were completely dissolved in distilled water.

4.3 Preparation of Soil Samples

The soil samples were artificially contaminated in the laboratory to perform the batch and column tests. Prepared metal salt solutions were containing 1295.17 mg/L of K_2CrO_4 [40meq/L of Cr (VI)], 4752 mg/L of $NiCl_2$ [40meq/L of Ni (II)] and 2726 mg/L of $ZnCl_2$ [40meq/L of Zn (II)]. The metallic solutions were then added to the bentonite. The solution to bentonite ratio was 1L : 0.1kg. The metal solution and bentonite were added to 50mL plastic Nylon centrifuge tubes. Following this, the tubes were shaken on a wrist action shaker at 60 oscillations/min for 24 hours at a room temperature (25 ± 2^0C). After centrifugation at 3000 rpm for 15 minutes, the supernatant was removed and the metal contaminated bentonite was dried in the oven at 105^0C for 48 hours. Following this, the contaminated bentonite was kept for one month.

The last operation is the preparation of soil samples for the batch tests involved the addition of 0.1g of contaminated bentonite and 4.9g of sand to each of the 50mL plastic Nylon centrifuge tubes. Since the quantity of metal retained in the bentonite is quite small it is reasonable to assume that the soil samples still contained 98 % of sand and 2 % of bentonite.

The Atomic Absorption (AA) Spectrophotometer (Perkin Elmer AAanalyst 100, PerkinElmer Inc., ON, Canada) analysis the supernatant to yield the metal concentrations. Performing simple mass balance, the soil contamination levels stood as the followings:

Table 4-4. Soil contamination levels: *[Soil = 2 % bentonite & 98 % sand]*

Cr (VI), mg/kg Soil	Ni (II), mg/kg Soil	Zn (II), mg/kg Soil
18.2	111.4	210.5

4.4 Batch Studies

Batch extraction studies were performed at a room temperature of 25 ± 2^0C. Three different surfactants (SDS, AOT and Tx-100) at different concentrations below and above the CMC, and the different concentrations of the chelating agent (EDTA salt) were used to determine their effects on extraction of Cr (VI), Ni (II) and Zn (II) from contaminated soil. The combinations of the most effective concentration of each surfactant and different concentrations of the chelating agent were also performed. The distilled water was also considered as an extracting agent.

In all batch tests, soil (98 % of sand + 2 % of bentonite) to solution ratio was 5.0g : 40mL. The samples were placed in a series of 50 mL plastic Nylon centrifuge tubes. Typically, 5.0g of contaminated soils were weighed out into the tube and 40mL of solutions were added at varying concentrations. The series of reactors (tubes) were equilibrated in a wrist action shaker at 60 oscillations/min for 24 hours. Later equilibrated samples were centrifuged at 3000 rpm for 15 minutes. A pH meter was used to measure the supernatants pH to the nearest 0.01 pH unit. The supernatants were digested with 70 % HNO_3 and shaken at 60 oscillations/min for 24 hours. The supernatants were then taken for AA analysis to yield the metal concentration. The batch tests related to metal extraction were performed in duplicate and the tests related to contaminant aging were done in triplicate. The reported values in the table denote average metal concentrations.

4.5 Column Tests

The laboratory column studies were conducted at a room temperature of 25 ± 2^{0}C. The experimental set-up for the column tests is shown in Figure 4.2. The Plexiglas columns were 4.0 cm in diameter and 20.5 cm in length. Both ends of the column were equipped with a pore stone filter and a Whatman filter paper to ensure uniform distribution at the column inlet and prevent soil dispersion at the column outlet. A submerged pump and an overhead container were used to maintain a steady flow through the column.

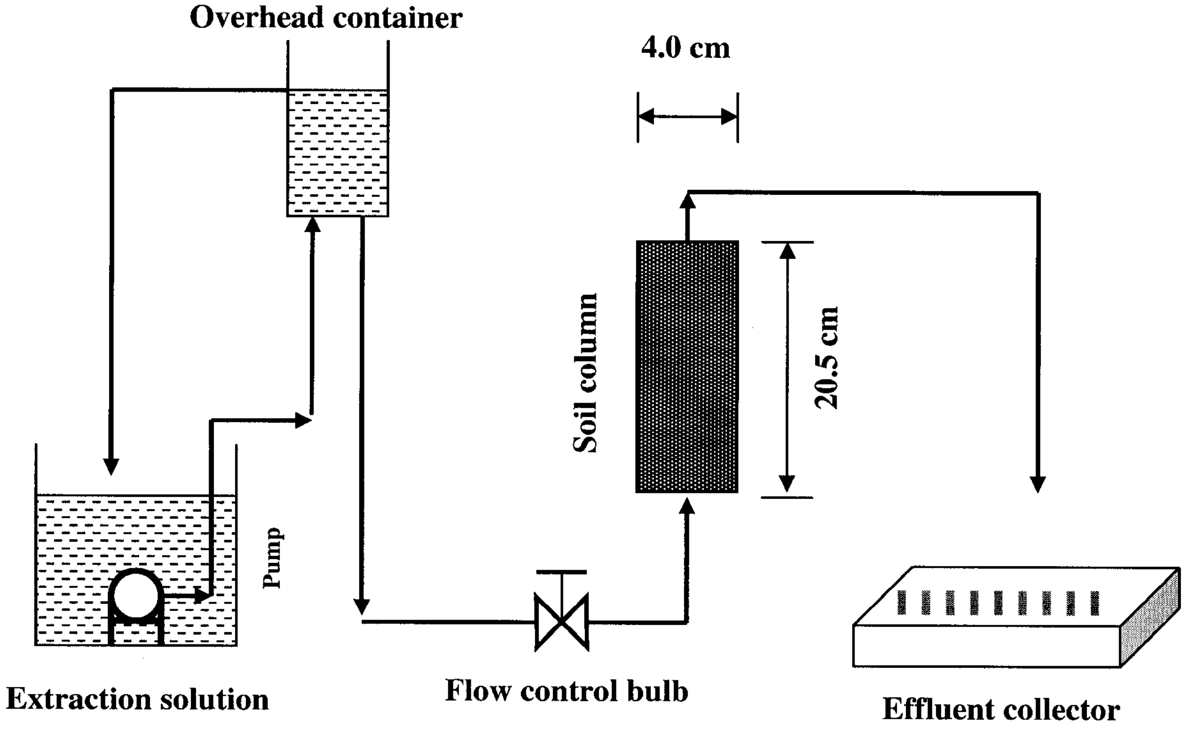

Figure 4-2. Experimental setup for column studies.

The soil samples for each column test were prepared separately, by mixing 2 % of bentonite and 98 % of sand. The columns were packed with soil, under continuous controlled tapping against the column wall as the soil was added. The soil was placed in the column in several layers. The purpose of tapping the column and layers of soil in the column was to pack the soil uniformly. The pore volume of the packed column was determined by the weight difference between the water-saturated column and the dry soil column, assuming complete saturation. The measured pore volume (P_V) of the soil column was 95 mL (See Appendix).

Surfactant systems (SDS, AOT, Tx-100) that exhibited good metal removal efficiencies in batch studies were selected for use in column studies. The solution was pumped through the soil column. The column effluent was collected manually for a constant time at regular intervals. A pH meter was used to measure the effluents pH. All the effluents were digested with 70 % HNO_3 and shaken at 60 oscillations/min for 24 hours at a room temperature of 25 ± 2^0C. Following this, AA analysis was performed to measure the metal concentration in the effluent.

Chapter 5

Results and Discussion

5.1 General Remarks

In this study, distilled water, surfactants SDS, AOT and Tx-100 with and without a complexing agent (EDTA) are used to extract Cr (VI), Ni (II) and Zn (II) from an artificially contaminated sandy soil (98 % sand and 2 % bentonite).

5.2 Results of Batch Studies

5.2.1 Effect of Surfactant Concentration

The results of batch extraction studies by distilled water and surfactants are represented in Fig. 5-1 to Fig. 5-3. Table A-1 to Table A-3 summarizes the additional details related to the batch studies. The initial pH value denotes the pH value of surfactant solutions before they were added to the soil samples. Final pH is the pH value noted after shaking the soil samples for 24 hours. The amount of metal removed (mobilized) that is expressed in milligrams of metal per liter of solution (mg/L) is plotted against the initial surfactant concentration. As stated earlier, soil to solution ratio was 5g : 40mL.

Surfactant concentration is an important factor influencing the removal efficiency of heavy metals. Desorbed Cr (VI), Ni (II) and Zn (II) concentrations by SDS, AOT and Tx-100 increased with increases in their concentrations [Fig.5-1 to Fig.5-3]. However, the results indicate that at concentrations higher than the CMC, the extent of metal removal remained relatively constant in all cases.

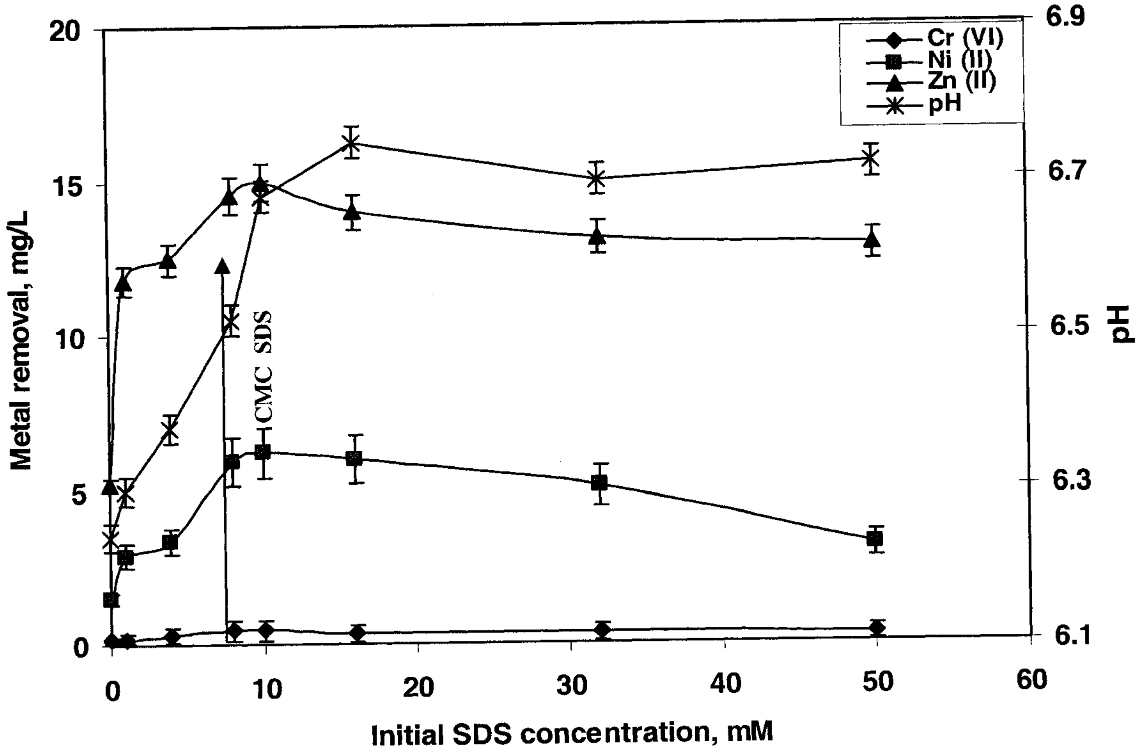

Figure 5-1. Extraction of metals from soil by SDS.

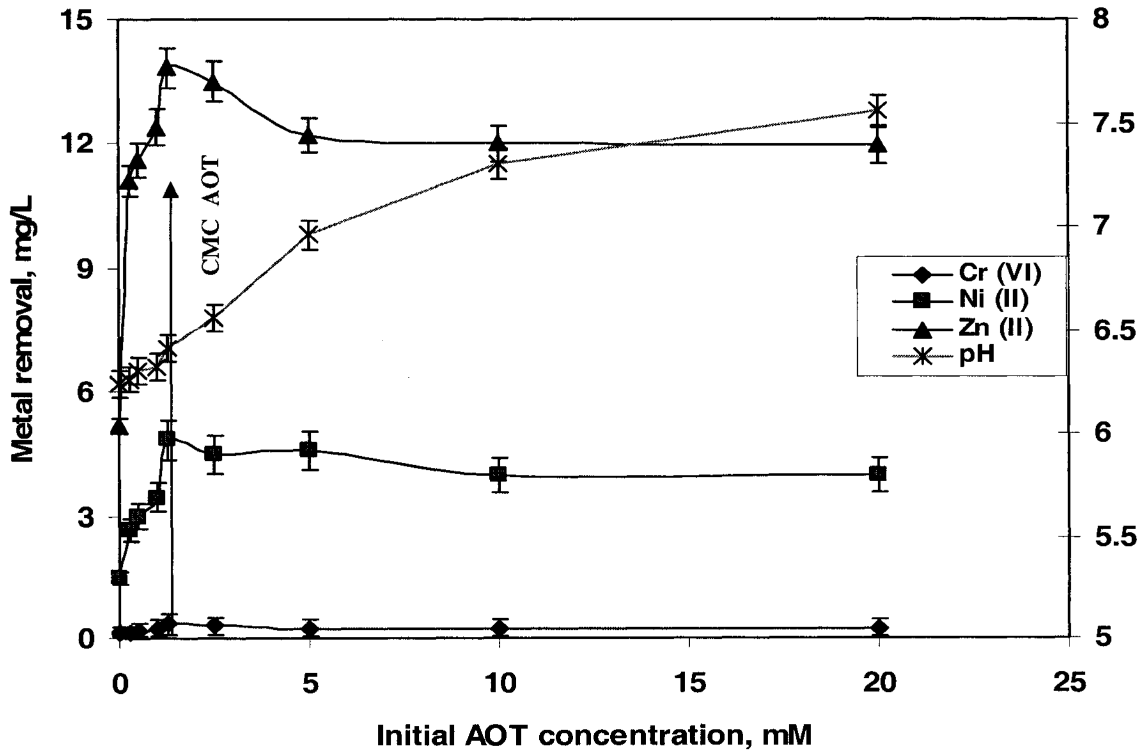

Figure 5-2. Extraction of metals from soil by AOT.

5.2.1.1 Cr (VI)

Possible mechanisms by which the aqueous Cr (VI) concentrations are enhanced by introduction of surfactants are ion exchange, precipitation, and counterion binding. For ionic micelles, the interfacial region between the aqueous solution and the micelle contains the ionic head groups, the Stern layer of the electrical double layer pertaining to these groups, more than one half of the counterions associated with the micelle, and water (Rosen, 1989). It is reasonable to suspect that, during extraction, the chromate anions may be attached to the counterions of the surfactant micelles. However, this effect would not be anticipated until concentrations exceeded the CMC of the surfactant. In addition, one would normally expect greater chromate removal as the surfactant concentration increases above the CMC due to the increase in the number of associated counterions. The results indicate that chromate removal increased up to the CMC and is almost constant above the CMC. As such, counterion binding does not appear to be major mechanism in Cr (VI) extraction.

Surfactants that precipitate with the cations of the insoluble mineral phases formed by Cr (VI) could enhance dissolution of the chromate anions. However, the soil used to prepare soil did not have chromate minerals. This suggests that precipitation-dissolution is not the primary mechanism in enhancing Cr (VI) extraction.

Rosen (1989) states that the other possible mechanism by which surfactants can enhance chromate removal from the soil is by ion exchange. He defines ion exchange as the replacement of counterions adsorbed onto the soil medium from the solution by similarly charged surfactants. Hence, if a negatively charged ion has adsorbed onto the substrate it can be replaced by negatively charged surfactant ions from solution. Since micelles unlike monomers are not directly involved in ion exchange, the amount of ion that can be replaced remains relatively constant above the CMC. From the results of batch studies [Fig.5-1 and Fig.5-2] it can be seen that Cr (VI) removal increases with increase in anionic surfactant (SDS or AOT) concentration up to the CMC, and remain relatively constant above the CMC. These results thus indicate ion exchange as the possible mechanism enhancing Cr (VI) extraction.

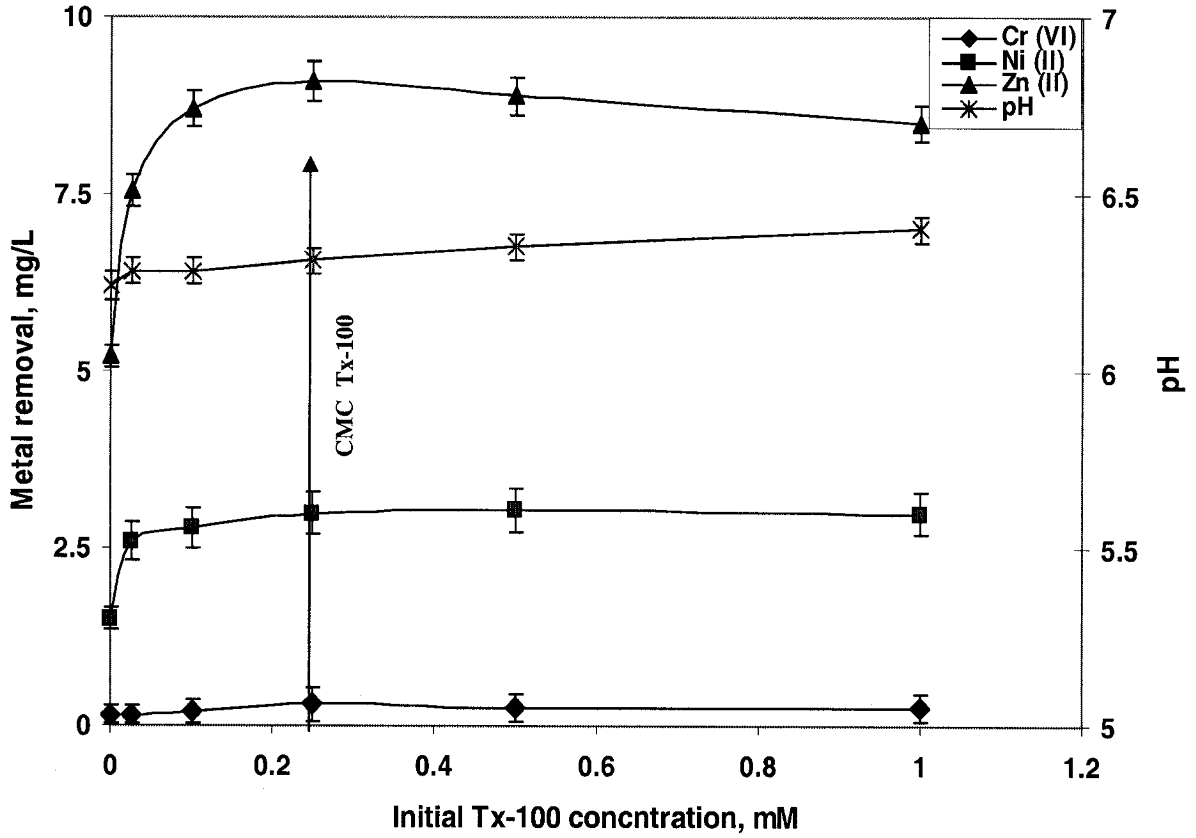

Figure 5-3. Extraction of metals from soil by Tx-100.

Also, when a nonionic surfactant (Tx-100, Fig. 5-3) was used, Cr (VI) removal in the vial was comparable to that obtained by distilled water alone. Nonionic surfactant would not be involved in ion exchange processes and counterion binding, and hence exhibited poor removal efficiency. These observations reinforce the conclusions that ion exchange is the likely principle mechanism enhancing Cr (VI) extraction from the soil by the anionic surfactants.

5.2.1.2 Ni (II) and Zn (II)

Since both Ni (II) and Zn (II) are cations, they could directly be replaced by the positively charged (cations) tail groups of the anionic surfactants. Because, the tail groups of anionic surfactants (SDS and AOT) contain the Na^+ cation. And according to metal activity series, Na^+ cation has the power to replace both Ni (II) and Zn (II). However, the exchangeable ions will increase until the CMC is reached and remain relatively constant above the CMC.

A counterion binding is another possible mechanism during Ni (II) and Zn (II) extractions, these cations may be attached to the counterions of the surfactant micelles (anions) in the Stern layer. This view is supported by the study of Gadelle et al (2001). They concluded that the probable mechanisms of metal extraction by a surfactant are mainly a result of counterion binding in the electrical double layer surrounding the micelles and to a lesser extent, dissolution of the soil matrix. The results obtained for two anionic surfactants in this batch study (Fig.5-1 and Fig.5-2) indicate that the enhancement of heavy metal extraction mainly occurs at the concentrations close to the CMC or at concentrations a little higher than the CMC. This concluded that it is the micelle that solubilizes metals through complexation and sorption of the surfactant on the soil surface and hence detachment of the metal occurs from the soil to the soil solution.

Unlike the tests dealing with the anionic surfactant (SDS and AOT), in tests involving nonionic surfactant (Tx-100, Fig.5-3) no metal precipitation was observed. Doong et al (1996) asserted that more Tx-100 is needed to reach the CMC in the soil-water system than in the presence of water alone, since a good portion of Tx-100 becomes sorbed on to the soil. Hence, it may be possible for the adsorbed surfactant on the soil particle to displace the bound metal.

5.2.2 Effect of Surfactant Type

Table 5-1 summarizes the results of batch extraction studies associated with the optimal surfactant concentration.

Table 5-1. Results of batch extraction studies by surfactant

Type of surfactant	Optimal concn., mM	Surfactant concn CMC (units)	Max. Cr (VI) removal, mg/L	Ratio to Cr (VI) removal by water	Max. Ni (II) removal, mg/L	Ratio to Ni (II) removal by water	Max. Zn (II) removal, mg/L	Ratio to Zn (II) removal by water
SDS	10	1.22	0.45	3.00	6.20	4.13	14.9	2.88
AOT	1.25	1.12	0.35	2.33	4.85	3.23	13.8	2.66
Tx-100	0.25	1.14	0.30	2.00	3.00	2.00	9.10	1.75

At equilibrium, distilled water was able to remove 0.15mg/L of Cr (VI), 1.50mg/L of Ni (II) and 5.20mg/L of Zn (II) through solubilization. The maximum desorbed concentrations of Cr (VI) were 0.45 mg/L, 0.35mg/L and 0.30mg/L in SDS (Fig.5-1), AOT (Fig.5-2) and Tx-100 (Fig.5-3) amended system respectively. This corresponds to 3.00, 2.33 and 2.00 times higher removal of Cr (VI) than that solubilized by distilled water. The desorbed concentrations of Ni (II) were 6.20 mg/L, 4.85mg/L and 3.00mg/L respectively in SDS (Fig.5-1), AOT (Fig.5-2) and Tx-100 (Fig.5-3). This corresponds to 4.13, 3.23 and 2.00 times higher removal of Ni (II) than that by distilled water alone. Similarly, the ratio of maximum Zn (II) removal by surfactants to that of distilled water ranged from 2.88 for SDS (Fig.5-1), 2.66 for AOT (Fig.5-2) and 1.75 for Tx-100 (Fig.5-3).

The results indicate that the optimal surfactant concentration generally occurs at a concentration slightly higher than the standard CMC. The reported CMCs are based on data related to CMC in water. As stated earlier, the CMC of a surfactant is strongly influenced by factors such as temperature, pH, hydrocarbon chain length, ionic strength and the presence of nonelectrolytes. However, the presence of soil constituents may affect the CMCs of surfactant systems. Further more, loss of surfactant occurs due to the sorption onto the soil media. Hence, one should expect that the surfactants form CMC at slightly higher concentration than the standard CMC.

5.2.3 Extraction by Surfactants with Complexing Agent

One of the hypotheses of this study is that extraction of metals from contaminated soil can be enhanced if complexing agents are used with surfactants. They are capable of forming stable complexes with metal ions and those metal-complexes are solubilized by surfactant micelles. A few tests were performed to know the effect of the addition of surfactant to EDTA in removing the heavy metal Cr (VI), Ni (II) and Zn (II). Surfactants (SDS, AOT, and Tx-100) were added individually to EDTA and the metal removal efficiency was determined.

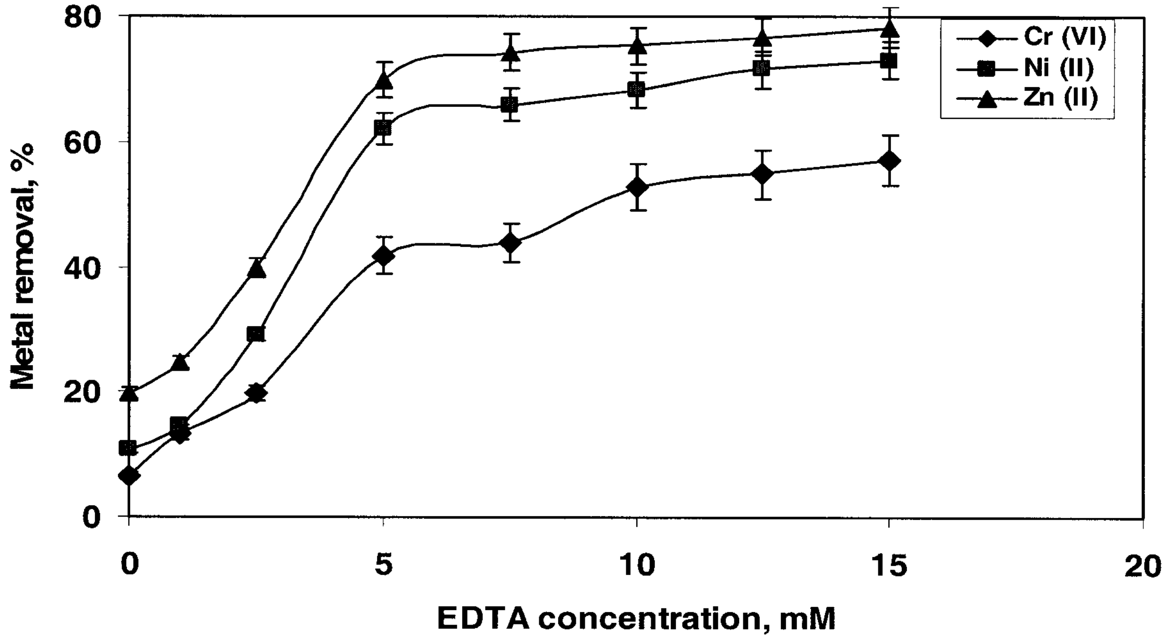

Figure 5-4. Extraction of metals by EDTA only.

Fig.5-4 and Table A-4 illustrate the removal of Cr (VI), Ni (II) and Zn (II) with EDTA salt only. EDTA salt does significantly enhance the removal of metal. The removal efficiency increased with increases in EDTA salt concentration. However, pH is also changing as the EDTA concentration increases, which affects the metal ion solubility. The final pH is 5.54 when 1mM is used and pH is 3.10 when 10mM is used. These indicate that EDTA becomes more acidic at an increased concentration. Acidic solutions have a higher tendency to extract metal ions.

Extraction efficiencies of Cr (VI), Ni (II) and Zn (II) by the combination of surfactants and EDTA salt (7.5mM) are represented in the Fig.5-5 to Fig.5-7. Table A-5 provides the additional data related to these tests. Surfactants with the complexing agent have demonstrated the various extractions capabilities of metal contaminants. Cr (VI) removal rate is increased by the addition of 7.5mM EDTA to 10mM SDS. The result shows that the removal rate of Cr (VI) is twice the rate of Cr (VI) removal by the EDTA alone (Fig.5-5). 72.5 % of Cr (VI) was removed by the mixture of EDTA and SDS. The removal of Cr (VI) was also improved by the addition of the other two surfactants to EDTA. However, addition of AOT and Tx-100 to EDTA did not significantly improve Cr (VI) removal compare to removal by EDTA alone. The combination of 7.5mM EDTA and 10mM SDS is extremely effective in removing Ni (II) and Zn (II). 87.0 % of Ni (II) and 97.6 % of Zn (II) were removed when EDTA and SDS mixture was used [Fig.5-6 and Fig.5-7 respectively]. Removal of Ni (II) and Zn (II) was also improved in cases where AOT and Tx-100 were added to EDTA.

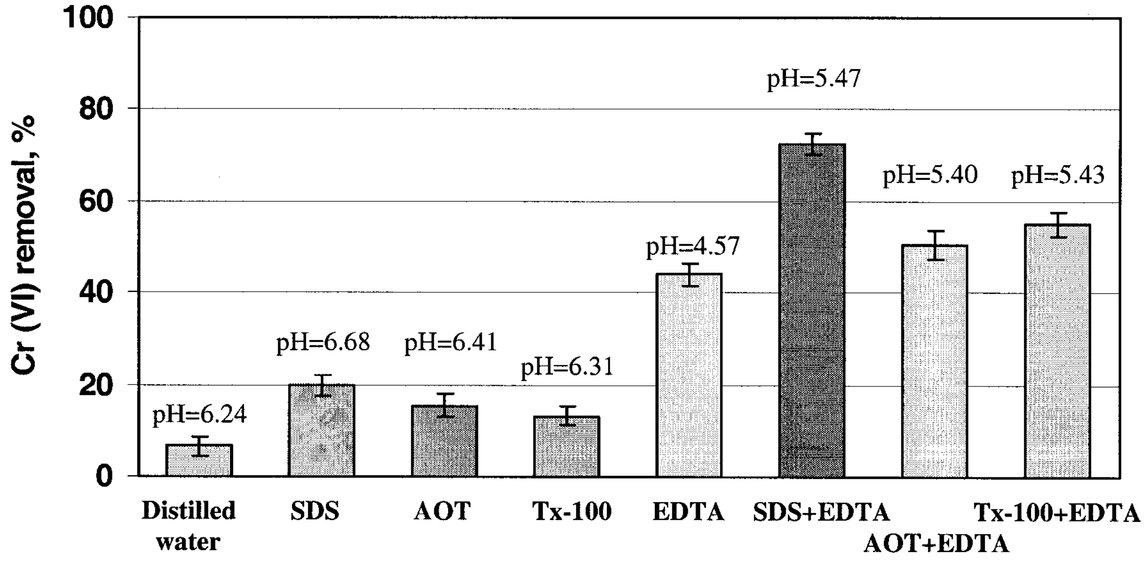

Figure 5-5. Batch extraction of Cr (VI) by water, surfactants, EDTA alone and surfactants with EDTA.

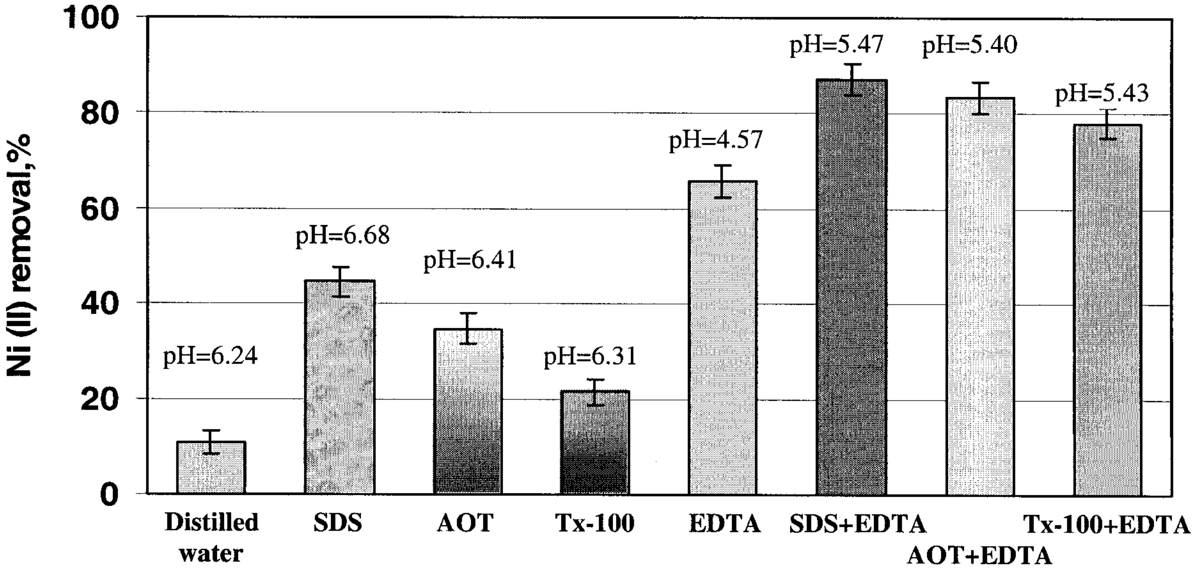

Figure 5-6. Batch extraction of Ni (II) by water, surfactants, EDTA alone and surfactants with EDTA.

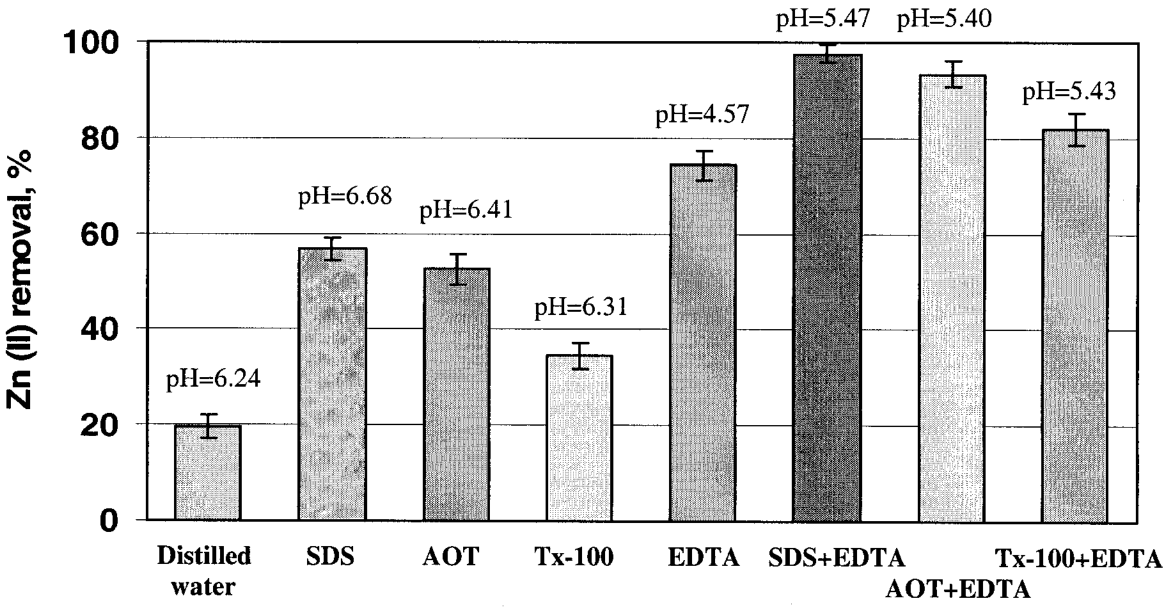

Figure 5-7. Batch extraction of Zn (II) by water, surfactants, EDTA alone and surfactants with EDTA.

5.2.4 Effect of Contaminant Aging

To study the effect of contaminant aging, water was used as the extracting solvent. As the contaminated soil ages, the soil-bound metal becomes less mobile. This is due to the formation of surface complexes or solids with the soil constituents (Reed, 1996).

Batch extraction experiments were conducted to observe the time dependent metal removal efficiencies. The age of contaminants varied from 2 weeks to 12 weeks. Strictly speaking, the difference in age of contaminants should be in terms of years rather than in terms of weeks. For the contaminants that were much older, there was a decreasing trend in metal removal rate due to the lower solubility of the contaminants. Over the study period of 4 months, the extractable metals from each soil sample appears to decrease with time from 0.15mg/L to 0.10mg/L for Cr (VI), 1.50mg/L to 0.95mg/L for Ni (II) and 5.20mg/L to 4.25mg/L for Zn (II) [Fig.5-8].

Additional tests are required to confirm the effects of contaminant aging on removal efficiency considering longer aging periods. Due to these limitations, the conclusions on aging drawn here are to be considered as tentative. Further additional tests should be conducted to study the aging effects of historically contaminated soils with metals.

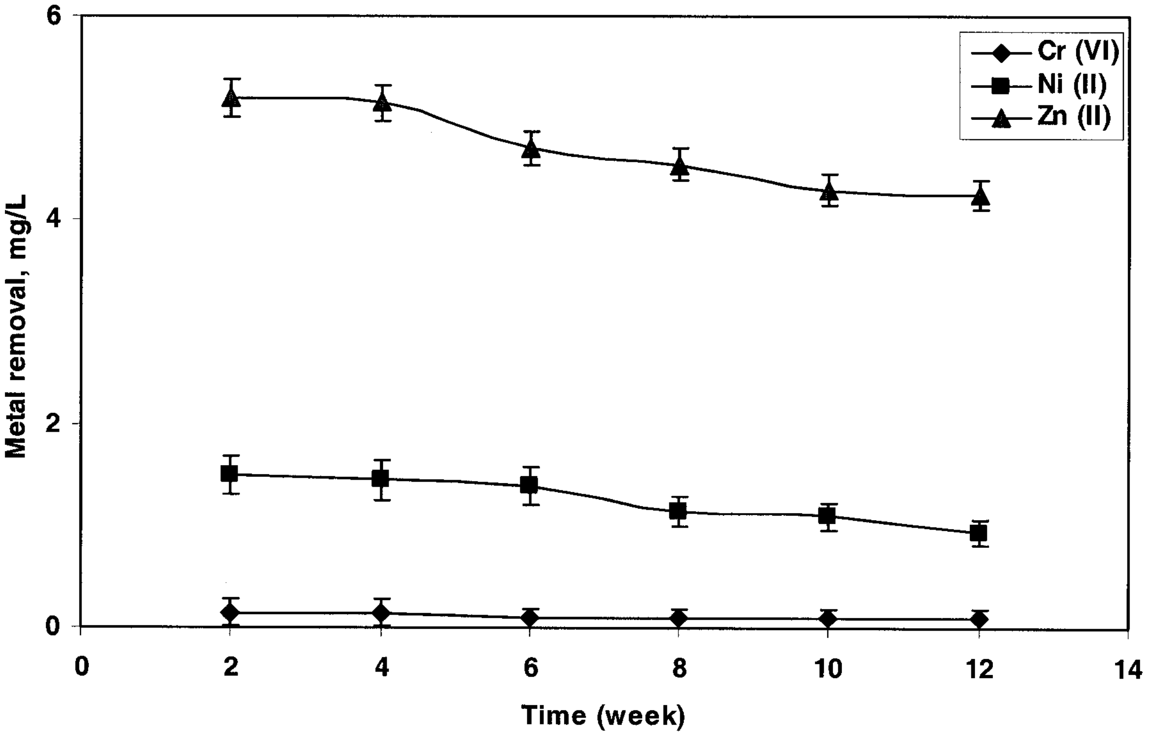

Figure 5-8. Effect of contaminant aging on the metal extractions.

5.2.5 Effect of Metal Affinities and Interaction

Many studies deal the adsorption and desorption processes for a single metal contaminant, when it is present in soils. However, the presence of multiple interacting metal ions is more frequently encountered in nature. Synergic effects could change the fate and transport of heavy metals, when they are present together.

To study the effect of metal affinities and interaction among the three metals Cr (VI), Ni (II) and Zn (II), parallel experiments were conducted to compare the results with and without metal interactions. A metal salt solution containing 346.8 mg/L [40meq/L] of only Cr (VI) was added to the bentonite. The prepared sample containing Cr (VI) contaminated bentonite is termed as soil sample 2. Similarly, 1174 mg/L [40meq/L] of Ni (II) and 1308 mg/L [40meq/L] of Zn (II) solutions were added to bentonite separately to prepare soil sample 3 and soil sample 4 respectively. The general procedure to prepare soil sample 2, soil sample 3 and soil sample 4 were identical to the procedure followed to prepare soil sample 1 (See chapter 4, section 4.3).

Table 5-2. Contamination level of soil samples

	Cr (VI), mg/kg	Ni (II), mg/kg	Zn (II), mg/kg
Soil sample 1	18.2	111.4	210.5
Soil sample 2	29.7	----	----
Soil sample 3	----	207.0	----
Soil sample 4	----	----	251.2

[Soil = 2 % bentonite & 98 % sand]

5.2.5.1 Interaction during adsorption

Fig.5-9 shows that in the soil sample 1 containing the three metals Cr (VI), Ni (II) and Zn (II), the amount of Zn (II) retained (210.5 mg/kg soil) is higher than the amount of Cr (VI) retained (18.2 mg/kg soil). This is also higher than the amount of Ni (II) retained (111.4 mg/kg soil). Fig.5-9 also shows that Zn (II) and Cr (VI) retention in the presence of Ni (II) is marginally affected. However, retention of Ni (II) is significantly reduced in the presence of Zn (II) and Cr (VI). These results confirm that Zn (II) has a greater affinity than the Cr (VI) and Ni (II), and that Ni (II) has a higher affinity than Cr (VI) to get adsorbed to the sites of the soil matrix.

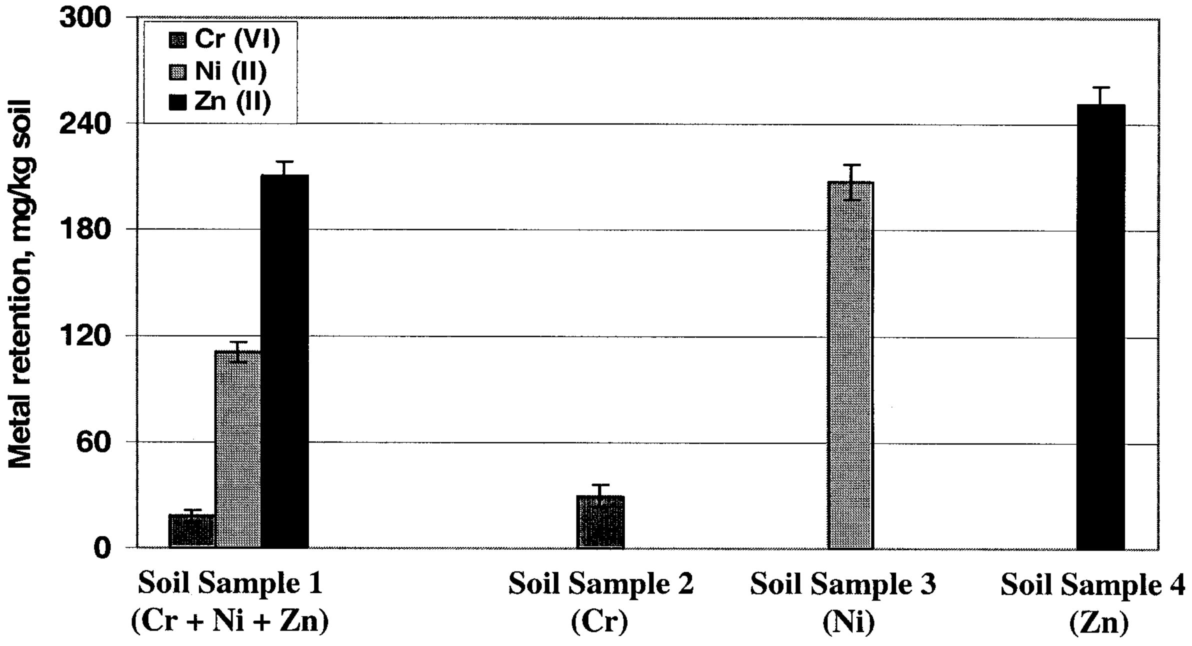

Figure 5-9. Interaction study related to metal retention.

5.2.5.2 Interaction during desorption

The interaction among the metals Cr (VI), Ni (II) and Zn (II) was also studied in the desorption mode. The desorption study for soil sample 1 (Fig.5-10) shows that in SDS, the percentage of Zn (II) desorption (56.8 %) is higher than that of Cr (VI) desorption (19.8 %). It is also higher that Ni (II) desorption (44.6 %). This behavior of metals can be traced to the fact that Zn (II) is less strongly bound to the soil than Cr (VI) and Ni (II). Also Ni (II) is not as strongly bound as Cr (VI).

To know more about the interaction among metals during desorption, additional desorption tests on soil samples 2, 3 and 4 were conducted using the same surfactant SDS. This result also shows that when the soil contains a single metal, the percentage of desorption of that metal is significantly reduced (Fig.5-10). Quantitatively, Cr (VI) desorption decreases to 11.8 % from 19.8 % in SDS (soil sample 2 and 1). Similarly, Ni (II) decreases to 29.7 % from 44.6 % (soil sample 3 and 1) and Zn (II) decreases to 34.6 % from 56.8 % (soil sample 4 and 1). A possible reason for this behavior of metals may be traced to the following facts. Cr (VI) and Ni (II) may be bound to most of the stronger soil adsorption sites such as organic phase sites. Possibly, Zn (II) is associated with the oxide fraction of the adsorption sites (Ramos et al. 1992). In the absence of other metals, all adsorption sites are available for any single metal. Hence, in this case, desorption of metal is more difficult (soil sample 2, 3 and 4). These observations hold good to describe the desorption of these metals by the surfactant SDS.

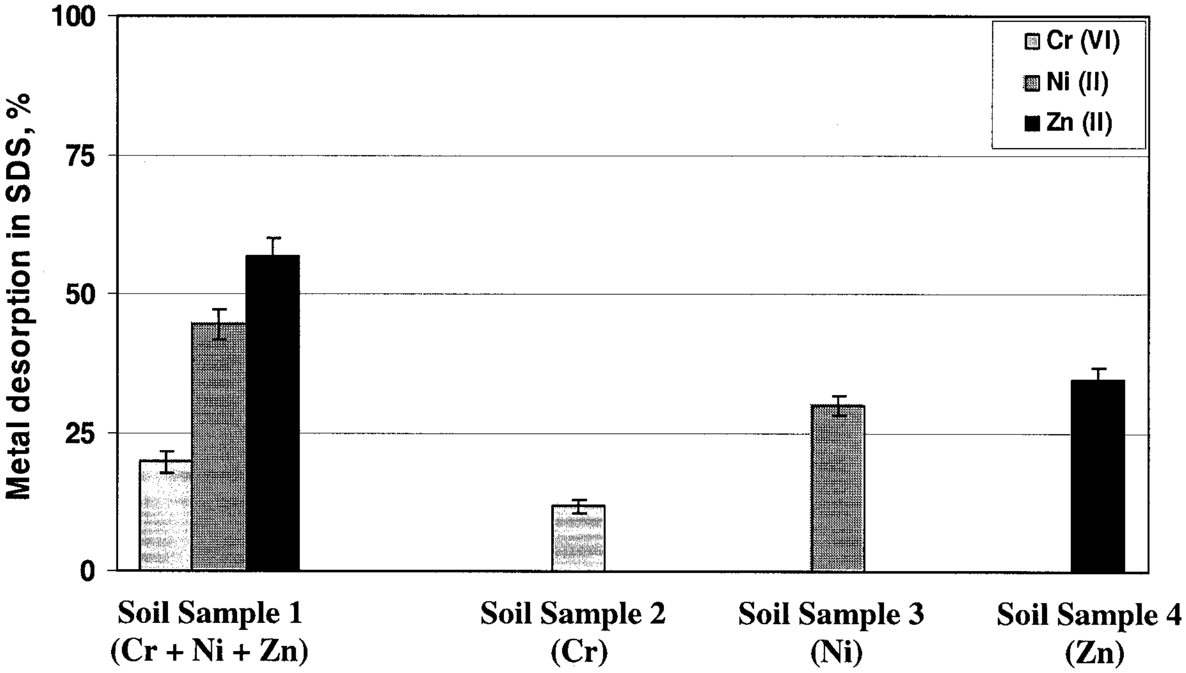

Figure 5-10. Interaction study related to metal desorption [solvent: 10 mM SDS].

5.3 Column Studies

Earlier batch tests indicated that surfactants enhance the removal of Cr (VI), Ni (II) and Zn (II) from the artificially contaminated sandy soil. Batch methods are simpler and are more easily reproducible compared to column tests. They will probably remain as the most common method for measuring equilibrium adsorption-desorption. However, the conditions in batch experiments are very different from those found in the field, where the soil is stationary. The column method is more realistic in simulating field conditions. In the field, the soil matrix is in a fixed position and the surfactant passes through it. Hence, to reproduce field conditions, column studies were conducted.

For column tests, the Plexiglas column (Fig.4-2) was initially packed uniformly with the soil. The extracting solvent was continuously introduced through the column at a fixed rate until a steady state flow was achieved. Metal extraction from the soil columns were evaluated by distilled water, surfactant, complexing agent EDTA and surfactant together with EDTA. The batch tests established that SDS was the most effective surfactant among the three surfactants in extracting metal contaminants. Hence, column tests were performed using the surfactant SDS only with and without EDTA to enhance the elution of Cr (VI), Ni (II) and Zn (II) from the soil column. However, column efficiency depends on the several factors including soil moisture, temperature history, contaminant concentration, age of contaminant, solvent flow rate and the extent of chemical reaction with the soil matrix.

Table 5-3 lists some of the relevant properties pertaining to the column studies. The last three column studies were performed using the same extracting solvent at different flow rates in order to investigate the effect of flow rates on contaminant elution efficiencies.

Table 5-3. Properties of the column

Extracting agent	Flow rate mL/min	Pore water velocity cm/min	Mass of soil, g	Density of soil, g/cm^3	One pore volume, mL	Hydraulic conductivity cm/min
Distilled water	12	2.59	458.2	2.82	95	0.2112 ±0.0035
SDS (10 mM)	12	2.59				
EDTA (7.5 mM)	12	2.59				
SDS (10 mM) + EDTA (7.5 mM)	12	2.59				
	40	8.63				
	4	0.86				

Porosity of soil = 0.3689

5.3.1 Column Test Results Using Distilled Water and SDS

Column results of metal [Cr (VI), Ni (II) and Zn (II)] removal using distilled water and SDS are shown in Fig.5-11 to Fig.5-14. Table B-1 and Table B-2 summarize the additional data related to these tests. In Fig.5-11 to Fig.5-13, the results are represented as the metal removed [effluent Cr (VI), Ni (II) and Zn (II) concentration, mg/L] versus the number of pore volumes of solution injected, while Fig.5-14 is on a mass percent removal basis.

In both cases (distilled water and SDS) the effluent concentration of all three metals [Cr (VI), Ni (II) and Zn (II)] was very high, when the first 3 pore volumes passed through the column (Fig.5-11 to Fig.5-13). This may partly due to the fact that the contaminant's age is not enough. The escape of some loose metals through the filters may also have contributed to this fact.

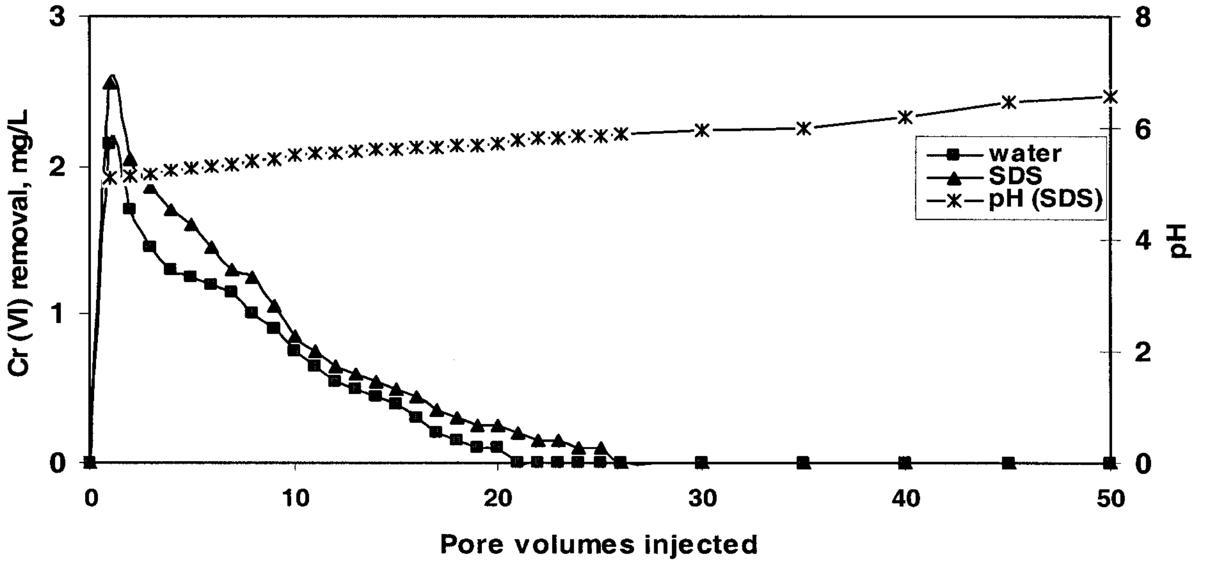

Figure 5-11. Removal of Cr (VI) from column by water and 10mM surfactant.

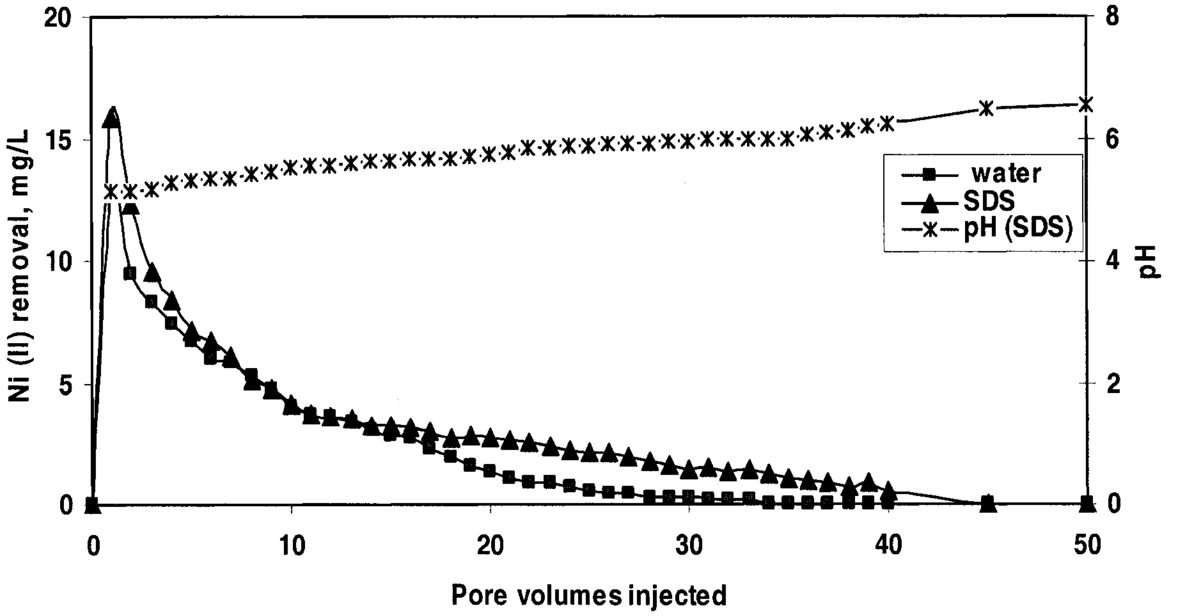

Figure 5-12. Removal of Ni (II) from column by water and 10mM surfactant.

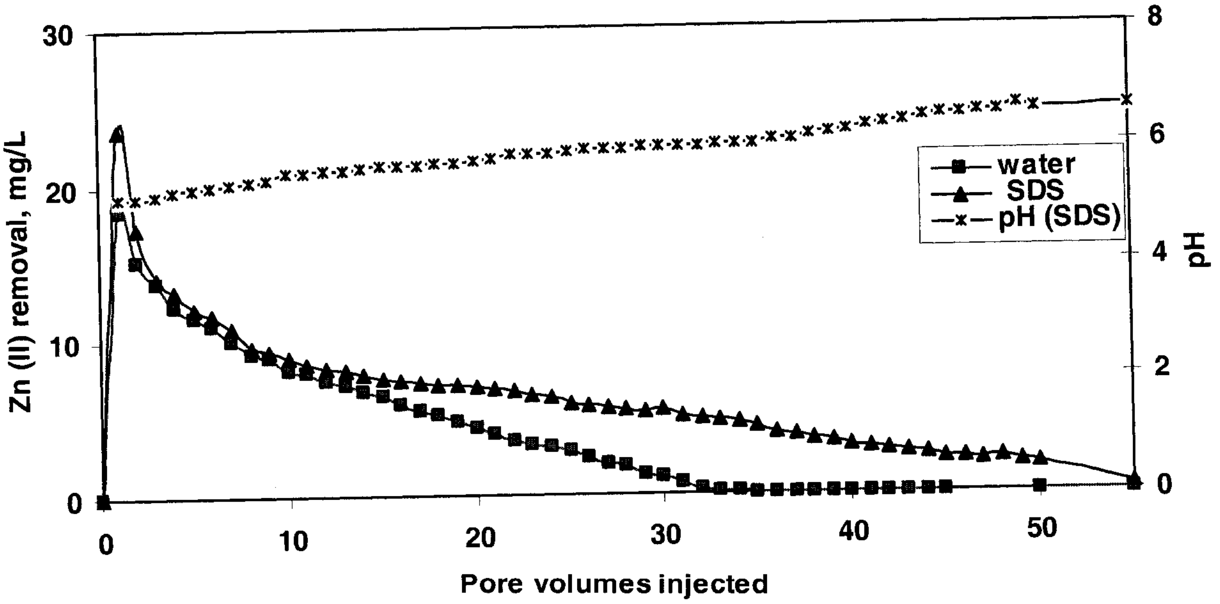

Figure 5-13. Removal of Zn (II) from column by water and 10mM surfactant.

Fig.5-14a and Fig.5-14b indicated that the percentage removal of metals by distilled water is quite less than the removal of metals by SDS. However, 50 pore volumes of water alone can remove 18.5 % of Cr (VI), 19.2 % of Ni (II) and 20.3 % of Zn (II). On the other hand, the amount of Cr (VI), Ni (II) and Zn (II) removal by SDS appears relatively high at 50 pore volumes 23.9 %, 26.6 % and 33.2 % respectively. These results indicated that SDS has marginally improved the percentage removal of Cr (VI) and Ni (II), but for Zn (II) there is a significant improvement. This may be traced to the earlier stated fact that Zn (II) is less strongly bound than Cr (VI) and Ni (II) to the soil matrix and gets removed more easily.

Based on the concentration ratio of metals extracted by the 10mM SDS to those extracted by the blank control system, a comparison of the batch and column results can be described as below. In batch studies, the enhancement ratios were found to be 3.00 for Cr (VI), 4.13 for Ni (II) and 2.88 for Zn (II). In column studies, injecting 50 pore volumes of solvent, the enhancement ratios were 1.29 for Cr (VI), 1.38 for Ni (II) and 1.64 for Zn (II). From these comparisons it is clear that batch systems are more efficient than column systems. This is probably due to the fact that equilibrium was not achieved, even after feeding 50 pore volumes in column tests.

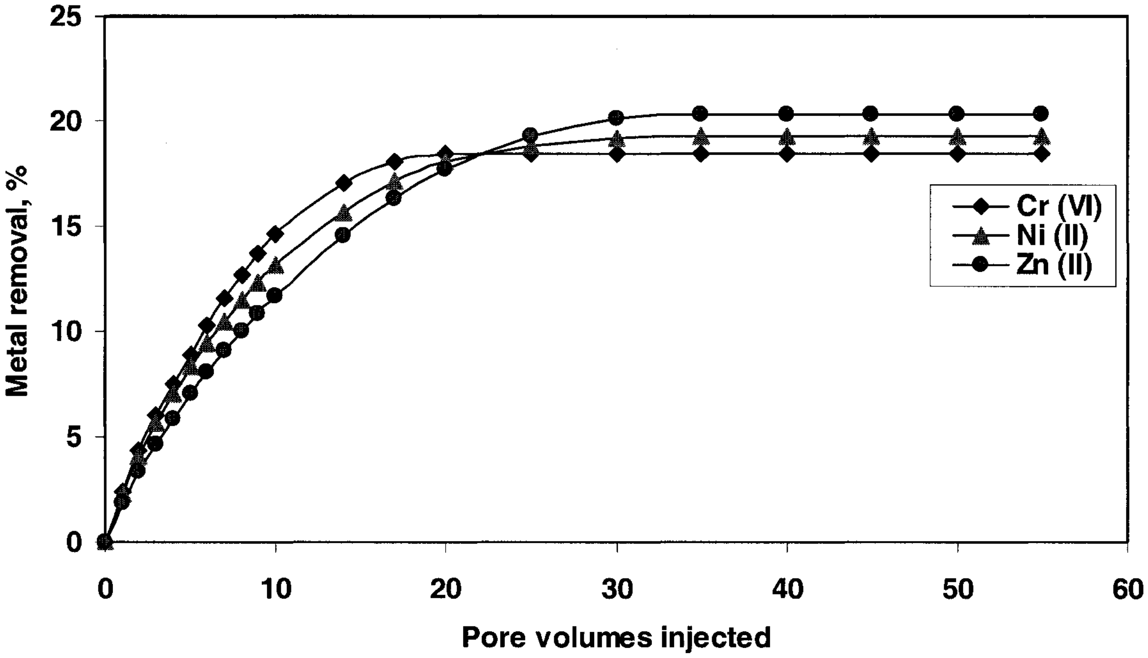

Figure 5-14a. Cumulative metal removal efficiencies by water.

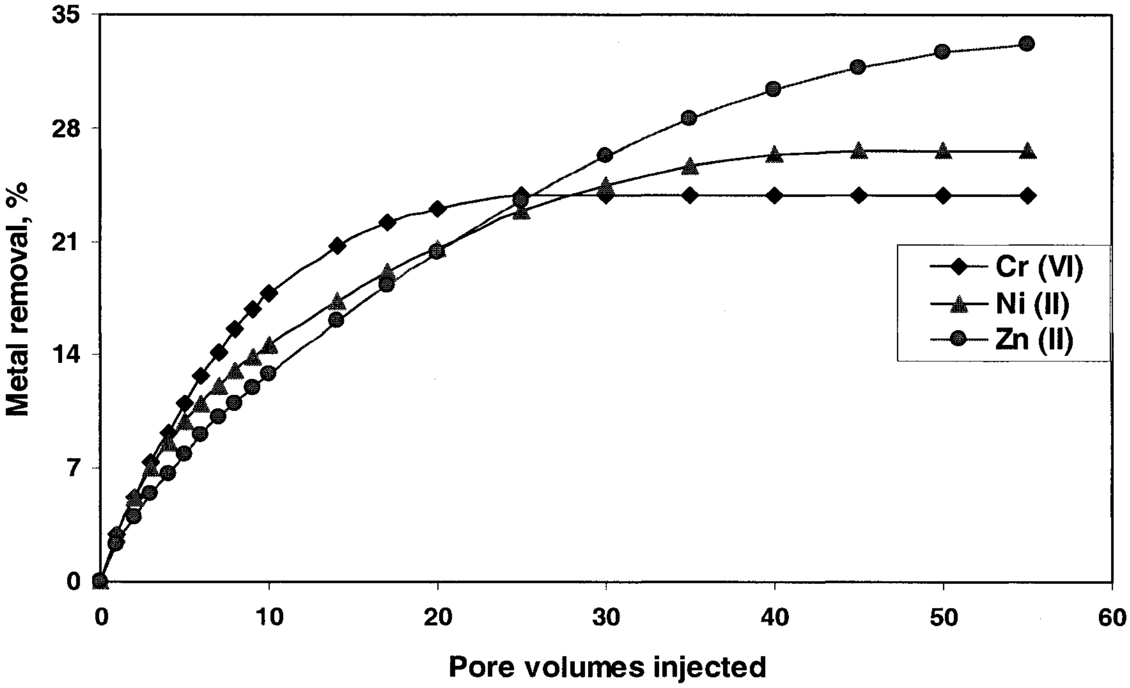

Figure 5-14b. Cumulative metal removal efficiencies by 10mM SDS.

5.3.2 Column Test Results Using Complexing Agent

Fig. 5-15 to Fig.5-17 show the metal removal rate by 7.5mM EDTA only and 10mM SDS with 7.5 mM EDTA. The results of these studies are outlined in Tables B-3 and B-4. For the case where SDS with EDTA is used, the maximum effluent concentration is 3.65mg/L for Cr (VI) at the15th pore volume, 21.2mg/L for Ni (II) at the12th pore volume and 32.75mg/L for Zn (II) at the 9th pore volume. When, only EDTA is used, the maximum concentration is 2.95mg/L for Cr (VI) at the 15th pore volume, 17.9 mg/L for Ni (II) at the 12th pore volume and 27.7mg/L for Zn (II) at the 11th pore volume. These indicates that Cr (VI), Ni (II) and Zn (II) removal in the effluent by surfactant with complexing agent is about 1.24, 1.18 and 1.18 times higher than that observed for the complexing agent alone, respectively. This indicates that two different mechanisms may be present for maximum metal removal in the combined systems of SDS and EDTA. The first is the formation of metal-EDTA complex; the second is the solubilization of the metal-EDTA complex into the micellar core of SDS. Hence, there is no rapid increase in the removal of metal in the earlier phases of injection. A pink coloration of the effluent was noted in the early phase of injection. This was caused by the formation of Cr (VI)-EDTA complex occurring during the earlier phases of injection. Ni (II) and Zn (II) also cormbined to form a complex as with EDTA. However, they were not discernible because of the formation of colorless complexes. However, the removal efficiency of both systems (EDTA with and without SDS) again starts to decrease at 15 pore volumes for Cr (VI), at 12 pore volumes of Ni (II) and at about 10 pore volumes for Zn (II). Probably this is due to the diminishing solubilization potential of SDS micelles.

Fig. 5-15 and Fig.5-16 also show that the peak concentration of Zn (II) removal occurs at an earlier stage of pore volumes than for the Ni (II) and Cr (VI). Also Ni (II) reaches a peak earlier than Cr (VI). This means that Zn (II) is less strongly bound than Cr (VI) and Ni (II) to the soil matrix and gets removed more easily. One also notes the fact that Zn (II) has less electronegativity, higher atomic weight and bigger ionic radius that the Cr (VI) and Ni (II).

Fig.5-17a and Fig.5-17b are derived from Fig.5-15 and Fig.5-16 respectively. It shows that the addition of EDTA to SDS does improve metal removal efficiency, as expected. However, at the injection of 50 pore volumes in column tests, removal efficiency increases from 46.1 % to 57.3 % for Cr (VI), 51.3 % to 67.5 % for Ni (II) and 58.5 % to 70.8 % for Zn (II).

In the batch system, addition of EDTA enhanced metal extraction from 43.9 % to 72.5 % for Cr (VI), 65.8 % to 87.0 % for Ni (II) and 74.3 % to 97.6 % for Zn (II) [Table A-5]. Hence, the enhancement in removal efficiency in column tests is clearly less than that in the batch systems.

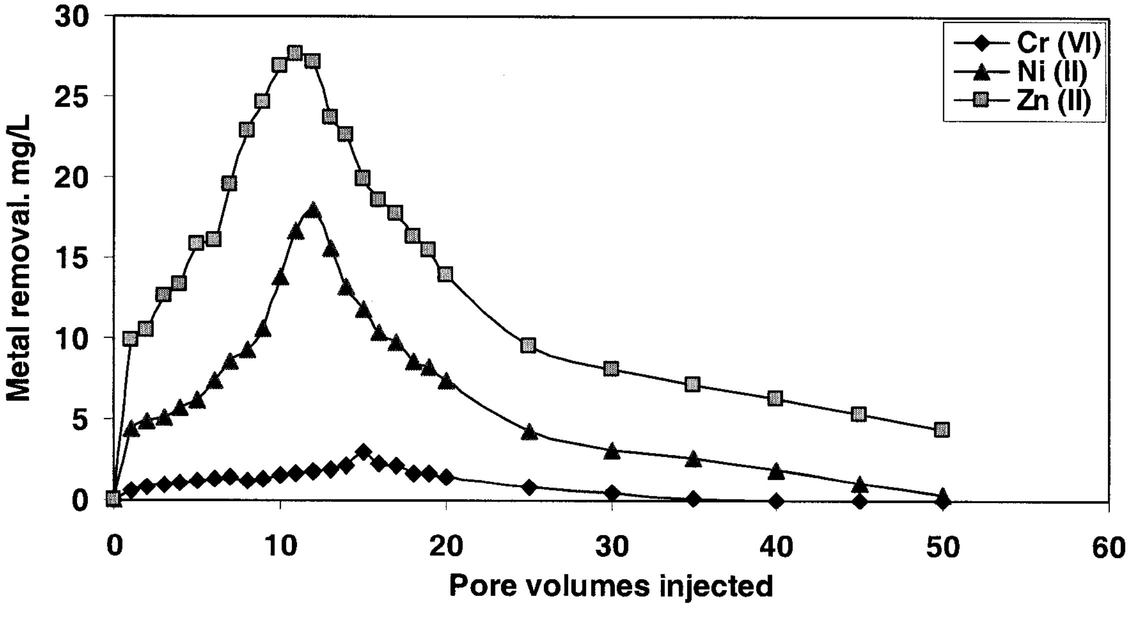

Figure 5-15. Removal of metal from column by 7.5mM EDTA.

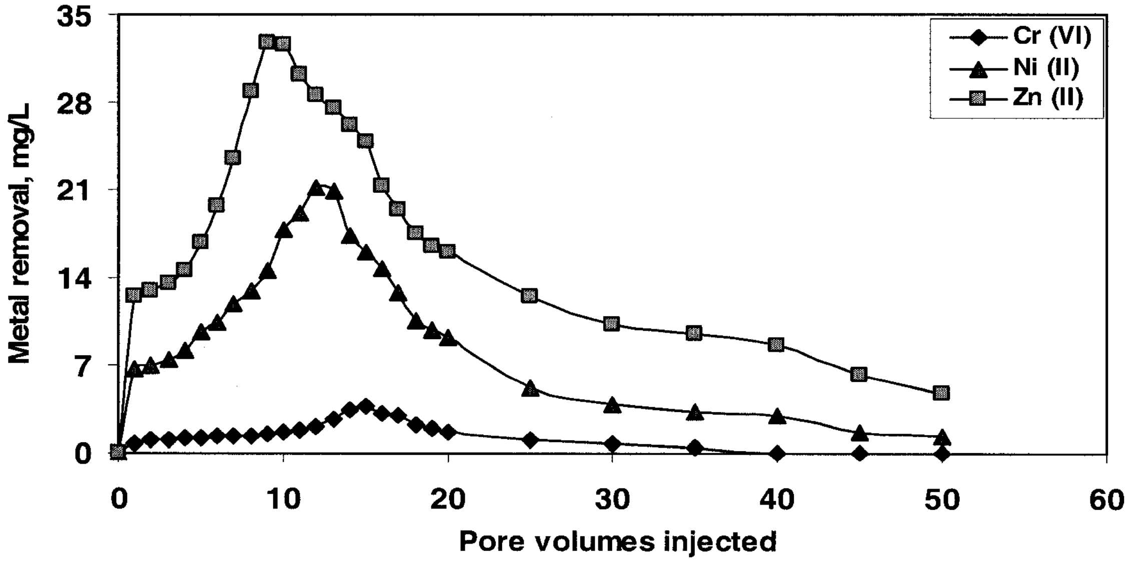

Figure 5-16. Removal of metal from column by 10mM SDS with 7.5mM EDTA

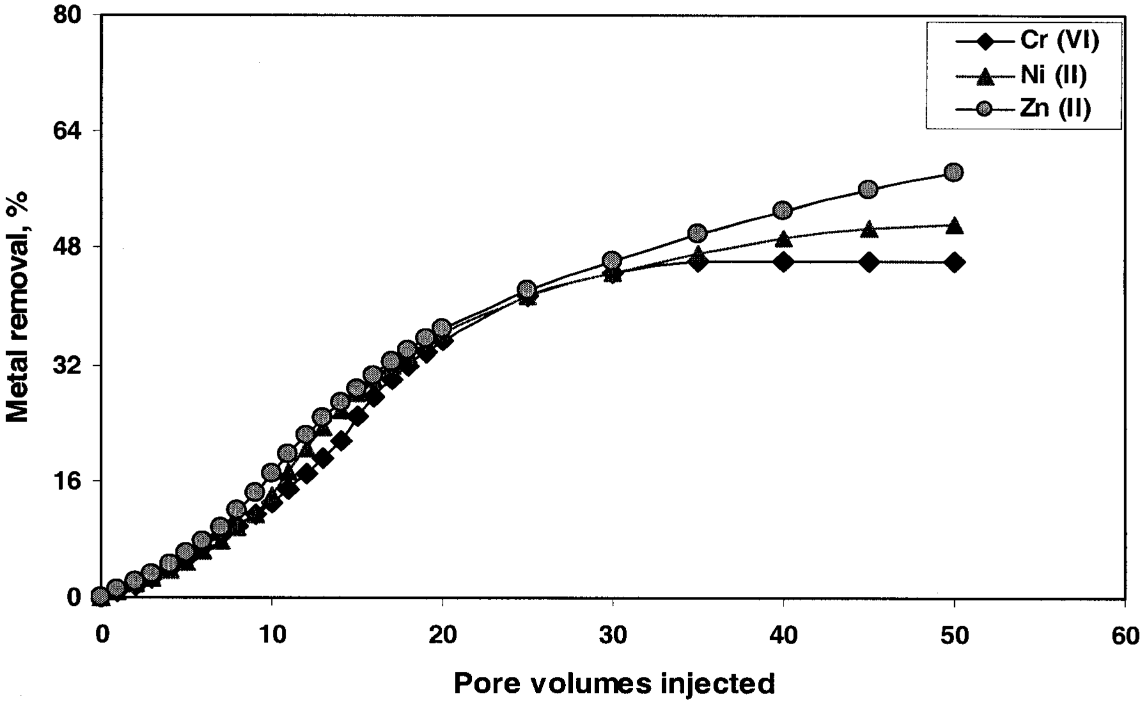

Figure 5-17a. Cumulative metal removal efficiencies by 7.5mM EDTA

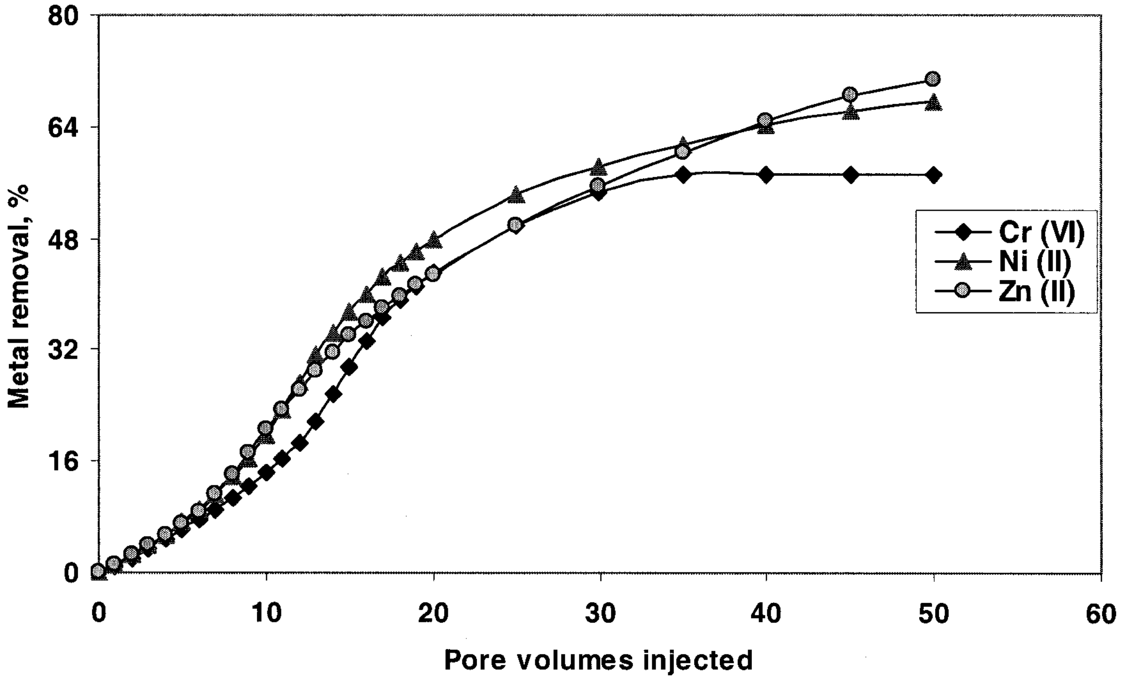

Figure 5-17b. Cumulative metal removal efficiencies by 10mM SDS with 7.5mM EDTA

5.3.3 Effect of Interruption in Injecting the Solvent

When the metal concentrations in the effluent were negligible, the injection of the solution was stopped. After 2 weeks of interruption, the pumping of the original SDS with EDTA was resumed. Fig. 5-18 and Table B-4 show that effluent metal concentrations increase drastically, when the test was resumed at the 50 pore volume level. The metal concentrations in the column effluent increased from 0 mg/L to 2.30 mg/L for Cr (VI), 1.40 mg/L to 13.7 mg/L for Ni (II) and 4.70 mg/L to 12.6 mg/L for Zn (II) after the flow interruption. Injecting 10 more pore volumes, 16.3 % more Cr (VI), 14.3 % more Ni (II) and 6.90 % more Zn (II) were removed. This is probably due to the fact that the increased residence times allowed the solvent to reach in the micro-pore spaces of the soils to diffuse the lattice-bound metals and release them.

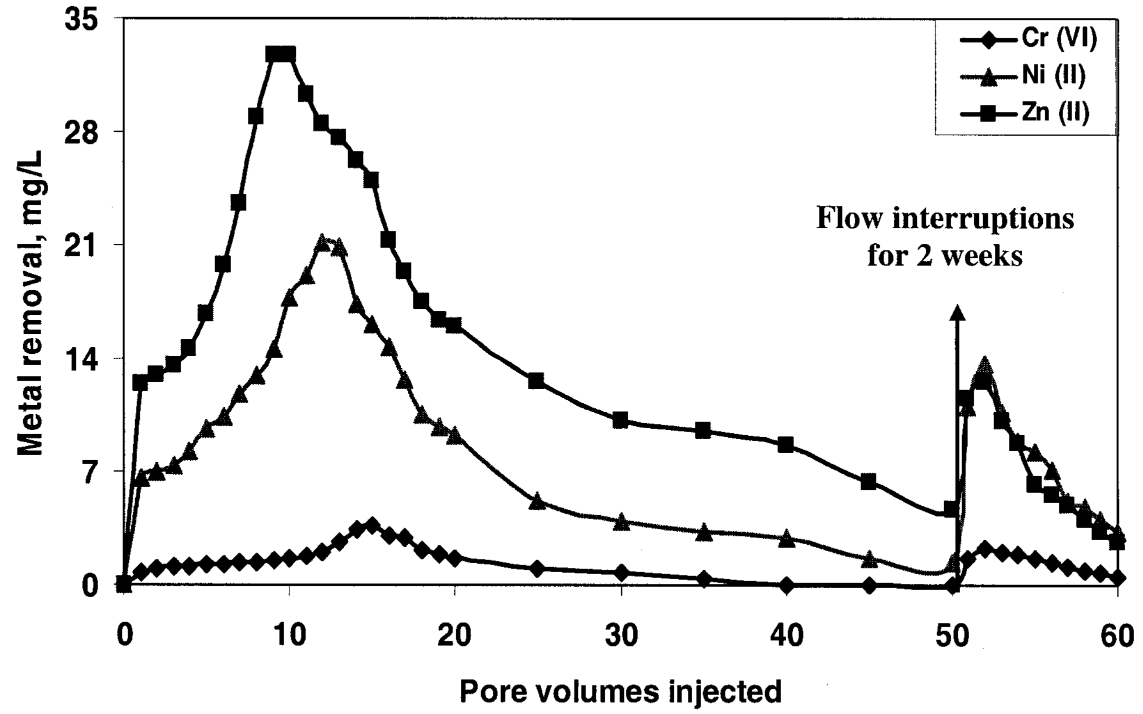

Figure 5-18. Removal of metal by10mM SDS with 7.5mM EDTA after flow being interrupted for 2 weeks.

5.3.4 Effect of Flow Rate

The flow rate through the column was varied over a range of 4 to 40mL/min using the fixed solution SDS (10mM) together with EDTA (7.5mM). The time of pumping varied from 20 hours to 2 hours. Fig.5-19 illustrates Zn (II) removal at different flow rates and table B-5 provides the additional data related to the tests.

Approximately, 78.3 %, 70.8 % and 60.5 % of Zn (II) was removed at the flow rate of 40mL/min, 12mL/min and 4mL/min respectively. Highest removal of Zn (II) appears at the higher flow rate of 40mL/min. Hence, it is clear that higher flow rate is desirable for the removal of heavy metals. This may be attributed to the higher fluid shear and increased dispersion of the metal in the soil media at higher flow rates.

The results demonstrated that the fastest flow rate performed better in washing efficiency tests. Operation at higher possible flow rate is recommended to extract the metal contaminants to minimize the treatment time. The column tests related to the flow rate may be further verified to ensure the trends seen in Fig. 5-19.

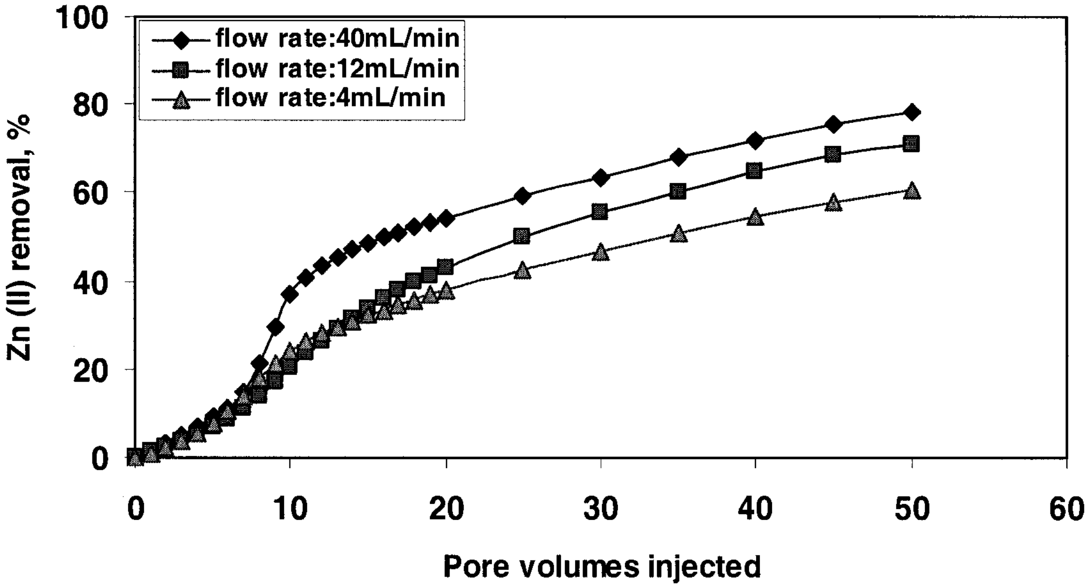

Figure 5-19. Removal of Zn (II) at different flow rates [solvent: 10mM SDS with 7.5mM EDTA].

5.3.5 Effect of pH

Desorption of metals depends to a great extent on the solution pH. Alloway (1990) notes that hydrogen ions are strongly attached to the negative charges of the soil surface, and they have the power to replace most of the cations. He showed that, activity of Zn^{2+} and solution pH have the following relation:

$$\text{Log } Zn^{2+} = 5.8 - 2\text{pH}$$

It describes that activity of Zn^{2+} in the solution is directly proportional to the square of the proton activity. This means that activity of Zn^{2+} increases with decreasing pH of the solution. However at low concentrations, activity is equal to the concentration.

In batch tests, final pH is the pH value noted after shaking the contaminated soil with either water or surfactants for 24 hours before conducting the AA analysis of the supernatant. Fig. 5-5 to Fig. 5-7 represented that extractions of metals are affected by the final pH. In case of SDS, the removal rate of metals is 19.8 % for Cr (VI), 44.6 % for Ni (II) and 56.8 % for Zn (II) at the final pH of 6.68. In case of EDTA, the removal rate of metals is 43.9 % for Cr (VI), 65.8 % for Ni (II) and 74.3 % for Zn (II) at the final pH of 4.57. However, the mixture of SDS and EDTA can remove 72.5 % of Cr (VI), 87.0 % of Ni (II) and 97.6 % of Zn (II) at the final pH of 5.47. This result shows that removal rate of metals is more at lower pH values. This effect is also occurs in the tests with other two surfactants AOT and Tx-100.

In column tests, Fig.5-20 shows that in the beginning, as the pore volumes increases, pH increases with the increase of effluent concentrations of metal. This is probably due to the fact that, hydrogen ions replace early most of the loosely bound metal fractions from the soil column. After maximum effluent concentrations of metal, pH generally drops till the pore volumes 50. The strongly bound metals are released slowly.

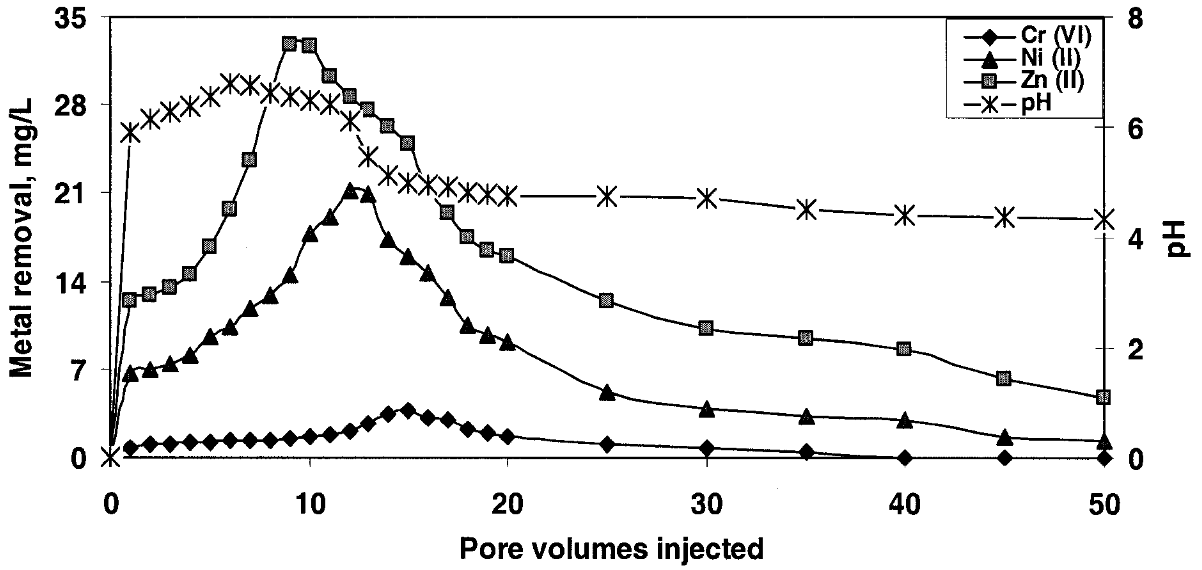

Figure 5-20. Effect of pH on metal removal from column [solvent: 10mM SDS with 7.5mM EDTA].

Chapter 6

Conclusions and Recommendations

6.1 Summary

The purpose of this study was to evaluate the potential of surfactant systems for enhancing the remediation of Cr (VI), Ni (II) and Zn (II) contaminated sandy soils. The sandy soil was selected to ensure that external factors present in natural soils did not unduly influence the adsorption-desorption processes related to interference and competition. For field applications, the specific natural soil should be used for tests. The results of the controlled experiments with the sandy soil can be used as a guideline for this purpose. The study demonstrated that surfactants can remove the adsorbed metals by ion exchange and or precipitation-dissolution mechanisms, and metal extraction is further enhanced when a complexing agent is used with surfactants. This hypothesis was evaluated through the batch and column tests. Based on the results of the study, the following conclusions and recommendations are made.

6.2 Conclusions

1. In batch systems, metal extraction from soils by surfactants increased with increase in surfactant concentrations, and remained generally constant above the CMC. Batch extraction studies showed that the surfactant SDS is more effective in metal extraction from soil than surfactant AOT and Tx-100. Cr (VI), Ni (II) and Zn (II) extractions by 10mM SDS were respectively 3.00, 4.13 and 2.88 times higher than metal extraction by distilled water alone.

2. Batch extraction studies also showed that addition of 7.5mM EDTA to 10 mM SDS was the optimal system for the extraction of Cr (VI), Ni (II) and Zn (II). This system

was able to remove 72.5 % of Cr (VI), 87.0 % of Ni (II) and 97.6 % of Zn (II). The acidic nature (initial pH = 4.24) of this system is another reason for higher efficiency of metal removal.

3. Metal adsorption and desorption in the soil matrix are affected due to their interaction and competition. In the presence of Cr (VI) and Zn (II), the retention of Ni (II) in the soil gets reduced by about 46.2 %. The retention of Zn (II) in soil gets reduced by about 16.2 % in the presence of Cr (VI) and Ni (II). Cr (VI) has a marginal retention affinity to the soil adsorption sites in the presence of Ni (II) and Zn (II).

4. The study suggests that ion exchange is the dominant mechanism for the extraction of Cr (VI) and counterion binding in the possible mechanism for the extraction of Ni (II) and Zn (II).

5. SDS was found to be the most effective surfactant for the extraction of metal in batch studies. Hence, it was selected for tests in column studies.

6. In cases involving distilled water and SDS, the effluent concentration of all three metals were very high for the first 3 pore volumes. The maximum effluent concentration of metals for the case of EDTA with or without SDS was in the range of 9 to 15 pore volumes of injection. SDS with EDTA was also the effective surfactant system to remediate metals in column tests.

7. Column tests indicate that pH generally rises to begin with and drops with increasing pore volumes of the surfactant system used.

8. Metal elution rate in column tests increased with an increase in flow rate. This was possibly due to the higher fluid shear and increased dispersion of the metal in the soil media.

6.3 Recommendations for further studies

1. Effective use of surfactant to extract heavy metal from soils other that Cr (VI), Ni (II) and Zn (II) may be investigated.

2. Since field soils contain both organic and inorganic contaminants, their simultaneous removal using surfactant may be studied.

3. Based on the results of adsorption and desorption studies involving surfactants, the development of a predictive mathematical model is desirable.

References

Ahmadi, S., Huang, Yi-C., Batchelor, B., Koseoghu, S.S. 1995. " Binding of Heavy Metals to Derivatives of Cholesteral and Sodium dodecyl sulfate". J. Environmental Engineering. 121, pp. 645-652

Ahmed, I. 2005. "Heavy Metal Contamination of Soil", Problems and Remedies. Science Publishers, Inc. U.S.A.

Alloway, B.J. 1990. "Heavy Metals in Soils". John Wiley & Sons, Inc. New York.

Anderson, W.C. and Dee, P.E.1993. "Innovative Site Remediation Technology", Soil Washing/Soil Flushing. American Academy of Environmental Engineers.

Bedient, P.B., Rifai, H.S. and Newell, R.C. 1994. " Groundwater Contamination, Transport and Remediation" Prentice Hall, U.S.A.

Benefield, L.D., Judkins, J.F. and Weand, B.L. 1982. " Process Chemistry for Water Wastewater Treatment". Prentice-Hall, Englewood cliffs, N.J.

Cheah, E., Reible, D.D., Valsaraj, K.T., Constant, W.D., Walsh, B.W. and Thibodeaux, L.J. 1998. "Simulation of Soil Washing with Surfactant". J. Hazardous Materials. 59, pp.107-122.

Chiou, C.T., Kile, D.E., Brinton, T.I., Malcolm, R.L., Leenheer, J.A. and Maccarthy, P. 1987. "A Comparison of Water Solubility Enhancements of Organic Solutes by Aquatic Humic Materials and Commercial Humic Acids." Environmental Science and Technology. 21, pp 1231-1245.

Chu, W. 2003. "Remediation of Contaminated Soils by Surfactant Aided Soil Washing". Practice periodical of hazardous, toxic, and radioactive waste management. 7, pp 19-24.

Connor, S.C., Lepp, N.W., Edwards, R. and Sunderland, R. 2003. " The Combined Use of Electrokinetic Remediation and Phytoremediation to Decontaminate Metal-Polluted Soils". Environmental Monitoring and Assessment. 84. pp 141-158.

Davis, A.P. and Inderbir Singh. 1995. "Washing of Zinc (II) from Contaminated Soil Column". J. Environmental Engineering. 121, pp. 174-18.

Deuren, J.V., Lloyd, T., Chhetry, S., Liou, R. and Pee, J. 2002. "Remediation Technologies Screening Matrix and Reference Guide". 4th Edition. Source, www.frtr.gov/matrix2/section4.

Drew Myers. 2006. "Surfactant Science and Technology". John Wiley & Sons, Inc. U.S.A.

Doong. R.A., Wu, Y.W. and Lei, W.G. 1998. “Surfactant Enhanced Remediation of Cadmium Contaminated Soils”. Water Science and Technology. 37, pp.65-71.

Duffield, A.R., Ramamurthy, A.S. and Campanelli, J.R. 2003. “Surfactant Enhanced Mobilization of Mineral Oil within Porous Media”. Water, Air and Soil Pollution. 143, pp 111-122.

Edwards, D.A., Adeel, Z. and Luthy, R.G. 1994. “Distribution of Nonionic Surfactant and Phenanthrene in a Sediment/Aqueous System”. Environmental Science and Technology. 28, pp 1550-1560.

Faisal I. Khan, Tahir Husain and Ramzi Hejazi. 2004. “An overview and Analysis of Site Remediation Technologies”. J. Environmental Engineering. 71, pp 95-122.

Gadelle, F., Wan, J. and Tokunaga, T.K. 2001. “ Remediation of Uranium (VI) from Contaminated Sediments by Surfactants” J. Environmental Quality. 30, pp.470-478

Gomes, P.C., Fontes, M.P.F., Silva, A.G., Mendonea, E.S. and Netto, A.R. 2001. “Selectivity Sequence and Compititive Adsorption of Heavy-Metals by Brazilian Soils”. Soil Science SOC. Am.J. 47, pp 47-51.

Griffiths, R.A. 1995. " Soil- Washing Technology and Practice". J. Hazardous Materials. 40, pp 175-189.

Grim, R.E. 1962. "Applied Clay Mineral". McGraw-Hill, New York.

Gzara, L. and Dhahbi, M. 2001. "Removal of Chromate anions by Micellar-Enhanced Ultrafiltration using Cationic Surfactant". Elsevier Science. Desalination. 137, pp241-250.

Huang, C., Van Benschoten, T.C., Healy, T.C. and Ryan, M.E. 1997. " Feasibility Study of Surfactant Use for Remediation of Organic and Metal Contaminated Soils". J. Soil Contamination. 6, pp 537-556.

James, B.R. 1996. "The Challenge of Remediating Chromium-Contamianted Soils. Environmental Science and Technology. 30, pp 248-262

Khodadoust, A.P., Reddy, K.R. and Maturi, K. 2004. "Removal of Nickel and Phenanthrene from Kaolin Soil using Different Extractants". Environmental Engineering Science. 21, pp 692-704.

Khodadoust, A.P., Reddy, K.R. and Maturi, K. 2005. "Effect of Different Extracting agents on Metal and Organic Contaminant Removal from a Field Soil". J. Hazardous Materials. 117, pp15-24.

Krishna R. Pagilla and Canter, L.W. 1999. “Laboratory Studies on Remediation of Chromium Contaminated Soils”. J. Environmental Engineering. 125, pp 243-248.

Lim, T.T., Joo-Hwa, Jing-Yuan Wang. 2004. “ Chelating Agent Enhanced Heavy Metal Extraction from a Contaminated Acidic Soil”. J. Environmental Engineering. 130, pp 59-66.

Lin, Su-Hsia and Juang, R.S. 2002. “Heavy Metal Removal from Water by Sorption Using Surfactant-Modified Montmorillonite”. J. Hazardous Materials 92, pp 315-326.

Merian, E. 1991. “Metals and their Compounds in the Environment”. Germany.

Mulligan, C.N. 1998. “On the Capability of Biosurfactants for the Removal of Heavy Metals from Soil and Sediments”. PhD. thesis. McGill University, Montral, Quebec.

Mulligan. C.N., Yong, R.N. and Gibbs, B.F. 2001a. “Heavy Metal Removal from Sediments by Biosurfactants”. J. Hazardous Materials. 85, pp 111-125.

Mulligan. C.N., Yong, R.N. and Gibbs, B.F. 2001b. “Surfactant Enhanced Remediation of Contaminated Soil: a review”. Engineering Geology. 60, pp 371-380.

Myers, D. 2006. “ Surfactant Science and Technology” John Wiley & Sons, Inc. New Jersey.

Nazaroff, W.W. 2001. “Environmental Engineering and Science”. John Wiley & Sons, Inc. U.S.A.

Nivas, B.T., Sabatini, D.A., Shiau, B. and Harwell, J.H. 1996. “Surfactant-Enhanced Remediation of Subsurface Chromium Contamination”. Water research. 30, pp 511-520

Puls, R.W., D.A. Clark, C.J.Paul and J. Vardy. 1994. “Transport and Transformation of Haxavalent Chromium through Soils and into Groundwater”. J. Soil Contamination. 3, pp 203-224.

Pump, H.H. and Krist, H. 1998. “Laboratory Mannual for the Examination of Water, Wastewater and Soil”. VCH Publishers. Pp154.

Rosen, M.J. 1989. “ Surfactant and Interfacial Phenomena”. Wiley-Interscience, 2nd Edition, New York

Roundhill, D.M. 2001. “Extraction of Metals from Soils and Waters”. Kluwer Academic/Plenum Publishers, New York.

Sabatini, D.A., Knox, R.C. and Harwell, J.H. 1995. “ Surfactant-Enhanced Subsurface Remediation”, Emerging Technologies. American Chemical Society (ACS) Symposium Series 594.

Sinex, C.A. 2004. “EDTA – A Molecule with a Complex Story”. Source, www.chm.bris.ac.uk/motm/edtah.htm.

Shin, M. and Barrington, S. 2005. “Effectiveness of the iodide ligand along with two surfactants on desorbing heavy metals with soils”. Water, Air And Soil Pollution. 161, pp 193-208.

Smith, L.A., Means, L.J., Chen, A., Atteman, B., Chapman, C.C., Tixier, S.J., Brauning, S.E., Gavaskar, A.R. and Royer, M.D. 1995. “Remedial Options for Metals Contaminated Sites”. Lewis Publishers. CRC press, Inc.

Tan, K.H. 1998. “Principles of Soil Chemistry”. Marcel Dekker, Inc. U.S.A.

Watts, R.J. 1997. “Hazardous Wastes”. Sources, Pathways, Receptors. John Wiley & Sons, Inc. New York.

West, C.C. and Harwell, J.H. 1992. “Surfactant and Subsurface Remediation”. Environmental Science and Technology. 26, pp 2324-2330.

Yaron, B., R. Calvet and R. Prost. 1996. “Soil pollution, Process and Dynamics”. Scientific publishing services Ltd. Madras.

Yurlova, L., Kryvoruchko, A. and Kornilovich, B. 2002. " Removal of Ni (II) ions from Wastewater by Micellar-Enhanced Ultrafiltration. Elsevier. Desalination. 144, pp 255-260.

Yong, R.N. 1992. " Principles of Contaminant Transport in Soils". Elsevier Science Publishers. Netherlands.

Appendix A

Results of Batch Extraction Studies

Table A-1. Extraction of metals by SDS

No	Surfactant concn. mM	Surfactant concn. CMC (units)	Cr (VI) removal mg/L	Ratio to Cr (VI) removal by water	Ni (II) removal mg/L	Ratio to Ni (II) removal by water	Zn (II) removal mg/L	Ratio to Zn (II) removal by water	Initial pH	Final pH
1	0	0.00	0.15	1.00	1.50	1.00	5.20	1.00	5.52	6.24
2	1	0.12	0.20	1.33	2.90	1.93	11.8	2.27	5.58	6.30
3	4	0.49	0.30	2.00	3.35	2.23	12.5	2.40	5.62	6.38
4	8	0.98	0.45	3.00	5.95	3.97	14.6	2.79	5.67	6.52
5	10	1.22	0.45	3.00	6.20	4.13	14.9	2.88	5.72	6.68
6	16	1.95	0.35	2.33	6.00	4.00	14.0	2.69	5.87	6.75
7	32	3.90	0.35	2.33	5.10	3.40	13.1	2.52	5.98	6.70
8	50	6.09	0.30	2.00	3.20	2.13	12.9	2.47	6.13	6.72

Soil to Solution Ratio. [5g : 40 mL]

Table A-2. Extraction of metals by AOT

No	Surfactant concn. mM	Surfactant concn. CMC (units)	Cr (VI) removal mg/L	Ratio to Cr (VI) removal by water	Ni (II) removal mg/L	Ratio to Ni (II) removal by water	Zn (II) removal mg/L	Ratio to Zn (II) removal by water	Initial pH	Final pH
1	0	0.00	0.15	1.00	1.50	1.00	5.20	1.00	5.42	6.24
2	0.25	0.22	0.15	1.00	2.65	1.77	11.1	2.13	5.80	6.26
3	0.50	0.45	0.20	1.33	3.00	2.00	11.6	2.23	5.95	6.30
4	1	0.89	0.25	1.67	3.45	2.30	12.4	2.38	5.90	6.32
5	1.25	1.12	0.35	2.33	4.85	3.23	13.9	2.66	6.20	6.41
6	2.50	2.23	0.30	2.00	4.50	3.00	13.5	2.60	6.25	6.56
7	5	4.46	0.25	1.67	4.60	3.06	12.2	2.35	6.58	6.96
8	10	8.93	0.25	1.67	4.00	2.67	12.0	2.31	6.76	7.30
9	20	17.9	0.25	1.67	4.00	2.67	11.9	2.30	7.10	7.56

Soil to Solution Ratio. [5g : 40 mL]

Table A-3. Extraction of metals bv Tx-100

No	Surfactant concn. mM	Surfactant concn. CMC (units)	Cr (VI) removal mg/L	Ratio to Cr (VI) removal by water	Ni (II) removal mg/L	Ratio to Ni (II) removal by water	Zn (II) removal mg/L	Ratio to Zn (II) removal by water	Initial pH	Final pH
1	0	0.00	0.15	1.00	1.50	1.00	5.20	1.00	5.42	6.24
2	0.025	0.12	0.15	1.00	2.60	1.73	7.55	1.45	5.20	6.28
3	0.10	0.49	0.20	1.33	2.80	2.86	8.70	1.67	5.22	6.28
4	0.25	0.98	0.30	2.00	3.00	2.00	9.10	1.75	5.30	6.31
5	0.50	1.22	0.25	1.67	3.05	2.03	8.90	1.71	5.46	6.35
6	1	1.95	0.25	1.67	3.00	2.00	8.50	1.63	5.51	6.40
7	8	3.90	0.25	1.67	2.70	2.00	8.50	1.63	5.66	6.52

Soil to Solution Ratio. [5g : 40 mL]

Table A-4. Extraction of metals by EDTA

No	EDTA concentration mM	Cr (VI) removal, mg/L	Ni (II) removal, mg/L	Zn (II) removal, mg/L	Percentage removal of metals			Initial pH	Final pH
					Cr (VI)	Ni (II)	Zn (II)		
1	0	0.15	1.50	5.20	6.58	10.8	19.8	5.42	6.24
2	1	0.30	2.00	6.50	13.2	14.4	24.7	4.42	5.54
3	2.5	0.45	4.05	10.5	19.8	29.1	39.9	4.20	5.10
4	5	0.95	8.65	18.4	41.7	62.2	69.9	3.50	4.83
5	7.5	1.00	9.15	19.6	43.9	65.8	74.3	3.26	4.57
6	10	1.20	9.50	19.8	52.7	68.3	75.2	3.10	4.42
7	12.5	1.25	9.95	20.2	54.9	71.6	76.8	3.00	4.37
8	15	1.30	10.2	20.6	57.1	72.9	78.3	2.85	4.20

Soil to Solution Ratio. [5g : 40 mL]

Table A-5. Comparison of metal extractions by D.I. water, surfactant, EDTA and surfactant with EDTA

NO	Surfactant concentration mM	Cr (VI) removal, mg/L	Ni (II) removal, mg/L	Zn (II) removal, mg/L	Percentage removal of metals			Initial pH	Final pH
					Cr(VI)	Ni(II)	Zn(II)		
1	Distilled Water	0.15	1.50	5.20	6.58	10.8	19.8	5.42	6.24
2	10 mM SDS	0.45	6.20	14.9	19.8	44.6	56.8	5.72	6.68
3	1.25mM AOT	0.35	4.85	13.9	15.4	34.9	52.6	6.20	6.41
4	0.25mM Tx- 100	0.30	3.00	9.10	13.2	21.6	34.6	5.30	6.31
5	7.5mM EDTA	1.00	9.15	19.6	43.9	65.8	74.3	3.26	4.57
6	10mM SDS + 7.5mM EDTA	**1.65**	**12.1**	**25.7**	**72.5**	**87.0**	**97.6**	4.24	5.47
7	1.25mM AOT + 7.5mM EDTA	1.15	11.6	24.6	50.5	83.4	93.5	4.29	5.40
8	0.25mM Tx-100 + 7.5mM EDTA	1.25	10.9	21.6	54.9	78.0	82.0	4.26	5.43

Soil to Solution Ratio. [5g : 40 mL]

Sample Calculation for Row 1.
Cr (VI) removal = 0.15 mg/L x 40mL ÷ 5g soil x 18.21mg/kg soil = 6.58 %
NI (II) removal = 1.50 mg/L x 40mL ÷ 5g soil x 111.38mg/kg soil = 10.77 %
Zn (II) removal = 5.20 mg/L x 40mL ÷ 5g soil x 210.45mg/kg soil = 19.76 %

Appendix B

Results of Column Extraction Studies

One Pore Volume (PV) = 95 mL

Tables B-1. Removal of metals by distilled water

Flow Rate = 12 mL/min

PV	Cr (VI) removal (mg/L)	Cr (VI) removal percent, %	Ni (II) removal (mg/L)	Ni (II) removal percent, %	Zn (II) removal (mg/L)	Zn (II) removal percent, %	pH
0	0.00	0.00	0.00	0.00	0.00	0.00	---
1	**2.15** [a]	**2.44** [a]	12.7	2.36	18.5	1.81	6.31
2	**1.70** [b]	**4.37** [b]	9.45	4.11	15.0	3.30	6.32
3	1.45	6.02	8.30	5.65	13.8	4.65	6.29
4	1.30	7.50	7.45	7.04	12.3	5.87	6.33
5	1.25	8.92	6.75	8.29	11.7	7.01	6.35
6	1.20	10.3	6.00	9.41	11.1	8.10	6.37
7	1.15	11.6	5.80	10.5	10.0	9.08	6.39
8	1.00	12.7	5.35	11.5	9.25	9.99	6.35
9	0.90	13.8	4.75	12.4	8.95	10.9	6.51
10	0.75	14.6	4.05	13.1	8.15	11.7	6.55
14	0.45	17.0	3.10	15.7	6.75	14.6	6.73
17	0.20	18.0	2.30	17.1	5.40	16.3	6.86
20	0.10	18.5	1.35	18.0	4.30	17.7	7.03
25	0	18.5	0.50	18.8	2.85	19.3	7.12
30	0	18.5	0.25	19.1	1.05	20.1	7.13
35	0	18.5	0	19.2	0.15	20.3	7.15
40	0	18.5	0	19.2	0	20.3	7.15
45	0	18.5	0	19.2	0	20.3	7.15
50	0	**18.5**	0	**19.2**	0	**20.3**	7.15

Sample Calculation for Rows 2&3:

$(2.15 mg/L \times 95 mL) \div (459.18 g\ soil \times 18.21 mg/kg\ soil) = 2.44\ \%^{a}$

$2.44\ \%^{a} + (1.70 mg/L \times 95 mL) \div (459.18 g\ soil \times 18.21 mg/kg\ soil) = 4.37\ \%^{b}$

Tables B-2. Removal of metals by 10mM SDS

Flow Rate = 12 mL/min

PV	Cr (VI) removal (mg/L)	Cr (VI) removal percent, %	Ni (II) removal (mg/L)	Ni (II) removal percent, %	Zn (II) removal (mg/L)	Zn (II) removal percent, %	pH
0	0.00	0.00	0.00	0.00	0.00	0.00	---
1	2.55	2.89	15.9	2.94	23.7	2.32	5.12
2	2.05	5.23	12.3	5.23	17.4	4.03	5.14
3	1.85	7.33	9.55	7.00	14.1	5.41	5.18
4	1.70	9.26	8.45	8.57	13.3	6.71	5.26
5	1.60	11.1	7.15	9.90	12.2	7.91	5.30
6	1.45	12.7	6.10	11.0	11.8	9.06	5.33
7	1.30	14.2	5.65	12.1	10.9	10.1	5.35
8	1.25	15.6	5.15	13.0	9.65	11.1	5.41
9	1.05	16.8	4.80	13.9	9.30	11.9	5.45
10	0.85	17.8	4.15	14.7	9.00	12.8	5.53
14	0.55	20.7	3.30	17.3	7.75	16.1	5.62
18	0.30	22.5	2.75	19.6	7.15	18.9	5.68
20	0.25	23.1	2.75	20.6	7.00	20.4	5.74
22	0.15	23.5	2.55	21.6	6.75	21.7	5.83
25	0.10	23.9	2.10	22.9	5.90	23.5	5.88
30	0	23.9	1.45	24.5	5.50	26.3	5.95
35	0	23.9	1.05	25.7	4.35	28.6	6.00
40	0	23.9	0.55	26.4	3.10	30.4	6.22
43	0	23.9	0.15	26.6	2.60	31.2	6.37
45	0	23.9	0	26.6	2.20	31.7	6.48
50	0	23.9	0	26.6	1.75	32.7	6.56
55	0	**23.9**	0	**26.6**	0.40	**33.2**	6.58

Tables B-3. Removal of metals by 7.5 mM EDTA

Flow Rate = 12 mL/min

PV	Cr (VI) removal (mg/L)	Cr (VI) removal percent, %	Ni (II) removal (mg/L)	Ni (II) removal percent, %	Zn (II) removal (mg/L)	Zn (II) removal percent, %	pH
0	0.00	0.00	0.00	0.00	0.00	0.00	---
1	0.60	0.68	4.45	0.83	9.85	0.96	5.62
2	0.85	1.65	4.90	1.74	10.5	2.00	5.61
3	1.00	2.78	5.10	2.68	12.6	3.24	5.65
4	1.05	3.98	5.70	3.74	13.3	4.55	5.71
5	1.20	5.34	6.15	4.88	15.8	6.10	5.85
6	1.30	6.82	7.35	6.25	16.1	7.68	6.00
7	1.45	8.46	8.55	7.83	19.6	9.60	5.63
8	1.25	9.88	9.30	9.56	22.9	11.9	5.58
9	1.30	11.4	10.6	11.5	24.7	14.3	4.50
10	1.50	13.1	13.8	14.1	26.9	16.9	5.17
11	1.65	14.9	16.7	17.2	27.7	19.6	4.93
12	1.80	16.9	17.9	20.5	27.2	22.3	4.80
13	1.90	19.1	15.6	23.4	23.7	24.7	4.68
14	2.20	21.6	13.2	25.9	22.6	26.9	4.52
15	2.95	24.9	11.8	28.1	19.9	28.8	4.43
16	2.30	27.6	10.4	30.0	18.6	30.7	4.26
17	2.15	30.1	9.75	31.8	17.7	32.4	4.10
18	1.70	31.9	8.60	33.4	16.3	33.9	4.00
19	1.65	33.9	8.25	34.9	15.5	35.5	3.92
20	1.40	35.5	7.40	36.3	13.9	36.9	3.82
25	0.85	41.5	4.25	41.4	9.50	42.2	3.70
30	0.45	44.8	3.15	44.7	8.05	46.4	3.53
35	0.15	46.1	2.60	47.3	7.10	50.0	3.41
40	0	46.1	1.90	49.3	6.30	53.3	3.35
45	0	46.1	1.05	50.7	5.40	56.2	3.31
50	0	**46.1**	0.30	**51.3**	4.40	**58.5**	3.26

Tables B-4. Removal of metals by 10 mM SDS with 7.5 mM EDTA

Flow Rate = 12mL/min

PV	Cr (VI) removal (mg/L)	Cr (VI) removal percent, %	Ni (II) removal (mg/L)	Ni (II) removal percent, %	Zn (II) removal (mg/L)	Zn (II) removal percent, %	pH
0	0.00	0.00	0.00	0.00	0.00	0.00	---
1	0.75	0.85	6.60	1.23	12.5	1.22	5.89
2	1.05	2.04	6.95	2.52	12.9	2.49	6.14
3	1.10	3.29	7.40	3.89	13.6	3.82	6.26
4	1.20	4.65	8.20	5.41	14.6	5.25	6.37
5	1.25	6.08	9.60	7.19	16.8	6.91	6.55
6	1.30	7.55	10.5	9.14	19.8	8.85	6.77
7	1.35	9.08	11.8	11.3	23.7	11.2	6.73
8	1.40	10.7	12.9	13.7	28.9	14.0	6.61
9	1.55	12.4	14.6	16.5	32.8	17.2	6.53
10	1.60	14.3	17.8	19.7	32.7	20.5	6.46
11	1.75	16.3	19.2	23.3	30.3	23.4	6.39
12	2.05	18.6	21.2	27.3	28.6	26.2	6.09
13	2.70	21.6	20.9	31.1	27.6	28.9	5.45
14	3.40	25.5	17.4	34.4	26.2	31.5	5.12
15	3.65	29.7	16.1	37.3	24.9	33.9	5.00
16	3.10	33.2	14.7	40.1	21.3	36.1	4.95
17	2.95	36.5	12.7	42.4	19.4	37.9	4.93
18	2.20	39.0	10.5	44.4	17.6	39.7	4.82
19	1.95	41.2	9.80	46.2	16.4	41.3	4.78
20	1.70	43.2	9.20	47.9	15.9	42.9	4.75
25	1.00	49.9	5.20	54.3	12.5	49.8	4.73
30	0.70	54.5	3.90	58.2	10.2	55.5	4.70
35	0.40	57.3	3.30	61.5	9.45	60.3	4.51
40	0	57.3	2.95	64.4	8.65	64.7	4.39
45	0	57.3	1.70	66.1	6.30	68.3	4.37
50	**0**	**57.3**	**1.40**	**67.5**	**4.70**	**70.8**	**4.35**
Flow interruptions for 2 weeks							
51	1.65	59.1	11.2	69.6	11.6	71.9	6.23
52	2.30	61.8	13.7	72.1	12.6	73.1	6.11
53	2.05	64.1	10.7	74.1	10.2	74.1	6.00
54	1.90	66.2	8.90	75.8	8.70	74.9	5.86
55	1.60	68.1	8.30	77.3	6.25	75.6	5.63
58	0.95	72.0	4.85	80.5	4.05	77.0	5.10
60	**0.55**	**73.6**	**3.30**	**81.8**	**3.00**	**77.7**	**4.96**

Tables B-5. Removal of Zn (II) at different flow rates by 10 mM SDS with 7.5 mM EDTA

PV	Flow rate, 40mL/min		Flow rate, 12mL/min		Flow rate, 4mL/min	
	Zn (II) removal (mg/L)	Zn (II) removal percent, %	Zn (II) removal (mg/L)	Zn (II) removal percent, %	Zn (II) removal (mg/L)	Zn (II) removal percent, %
0	0.00	0.00	0.00	0.00	0.00	0.00
1	15.4	1.51	12.5	1.22	10.8	1.06
2	17.7	3.25	12.9	2.49	12.5	2.28
3	18.2	5.04	13.6	3.82	13.7	3.63
4	19.8	6.98	14.6	5.25	17.4	5.34
5	20.8	9.03	16.8	6.91	26.9	7.98
6	22.3	11.2	19.8	8.85	28.9	10.8
7	35.2	14.7	23.7	11.2	33.6	14.1
8	65.8	21.2	28.9	14.0	37.9	17.8
9	87.6	29.8	32.8	17.2	33.3	21.1
10	74.9	37.1	32.7	20.5	29.8	24.0
11	37.4	40.8	30.3	23.4	24.6	26.5
12	25.9	43.3	28.6	26.2	18.3	28.3
13	22.4	45.5	27.6	28.9	14.9	29.7
14	17.6	47.3	26.2	31.5	13.5	31.0
15	14.7	48.7	24.9	33.9	12.9	32.3
16	12.2	49.9	21.3	36.1	12.3	33.5
17	11.7	51.1	19.4	37.9	11.8	34.7
18	10.9	52.1	17.6	39.7	11.1	35.8
19	10.8	53.2	16.4	41.3	10.8	36.8
20	10.7	54.2	15.9	42.9	10.2	37.8
25	9.6	59.1	12.5	49.8	9.25	42.5
30	9.10	63.6	10.2	55.5	8.65	46.8
35	8.15	67.9	9.45	60.3	7.95	50.8
40	7.75	71.8	8.65	64.7	7.25	54.5
45	6.65	75.3	6.30	68.3	6.30	57.7
50	5.35	**78.3**	4.70	**70.8**	5.20	**60.5**

Appendix C

C-1. Measurement of pore volume & pore water velocity

The pore volume (P_V) of the packed column was determined by the weight difference between the water-saturated column (W_{sat}) and the dry soil column (W_{dry}):

$P_V = W_{sat} - W_{dry}$

Pore water velocity (V) was calculated using the following formula:

$V = QL/ P_V$

Here, Q is the average flux of water through the column (mL/min), L is the column length (cm), and P_V is the pore volume (mL).

C-2. Measurement of soil hydraulic conductivity

1. Procedure

Step 1. Measure the column's diameter (D) and length (L). Calculate the column section area (F). Pack the soil sample into the column, tap gently on the side of the column to pack the soil uniformly.

Step 2. Install the experimental setup as in Fig.4-2. Record the height difference between the water surface of a high level container and the top of the column (H).

Step 3. Collect the outflow in a graduated cylinder. Record the outflow vs. time (at 10mL intervals) until the time interval for 10mL outflow remains constant for five consecutive samples.

Step 4. Calculate the hydraulic conductivity K by the following equations:

$q = Q/t$ (Ci) $v = q/F$ (Ciii)

$I = H/L$ (Cii) $K = v/I$ (Civ)

Step 5. Reload the column, repeats steps 1-4, and duplicate the experiments. Calculate hydraulic conductivity as the average value.

2. Experimental results and calculations

Diameter, D = 4.0 cm, Section area, F = 12.56 cm^2

Length, L = 20.5 cm

H = 84 cm

Table C-1. Calculation of soil hydraulic conductivity

Reading	Q (mL)	Time, T (min)	q (mL/min)	v (cm/min)	I	Hydraulic conductivity (cm/min)
1	400	37.50	10.67	0.84952	4.09	0.207706
2	300	27.20	11.03	0.87818		0.214714

The hydraulic conductivity (K) was calculated as the average of the two values:

K = (0.207706 + 0.214714)/2 = 0.2112

Standard deviation (STDEV),

STDEV
$= [\{(0.207706 - 0.21121)^2 + (0.214714 - 0.21121)^2\}/2]^2 = 0.0035$ cm/min

Estimated hydraulic conductivity of the soil is**:** 0.2112 ± 0.0035 cm/min

Reference

Cook, F.J., and Broeren, A, 1994. Six methods for determining sorptivity and hydraulic conductivity with disc permeameter, Soil sci. (157,1): pp.2-11