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Surfactant Enhanced Washing of Cu (II) and Zn (II)
from a Contaminated Sandy Soil

Xiaojie Li

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)

Concordia University, Montreal, Quebec, Canada

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ABSTRACT

Surfactant Enhanced Washing of Cu (II) and Zn (II)

from a Contaminated Sandy Soil

Xiaojie Li

The role of surfactants in the remediation of metal contaminated sites has remained unclear due to the limited number of earlier investigations devoted to surfactant enhanced metal removal from soils. In the present study, distilled water, surfactants with and without a complexing agent are used to remove Zn (II) and Cu (II) from an artificially contaminated sandy soil. SDS (sodium dodecyl sulfate), AOT (sodium dioctyl sulfosuccinate) and Tx-100 (Triton X-100) are the surfactants used in this study. EDTA (ethylenediaminetetraacetic acid) is the complexing agent selected for soil washing. In batch tests, it is shown that extraction by all surfactants is nearly 6 times more effective for copper removal, and 1.2 to 1.4 times more effective for zinc removal than extraction by distilled water alone. The use of surfactants together with the complexing agent EDTA is shown to considerably improve the efficiency of metal removal by EDTA. It is suggested that surfactants do improve the performance of soil washing by enhancing elution of metallic compounds and the reduction of interfacial tension.

Column tests indicated that the removal of Cu (II) unlike Zn (II) is quite small when water alone is used. SDS at concentration of 10 mM removes 13% of Cu (II) and 21% of Zn (II) after 50 pore volumes. Up to 60 pore volumes, the removal of copper by the complexing agent EDTA (5 mM) alone is 50%. With the addition of SDS (10 mM),

Cu (II) removal increases to 59%. Similarly, Zn (II) removal rate also increases from 61% to 70% when SDS is added to EDTA.

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List of Abbreviations

AA	The Atomic Absorption Spectrophotometer
AOT	Aerosol-OT, Sodium Dioctyl sulfosuccinate
CEC	Cation Exchange Capacity
CMC	Critical Micelle Concentration
CTAB	Cetyltrimethylammonium bromide
DPC	Diphenyl Carbazone
EDTA	Ethylenediaminetetraacetic Acid
ER	Electrokinetic Remediation
ISV	In situ vitrification
NAPL	Non-Aqueous phase Liquid
NTA	Nitrilotriacetate
PAHs	Polynuclear Aromatic Hydrocarbon
PCBs	Polychlorinated Biphenyls
PV	Pore Volume
SCMC	S-carboxymethylcysteine
SDS	Sodium Dodecyl Sulphate
Tx-100	Triton X-100

CHAPTER 1

INTRODUCTION

1.1 Introduction and background

Heavy metals are metals with densities generally larger than 5g/cm^3 . There are nearly 70 elements with the atomic numbers varying from 23 to 106 (Yaron, 1984). Cadmium, copper, lead, and zinc are the most hazardous heavy metals. They are in the EPA's list of priority pollutants (Mulligan, 2001a; Cameron 1992). The production and use of copper, and zinc have increased a great deal to keep pace with the demand of the industry. One can measure the metal concentration very accurately with modern scientific equipment. The public is more aware of the presence of heavy metal present in the environments (Alloway, 1990). Cu and Zn are important trace elements for living organisms. However, at concentrations above a threshold, they are harmful to human beings, animals and plants (Alloway, 1990).

Organic and inorganic colloids in surface soils can sorb Cu (II). Generally, the total Cu concentration in the soil solution varies from 0.01-0.06 μM . When the Cu (II) concentration is in the range of 1.5 to 4.5 μM , roots of the growing plant get adversely affected by Cu (II) (Alloway, 1990).

Both surface and subsurface environments have been subjected to heavy metal pollution. Various techniques have been used for the remediation of contaminated soils. These include thermal extraction for volatile metals, solidification /stabilization, chemical

oxidation, and soil washing. Recently the use of surface-active agents (surfactants) have found a use in enhancing remediation of contaminants from soils in situ or during soil washing (Abdul et al., 1991, Kile, E., 1989, Hong et al., 1999). At lower concentrations, surfactants are able to increase the mobility of hydrophobic organic compounds. At higher concentrations, they can enhance the solubilization of many hydrophobic organic compounds, such as polynuclear aromatic hydrocarbon (PAHs), and chlorinated hydrocarbons by increasing the solubility of the contaminants via micellar solubilization (Edward et al., 1994). Surfactants are shown to have some potential for the removal of heavy metals. Their use is site specific. Their performance is linked to the matrix of soil, its pH, organic content hydraulic conductivity and speciation of metal. The modeling and mechanisms of surfactants in the remediation of soils contaminated with Zn (II) and Cu (II) is still not very clear due to the complexity of a soil system and the variety of factors involved.

The present study attempts to evaluate the potential of surfactants to enhance the remediation of sandy soils contaminated by Cu (II) and Zn (II). To this end, both batch and column experiments were conducted to investigate the sorption/desorption and transport behavior of these two heavy metals. Both the effects of competition as well as interaction associated with the sorption/desorption of these metals were studied. Two anionic surfactants sodium dodecyl sulfate (SDS) and sodium dioctyl sulfosuccinate (AOT), In addition to a nonionic surfactant (Tx-100) and a complexing agent ethylenediaminetetraacetic acid (EDTA) were used in this study as extracting agents.

This thesis consists of six chapters devoted to the following topics:

- Chapter 1 gives an introduction to the subject of study.
- Chapter 2 provides a brief review of the important existing studies on site remediation and surfactant-enhanced extraction of heavy metal from soils.
- Chapter 3 deals very briefly with the fate and transport of heavy metal in soils.
- Chapter 4 discusses the specifics of the material used and the experimental procedure adopted in the study.
- Chapter 5 provides a discussion of the results related to batch and column tests.
- Chapter 6 includes the sections dealing with the summary, conclusions and recommendations for future work.

1.2 Research objectives

The overall objectives of this study are stated below:

Main objectives:

- 1) Determination of an optimal washing system for enhancing the removal of Cu (II) and Zn (II) from an artificially contaminated sandy soil.
- 2) Determination of the mechanism of surfactant-enhanced extraction of heavy metals Cu (II) and Zn (II) from contaminated soils.
- 3) Investigation of the effects of interaction and competition between Cu(II) and Zn (II) during site remediation.

Secondary objectives:

- 1) Determination of the effect of aging of the contaminated soil on metal removal.
- 2) Study of the effect of flow rate on the desorption characteristics of a sandy soil containing a mixture of Cu (II) and Zn (II).

CHAPTER 2

LITERATURE REVIEW

2.1 Remediation technologies for metal-contaminated soils.

Soil remediation is becoming an important industrial activity in the world. Many in situ and ex situ heavy metal remediation techniques are used in practice. The contaminants can be rendered harmless by two distinct methods (Rampley et al., 1998). In one case, the metals can be immobilized in the soil matrix. Immobilization involves solidification/stabilization or vitrification. Alternatively, one can resort to separation, soil washing and soil flushing. Here, desorption and solubilization will transform the contaminants to a liquid form (Rampley et al., 1998). More recently, some relatively new technologies such as electrokinetic processes and phytoremediation are coming into vogue, to clean a contaminated site (Deuren, et al., 2002).

Separation, soil flushing and soil washing (Deuren, et al., 2002):

Separation, soil flushing and soil washing are the processes that are often used in soil remediation processes.

Separation: In this process of separation, one detaches the contaminant from the medium. The techniques involve gravity separation, sieving/physical separation and magnetic separation. The first two types of separation have long been the main methods for treating municipal wastewaters. The last one is a newer separation process that is still being tested.

Soil flushing: Water, or water containing an additive to enhance contaminant solubility is applied to the soil or injected into the ground water to raise the water table of the contaminated soil zone so that the contaminants are leached into the ground water. Following this, they are extracted and subjected to treatment (Fig. 2-1).

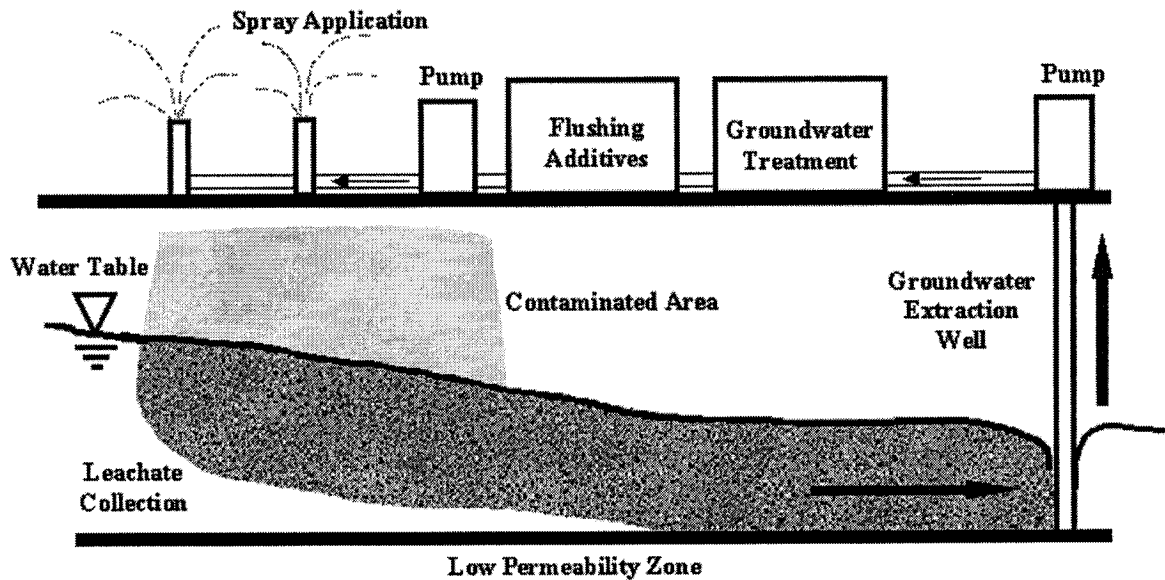


Fig. 2-1 System diagram of soil flushing technology (Deuren, et al., 2002)

Soil washing: This is an ex situ technology. Soil contaminants are separated from bulk soil in an aqueous-based system. The wash water may contain other ingredients (leaching agent, surfactant, pH adjustment, or chelating agent) to assist in the removal of heavy metals (Fig. 2-2). These mineral processing techniques are used in Northern Europe and America.

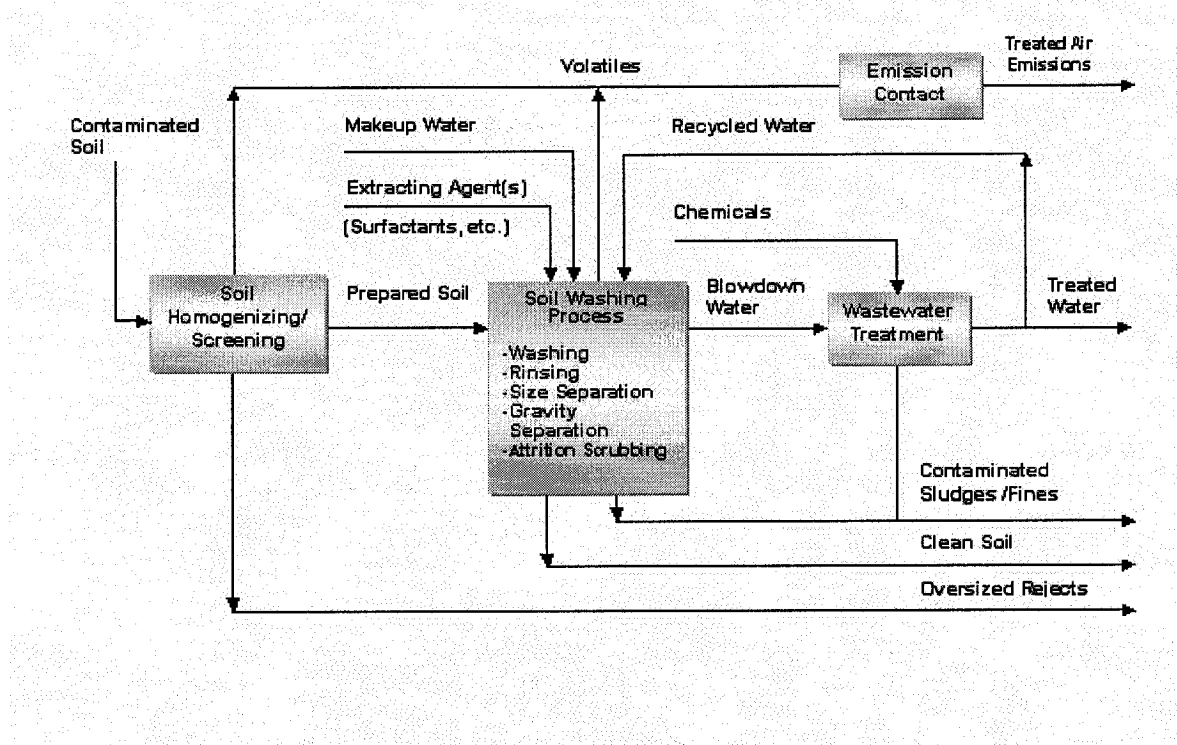


Fig. 2-2 System diagram of soil washing technology (Deuren, et al., 2002)

Deuren et al (2002) also suggested solidification/ stabilization, in situ vitrification, electrokinetic and phytoremediation as alternate methods for soil remediation which are described below:

Solidification/ stabilization: One can physically bind or enclose the contaminant within a stabilized mass (solidification). The stabilizing agent reacts with the contaminants and immobilizes them. Hazardous substances and contaminants in the environment can be rendered harmless through solidification/ stabilization.

In situ vitrification: The above process is achieved by passing an electric current to melt soil or other entrapped materials at extremely high temperatures (1,600 to 2,000 °C). This

process immobilizes most inorganic and destroys organic pollutants by pyrolysis. Inorganic pollutants form part of the vitrified glass-like and crystalline mass that is chemically stable. It is a leach-resistant, glass and crystal-like material similar to a metamorphic rock.

Electrokinetic Remediation: This is a recently introduced in situ process that is primarily a separation and removal technique for extracting contaminants from soils. Here, one removes metals from low permeability soil, mud, sludge, and marine dredging. It uses electrochemical and electrokinetic processes to desorb, and then remove metals and polar organics.

Phytoremediation: Phytoremediation is a process in which plants remove, transfer, stabilize, and destroy contaminants in soil. The process includes enhanced rhizosphere biodegradation, phyto-extraction, phyto-degradation, and phyto-stabilization. Fig. 2-3 shows the system diagram for a combined use of electrokinetic and phytoremediation technologies.

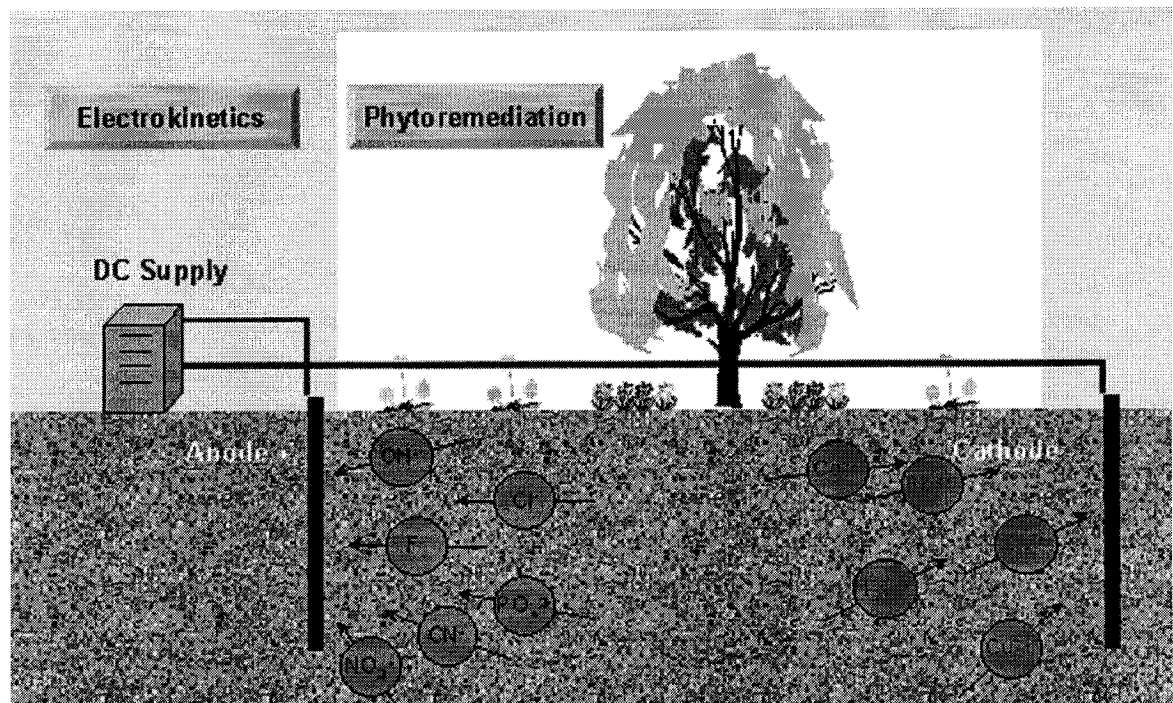


Fig. 2-3 System diagram of electrokinetics and phytoremediation technology

(Deuren, et al., 2002)

2.2 Soil washing/soil flushing technology

Various in situ and ex situ remediation techniques are used in engineering practice. The excavated soil is washed with chemical extractants in an aqueous solution. The aqueous solution removes the adsorbed/precipitated metals from the soil. Washing solution used can be mineral acids or organic acids, chelating agents such as EDTA and nitrilotriacetate (NTA) (Elliot et al., 1989, Peter and Shem, 1992, Reed et al., 1996, Hong et al., 1999; Peter, 1999).

Chelating agents in general are effective in metal extraction. In view of the toxic nature of chelates, surfactants are considered to be attractive for site remediation. Surfactants have low toxicity and relative favorable biodegradability (Deshpande, et al, 1999).

Soil washing is not often used for soils with different types of contaminants such as a mixture of metals, volatile organics, and nonvolatile organics (Dupont, 2001). Similarly, in situ flushing is not applicable when more than one type of contaminant is encountered. It is also not applicable to highly heterogeneous soils that have low permeability (Dupont, 2001).

The following factors influence the applicability and effectiveness of soil washing (Dupont, 2001):

- “Low permeability or heterogeneous soils are difficult to treat. The efficiency of extraction depends on the hydraulic conductivity of the soil. Soils with high permeability have better results (greater than 1×10^{-3} cm/s) in soil washing.
- Surfactants can adhere to soil and reduce effective soil porosity.
- Reactions of flushing fluids with soil can reduce contaminant mobility.
- The potential of washing the contaminant beyond the capture zone and the introduction of surfactants to the subsurface concern regulators. The technology should be used only where flushed contaminants and soil-flushing fluid can be contained and recaptured. Hydraulic control of the surfactant and contaminants must be maintained to prevent the migration of contamination to unpolluted regions.

- Above ground separation and treatment costs for recovering the solvents can be very expensive”.

The selection of a surfactant depends on its performances in mobilizing or solubilizing the contaminants besides cost considerations.

2.2.1 Chelating agent-enhanced soil washing/ flushing

Chelating agents form metal complexes and thus desorb heavy metals from soil particles. As such, they are used as solvents for soil remediation. The use of chelating agents in the extraction of heavy metals from contaminated sites has attracted a great deal of research interest. Ellis et al (1986), Eliot et al (1989), Peter and Shem (1992), and Reed et al (1996) investigated the removal of various heavy metals from contaminated soils and showed that the complexing agent EDTA can enhance most of the heavy metal removal.

Allen et al (1995) conducted several chemical column-washing experiments and concluded that efficient washing occurred while using the organic chelating agents at the lowest flow rate. The washing efficiency is strongly dependent on the zinc species present.

The chelator S-carboxymethylcysteine (SCMC) has been used to extract Cu (II) from a spiked soil by batch experiments (Hong et al, 1995). The result indicated SCMC could extract and release copper reversibly and SCMC preferred complexing with copper to competing with iron and calcium ions.

Reed et al. (1996) studied flushing Pb (II) from synthetically contaminated sandy loam using 0.1N HCl, 0.01 M EDTA and 1M CaCl₂ in the column mode. They found that Pb removal efficiencies for HCl, EDTA and CaCl₂ were 87% 100% and 78% respectively.

2.2.2 Surfactant background

Surfactants are organic chemical wetting, cleaning and disinfecting agents. They are used as flocculating, wetting and foaming agents (Mulligan, 2001a, Mulligan and Gibbs, 1993).

Surfactants are surface active because of their amphiphilic structure. In aqueous systems, a surfactant has a polar or ionic hydrophilic part and a nonpolar hydrophobic part, referred to as the head and tail groups respectively (Fig. 2-4) (Myers 1999).

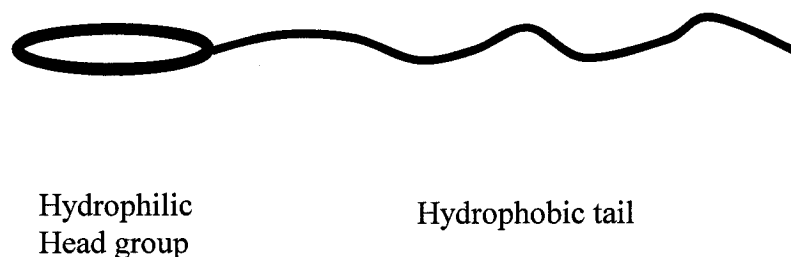


Fig. 2-4 Surfactant structure (Myers, 1999)

The common classification of surfactants given below is based on the nature of the hydrophilic part. It was described by Myers (1999).

- 1) Anionic: The hydrophilic group carries a negative charge. Typically it contains one or more of the following head groups: carboxyl, sulfonate or sulfate.
- 2) Cationic: The hydrophilic group has a positive charge. Example: Quaternary ammonium halides.
- 3) Nonionic: The hydrophilic group has no charge. It owes its water solubility to the highly polar groups. Example: Groups such as polyoxyethylene and sugars.
- 4) Amphoteric: The hydrophilic group has both a negative and a positive charge on the principal chain. Example: Sulfobetaines.

Micelles denote the clustering of surfactant molecules into a dynamic group (Fig. 2-5), when the surfactant concentration reaches critical value. This concentration of surfactant is referred to as the critical micelle concentration (CMC) and it is different for every surfactant (Rose, 1989). CMCs typically range between 0.1mM and 10 mM and depend on the structure of the surfactant, the temperature of the surfactant solution, and the concentration of added electrolytes. In a micelle, the individual monomers are oriented with their hydrophilic moieties in contact with the aqueous phase while their hydrophobic moieties get tucked into the interior of the micelle (Harwell, 1992).

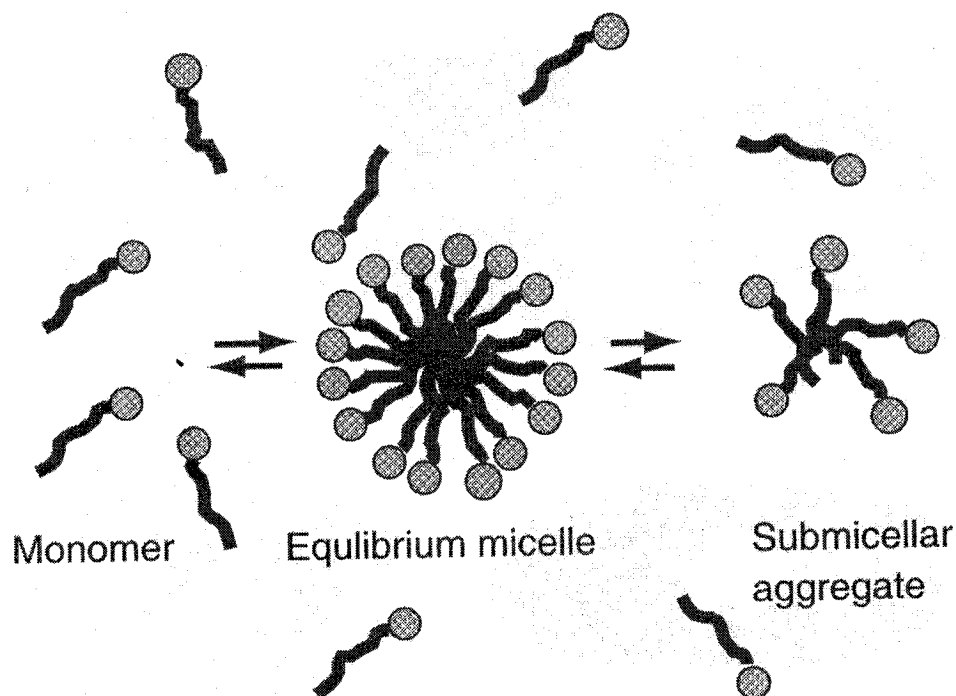


Fig. 2-5 Surfactant micellization (Myers 1999)

2.2.3 Previous investigations on the use of surfactants to enhance remediation of soil

2.2.3.1 Surfactant enhanced removal of organics

A chelating agent is a ligand. It contains two or more electron-donor groups enabling the formation of more than one bond between the metal ion and the ligand (Cline et al., 1995).

In the previous studies, acid washing and chelating agent washing were the two most prevalent removal methods. Recently, surfactants have been shown to have significant potential for enhancing the remediation of contaminated soil and groundwater. Numerous studies have been conducted on the surfactant enhanced remediation of organics (Harwell, 1992, Wilson and Clarke, 1994, Cheah et al., 1998).

Duffield et al. (2003) has studied non-aqueous phase liquid (NAPL) removal using surfactants. They concluded that surfactant could promote the enhanced removal of NAPL through mobilization, which is a mechanism that relies on the reduction of interfacial tension at the flushing solution/ NAPL interface.

Two very different mechanisms by which surfactants can enhance removal of organic contaminants are the following (Cheah et al, 1998):

(1) Mobilization: Surfactants reduce the oil-water interfacial tension and the capillary forces that trap the residual organics in the voids of the soil and reduce the residual oil saturation. Hence, more oil is mobilized than with simple water flushing.

(2) Solubilization: Above the CMC, the interior of a micelle incorporates hydrophobic organic molecules through the process of solubilization.

2.2.3.2 Surfactant enhanced remediation of metal contaminated soils

As previously mentioned, surfactants are used to assist the remediation of numerous types of hydrocarbon contaminants. The research in the area of metal removal from soils is still quite limited. Surfactants have shown some potential for soil remediation of heavy metals.

Nivas et al. (1996) noted that one of the mechanisms for the extraction of heavy metals (Cr O_4^{2-}) by surfactants is through ion exchange. The negatively charged ions such as

Cr O₄²⁻ [Cr (VI)] adsorbed by the soil are replaced by negatively charged surfactant ions. Nivas et al. (1996) also suspected that precipitation-dissolution was the second mechanism for metal removal.

Doong et al. (1998) studied the use of a surfactant to remediate cadmium-contaminated soils. They reported that anionic and nonionic surfactants enhance desorption rates of cadmium, lead and zinc. The addition of cationic surfactants appears to decrease the desorption efficiency of heavy metal. They found that below critical micelle concentration (CMC), the desorption efficiency increased linearly with the increasing surfactant concentration. However, above the CMC, it remained relatively constant. The extraction capacities of nonionic and anionic surfactants decreased with the increasing pH. In addition, they found that complexing agents such as EDTA and diphenylthiocarbazone (DPC) can change the removal efficiency.

Biologically produced surfactants, surfactin, rhamnolipids and sophorolipids have also been used to remove Cu (II) and Zn (II) from a hydrocarbon-contaminated soil by Mulligan et al (1999a). Their batch tests indicated that high levels of Zn (II) and Cu (II) removal rates occurred with the use of biosurfactants. Furthermore, the analysis indicated that the carbonate and oxide fractions accounted for over 90% of Zn (II) present in the soil, while the organic fraction constituted over 70% of Cu (II). Mulligan et al (2001b) also investigated the feasibility of biosurfactants for the removal of heavy metals from sediments by batch washing experiments. They stated that metal removal by the biosurfactant occurs through sorption of the surfactant onto the soil surface, and

detachment of the metal from the soil into the solution. This resulted in its association with surfactant micelles.

Peters (1999) studied surfactant-enhanced remediation of soils contaminated with metals. According to him, cationic surfactants modify soil surfaces to promote displacement of metal cations from the solid to the liquid phase. Ion exchange process is the process through which surfactants promote metal desorption from soil. He came to this conclusion based on the studies by Beveridge et al. (1983) and Kornecki et al. (1998). However, Huang et al. (1997) maintained that cationic surfactants are expected to form strong complexes with the negatively charged soil matrix itself, and hence may not be feasible for subsurface remediation.

Based on batch tests, Li (2000) has reported that the anionic surfactant SDS was more effective in the removal of Cu (II) than the nonionic surfactant Triton X-100. He also stated that desorption of Cu (II) increases with the decrease of pH.

Gadelle et al. (2001) evaluated the factors controlling desorption. They indicated that two anionic surfactants Witconate AOK (Witco Corporation, Greenwich, CT) and Geroon T77 (Rhone-Poutenc, Granbury, NJ) at the concentration from 60 to 20 mM are very effective in the removal of uranium [U (VI)] from acidic soils such as soils collected at the Melton Branch Watershed (Oak Ridge National Laboratory, TN). They concluded that the most probable mechanisms include mainly cation exchange in the electric double

layer surrounding the micelles and to a lesser extent, dissolution of the soil matrix. They also noticed that there was some loss of surfactant due to sorption by soil particles.

Mohammad et al. (2003) studied the separation of heavy metal cations on soil amended silica gel layers using surfactants SDS, CTAB (cetyl trimethyl ammonium bromide) and Tx-100 as the washing solution. They used thin-layer chromatography to determine the metal cation separation from multi component contaminants. 0.5 mM CTAB was found to be the most effective for the separation of heavy metal cations.

Previous studies have given an indication that surfactants can enhance metal removal. The pH, hydraulic conductivity, the texture of soil, the speciation of metal and the organic content of soil have an important role in the effectiveness of surfactant-based remediation of soil contaminated by metals. Due to these complexities, the role of surfactants in site remediation remains unclear. Further research based on the emerging technologies is also needed to improve the application of surfactants for site remediation.

CHAPTER 3

FATE AND TRANSPORT OF HEAVY METALS IN SOILS

3.1 Mobility of heavy metals in soil

The main sources of heavy metal pollution include runoff from farmlands on which municipal sludge is spread, atmospheric fallout from power plants and industries (Alloway, 1990). Once heavy metals are released into the soil matrix, they are retained by soil particles. Heavy metal salts 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.

It was noted that the mobilities and solubilities of heavy metal have a negative effect on the environment. However, the same properties of heavy metals can also be used for remediation of contaminated sites. The study of heavy metal migration is very important in many engineering applications.

As stated earlier, metal behavior in the soil is controlled scientifically by factors such as pH, organic content, permeability and moisture content of soil are the significant factors. Generally, heavy metals in soils can be grouped into five fractions: exchangeable, carbonate, Fe-Mn oxide, organic and residual fractions (Alloway, 1990). The presence of the hydrous metal oxides of Fe, Al and Mn can strongly influence metal concentration. These minerals can remove cations and anions from solution by ion exchange, specific adsorption and surface precipitation (Alloway, 1990).

3.1.1 Copper

Copper is a metal with an atomic number of 29, a molar mass of 63.5g, and a density of 8.9g/cm^3 . The use of copper combined with the associated burning of oil, coal, certain waste and cu-containing fungicides and algaecides contribute to Cu (II) pollution of soil. (Alloway, 1990). Excessive amount of copper is associated with the occurrence of chronic liver disease. Wilson's disease is known to occur due to excessive Cu accumulation in the liver (Nriagu, 1979). Alloway (1990) states that normal human diet provides 1-5 mg of Cu /day.

According to Alloway (1990), total Cu in soils can also be classified in terms of six "pools" based on their physical-chemical behaviors. The pools are (1) soluble ions and inorganic and organic complexes in soils solution; (2) exchangeable Cu; (3) stable organic complexes in humus; (4) Cu adsorbed by hydrous oxides of Mn, Fe and Al; (5) Cu adsorbed on the clay-humus colloidal complex; (6) the crystal lattice-bound Cu in soil minerals. In general, copper in the soil is strongly held on inorganic and organic exchange sites and in complexes with organic matter. This decreases its mobility (Nriagu, 1979). As such, it is more difficult to remove copper from soil.

3.1.2 Zinc

Zinc is a metal with an atomic number of 30, a molar mass of 65.39g, and a density of 7.13g/cm^3 . Zinc's physiological importance as a trace element stems from the fact that it is part of the animal nutrition. The enzyme carbonic anhydrase contains 0.33 percent zinc

and zinc is essential to the elimination of carbon dioxide (Mathewson, 1964). Zinc deficiency symptoms in humans and animals lead to poor appetite, severe growth depression, skin lesions and sexual immaturity (Alloway, 1990).

Zinc contamination in soil is traced to the industries dealing with zinc based alloys, galvanized products, rubber, copying paper, cosmetics, batteries, televisions, tires, metal coatings, glass and paints (Cameron, 1992). Cameron (1992) gives an excellent and exhaustive survey of soil contamination by Zn compounds. Agricultural use of sewage sludge and composted materials and the use of agrochemicals such as fertilizers and pesticides also are the main pollutant sources for Zn in soil (Alloway, 1990).

Zinc belongs to the group of trace metals that are the most hazardous to the biosphere. Most of the concern about excessive Zn concentration in soils is related to its possible uptake by crops and consequent adverse effects on the crops themselves and on livestock and human diets (Alloway, 1990). Zn is principally phytotoxic. So the concern about this metal is mainly related to its effects on crop yield and soil fertility (Alloway, 1990).

3.2 Fate and transport processes

Contamination exists in the soil in three forms. They are solubilized contamination in the soil moisture; adsorbed contamination on the soil surface and contamination fixed chemically as solid compounds (Evanko, 1997). The fate and transport of heavy metals in

soils depend significantly on the chemical form and speciation of the metal (Allen et al., 1991).

The main migration and transportation processes of solutes in groundwater include advection, diffusion, dispersion, adsorption, biodegradation and chemical reaction (Bedient et al., 1994). Among these six processes, adsorption of metals is an important process that significantly affects the transport of contaminants. It can significantly influence the ability to decontaminate polluted sites (Bedient et al., 1994).

3.3 Previous studies on sorption and desorption of metals

The most important chemical processes affecting the behavior and bioavailability of metals in soils are those concerned with their adsorption and desorption capabilities. They determine the concentration of metal ions and complexes in a soil solution. According to Alloway (1990), several mechanisms can be involved in the adsorption of ions including cation exchange, specific adsorption, organic complexation and co-precipitation. (1) Cation exchange: Cation exchange capacity (CEC) refers to the concentration of readily exchangeable cations. To maintain electroneutrality, the surface negative charge of soil has to be balanced by an equal quantity of oppositely charged ion called counter-ions. Ion exchange denotes the exchange between the counter-ions balancing the surface charge on the colloids and the ions in the soil solution. This mechanism is reversible. It is diffusion controlled and selective. (2) Specific adsorption. This refers to the exchange involving heavy metal cations and most anions with surface ligands. (3) Co-precipitation. It is defined as the

simultaneous precipitation of a chemical agent along with other elements. (4) Organic complexation: In this process, humic substances adsorb metals by forming chelate complexes. The extent of sorption is influenced by the chemical properties of the sorbent and the sorbate. The surrounding environmental conditions also modify the process (Alloway, 1990).

In spite of the importance of both adsorption and desorption of metals in affecting the mobility and fate of contaminants in soil, only a few studies are devoted to desorption studies. The observed behavior of desorption process is not always the reverse of the sorption process behavior. This is caused by the rearrangements of soil's natural organic matter as a result of contaminant sorption. The contaminant can be physically sequestered within the organic matrix. It may fail to get released under conditions predicted by equilibrium partitioning (Bedient et al., 1994).

Heavy metals may be either adsorbed to the various components of the soil matrix or as separate metal compounds. Since they have a higher surface area per unit volume, metal contamination is associated with the finer soil particles. Fine soil fraction usually contains the natural organic component of the soil and hence favor adsorption (Peters et al., 1992).

Erwin et al. (1994) studied the effect of pH on both the copper desorption from a sandy soil and the complexation of copper by dissolved organic fractions. Ultrafiltration data revealed that copper was bound by dissolved organic matter and was divided into a humic

and a fulvic fraction. Their Cu desorption isotherms were nonlinear and were dependent on pH. The exchangeable copper was less than 3% of the total copper in the soil. About 1% of exchangeable copper was complexed with nitrate. Free copper varied from 2% to 9%.

Atanassova (1995) investigated Cu adsorption-desorption in a vertisol and planosol and their clay fractions. They found that Cu sorption was well described by Langmuir isotherms. It was suggested that the observed decrease of the distribution coefficient (K_d) with increasing Cu concentration was attributed to a high affinity of the sorption sites for Cu at low surface coverage. Atanassova (1995) showed that Cu desorption was fully reversible for the planosol. Hysteresis was observed for the vertisol, which had a significantly higher organic content.

A study of Reed et al., (1996) revealed that the factors affecting heavy metal retention by soil include: pH, soil type and horizon, cation exchange capacity (CEC), natural organic matter, age of contaminant, and the presence of other inorganic contaminants.

Yin (1997) studied adsorption /desorption isotherms of Hg (II) in 15 soils. His results indicated that all soils with a large organic matter content had an S-type isotherm, whereas all soils with low organic matter content had an L-type isotherm. The locus of the adsorption and desorption isotherm were not identical. Soil organic matter was the main component responsible for the observed hysteresis. He stated that restricted

diffusion of Hg through organic matter was probably the major factor that resulted in the hysteresis.

Wu et al. (1999) found that copper was preferentially sorbed on organic matter associated with the coarse clay fraction. They attributed the observed adsorption-desorption hysteresis to the extremely high-energy bonding with organic matter and the layered silicate surface.

Base in batch experiments, Tran (2002) stated that the dissolved amount of cadmium (Cd) was low compared with the quantity of Cd adsorbed previously. The Freundlich isotherm coefficients of desorption experiments were different from the values determined from the corresponding adsorption experiments. The effect of pH on Cd desorption was not determined in the flow through experiments.

Desorption experiments are simple extensions of adsorption experiments. Still little metal desorption information is available. Moreover, competition among metal adsorption and desorption on soil surfaces plays a very crucial role on contaminant mobility in the environment. Few studies have dealt with the topic of competition related to heavy metal adsorption/desorption competition in soils. In a natural setting, the presence of multiple competing ions is more frequent than the existence of only one contaminant.

Christophi (2000) studied the competition among copper, lead and cadmium in relation to adsorption on a goethite surface. It was found that adsorption increased with metal

electronegativity: Cu>Pb>Cd. On the other hand, the equilibrium constant for lead was found to be greater than that for copper. This is in agreement with their hydrated radii (Pb>Cu>Cd).

3.4 Reaction and transport model

3.4.1 Freundlich isotherm

The Freundlich equation is frequently used to describe the sorption of reactive solute onto the soil matrix. It is given by (Selim, 1996):

$$S=K_fC^b \quad (3-1)$$

Here S is the amount of solute retained by the soil, in mg/kg, C is the solute concentration in mg/l. K_f is the distribution coefficient in ml/g, and the parameter b is dimensionless and typically has a value of $b<1$.

The distribution coefficient describes the partition of a solute species between the solid and the liquid phase over the concentration range of interest and is analogous to the equilibrium constant for a chemical reaction in the following equation.

$$\text{Log } S = \text{log } K_f + b \text{ log } C \quad (3-2)$$

All the equilibrium models assume that the rate of change of concentration due to sorption is very rapid and that the flow rate is low enough that equilibrium can be reached. However the kinetic models are linked to appropriate solute transport equations to describe the rate at which solute is adsorbed onto the solid surface and desorbed from

the surface. The reversible nonlinear first order kinetic sorption model is (Selim, et al., 1999):

$$dS /dt= K_{ads} C^b - K_d S \quad (3-3)$$

Here, K_{ads} and K_d are the forward rate constants of the Langmuir model (adsorption and desorption).

3.4.2 Langmuir isotherm

The Langmuir isotherm is a combination of the adsorption and desorption rate equations (Selim, et al., 1999):

$$\frac{\partial \theta}{\partial T} = K_{ads} CN(1 - \theta) - K_d N \theta \quad (3-4)$$

Here, N is the maximum number of adsorption sites occupied by the metal; θ is the dimensionless surface coverage ratio ($\theta=S/S_m$); C is the metal concentration in the liquid phase.

At equilibrium, Equation 3-3 becomes (Selim, 1996):

$$\frac{S}{S_m} = \frac{K_l C}{1 + K_l C} \quad (3-5)$$

Here, $K_l = K_{ads}/ K_d$ is the Langmuir constant, S_m is the maximum adsorption capacity, S is the amount of sorbed metal at equilibrium, and C is the metal concentration in the liquid phase at equilibrium.

CHAPTER 4

EXPERIMENTAL METHODS AND MATERIALS

4.1 Introduction

The experiments discussed in this study were performed using both batch and column tests to study the effect of surfactants on the removal of metal Cu (II) and Zn (II) from an artificially contaminated sandy soil. Soil samples, surfactant and target contaminants, Cu (II) and Zn (II) in the form of $\text{Cu}(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 7\text{H}_2\text{O}$, and HNO_3 (70%) for digestion before Atomic Absorption (AA) analysis, formed the experimental materials. Distilled water was used for washing, diluting and for use as a control.

4.2 Physical descriptions

4.2.1 Soil samples

The soil used in this study contained predominantly sand (40 mesh) mixed with a very small quantity of bentonite. The mineral montmorillonite is the commercial name for bentonite. All experimental soil samples used in this study were made of 98% of sand and 2% of bentonite by weight. The sand was obtained from Geneq Inc, Canada, and bentonite was purchased from Sial Inc, Canada. Commercially available bentonite has a particle size which pass through the 325 mesh. The sand grain size used in this study corresponds to 40 mesh and specific surface area has been reported to be $0.1\text{m}^2/\text{g}$. (Chiou et al. 1993). The characteristics of these two compositions are shown in the Table 4-1. The measured hydraulic conductivity of the soil sample (98 % sand and 2 % bentonite) was $3.63 \times 10^{-3} \text{cm/s}$ (See Appendix A).

Table 4-1 Characteristics of sand and Bentonite

	Bentonite	Sand
CEC (meq/100g)	110.5 (pH5.9) ⁽¹⁾	0
Organic matter content	3.1% ⁽²⁾	0.12%⁽²⁾
pH in water	6.7	9.4
Particle size	Mesh 325⁽³⁾ (Dm = 0.044mm)	Mesh 40⁽³⁾ (Dm = 0.42mm)

(1) Pump and Krist, 1998

(2) Li, 2000 (Determined at 550°C)

(3) U.S. standard sieve: Dm is the standard screen size

4.2.2 Surfactants and Complexing agent

The surfactant, SDS (sodium dodecyl sulfate), AOT (dioctyl sulfosuccinate), and Tx-100 (Triton X-100) were used to represent anionic and nonionic surfactants. Due to their high potential for sorption with the subsurface medium (Huang et al, 1997), cationic surfactants are not used in surface soil remediation. SDS, AOT and Tx-100 were obtained from SIGMA Chemical Co.; U.S.A. Tx-100 was produced from Octylphenol polymerized with ethylene oxide. The properties of these three surfactants are shown in the following tables.

Table 4-2 Properties of Tx-100 (Sigma, 1993)

Product name	Triton X-100 (99%)
Type	Nonionic surfactant
Molecular formula:	$C_8H_{17}C_6H_4(OC_2H_4O)_nOH$ (n=9-10)
M.W (g)	625
Appearance	Viscous colorless liquid
Specific Gravity at 25° C	1.065 g/mL
CMC	0.22-0.24 mM ⁽¹⁾

(1) Edwards et al., 1971

Table 4-3 Properties of SDS (Sigma, 1993)

Product name	Sodium dodecyl sulfate (> 98.5%)
Type	Anionic surfactant
Molecular formula:	$C_{12}H_{25}OSO_3Na$
M.W (g)	288.38
Appearance	Viscous colorless liquid
CMC	8.20 mM ⁽¹⁾

(1) Mukerjee and Mysels, 1971

Table 4-4 Properties of AOT (Sigma, 1993)

Product name	Sodium Dioctyl sulfosuccinate (96%)
Type	Anionic surfactant
Molecular formula:	$(C_9 H_{17} O_2)_2 CH_2 CH SO_3 Na$
M.W (g)	444.57
Appearance:	White solid
CMC	1.124 mM ⁽¹⁾

(1) Nivas et al. 1996

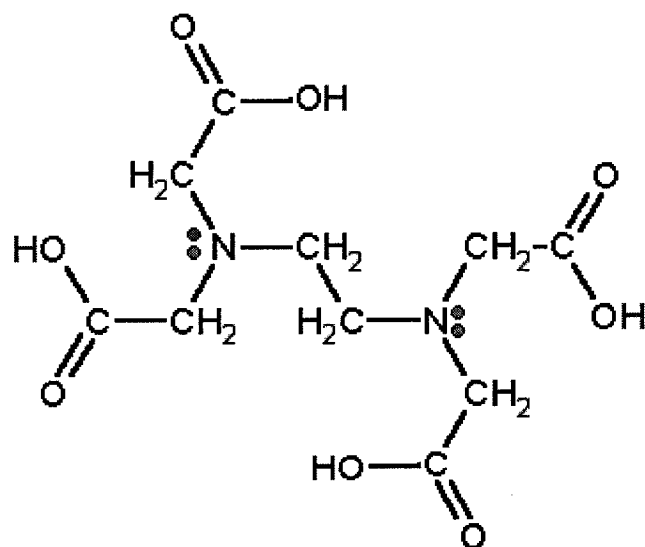


Fig. 4-1 Chemical structure of EDTA (Sinex, 2004)

Chemical structure of EDTA is shown in Fig. 4-1. EDTA used in this study was obtained from SIGMA Chemical Co.; U.S.A. The main property of EDTA is its ability to chelate or complex metal ions to form metal-to-EDTA complexes (Sinex, 2004).

4.2.3 Contaminants

The target contaminants Zn and Cu were added in the forms of $\text{Cu}(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 7\text{H}_2\text{O}$, which were purchased from Fisher Scientific. Montreal, Canada. They had a manufacturer's reported purity of 99%. They were dissolved in distilled water, before they were added to soil samples.

4.3 Experimental procedures

The soil samples were artificially contaminated in the laboratory. Batch and column experiments were then conducted to investigate different parameters involved in the surfactant-enhanced removal of heavy metal contaminated soils.

4.3.1 Soil contamination

Metal salt solution containing 4000 mg/L of $\text{Cu}(\text{NO}_3)_2$ and 4000 mg/L of $\text{Zn}(\text{NO}_3)_2$ were added to sand and bentonite separately. The solution to sand ratio was 1L:4kg and the solution to bentonite ratio was 1L:0.1kg. The addition of the metallic solution was followed by shaking them separately on a wrist action shaker (BURRELL, Burrell, Scientific, Pittsburgh, P.A., USA) at 60 Oscillations/min for 24 hours at a room temperature of $25^\circ\text{C} \pm 2^\circ\text{C}$. After centrifugation at 3000 rpm for 15 minutes, the supernatant was removed and the two soil samples were dried in the oven at 100°C for 48

hours. Following this, the dried contaminated sand and bentonite samples were kept for 1 month separately. The last operation in preparing the soil samples for batch testing involved the addition of 0.10 g contaminated bentonite and 4.90 g of contaminated sand to each sampling tube. Since the quantity of metal retained in both the soils is quite small, it is reasonable to assume that the combined soil still contained 2% of bentonite.

As stated earlier, It was possible to ensure that all samples contained very nearly 2% ($\pm 0.02\%$) bentonite and 98% sand in the sample, by initially segregating the sand and bentonite during the process of contamination and subsequently taking known quantities of the two soils for testing.

To measure the concentration of metals present in the soil, the soil sample was digested by 70% of HNO_3 and shaken at 60 rpm/min for 24 hours. Nitric acid is a strong oxidizing acid. It dissolves most of the common metals. The Atomic Absorption (AA) Spectrophotometer (Perkin Elmer AAnalyst 100, PerkinElmer Inc., ON, Canada) analysis of the digested sample yielded the metal concentrations. Following the detail instructions listed in the Perkin Elmer's analyze manual, one measure metal concentration to the nearest 0.1mg/L. These tests were performed in triplicate and did not vary by more than 5 %. The average results are presented in Table 4-5.

Table 4-5 Soil contamination levels: (Soil: 2 % bentonite and 98 % sand)

Cu (II) Concentration mg/kg Soil	Zn (II) Concentration mg/kg Soil
1216	1152

4.3.2 Batch experiments

Batch extraction experiments were conducted at a room temperature of $25^{\circ} \pm 2^{\circ}\text{C}$. All soil samples were dried at 105°C for a minimum of 24 hours before usage. Three different surfactants and a complexing agent solution (SDS, AOT, Tx-100, and EDTA) at different concentrations and combinations (Tables B-1 to B-5) were used to determine their effects on the extraction of Cu (II) and Zn (II) from the contaminated soil. Typically, in all batch experiments, 5.0 g (4.9 g of sand + 0.10 g of bentonite) of contaminated soil samples were weighed out into the reactor formed of 50 ml plastic Nylon centrifuge tubes. For each tests involving a washing solution, the volume of the solution chosen was 40 ml, because the tube size was 50 ml. 40 ml of solutions were added at varying concentrations to the reactors (tubes). All the gravimetric measurements were done with a Sartorius balance (0.001g). The samples were equilibrated in a wrist action shaker at 60 rpm for 24 h, and later centrifuged for about 20 minutes, and the supernatant was taken for subsequent AA analysis of metal concentration. All the batch experiments except those for tests related to contaminant aging were done in triplicate and the reported values denote average metal concentrations.

4.3.3 Column experiment

All column experiments were conducted at room temperature ($25 \pm 2^{\circ}\text{C}$). The experimental set-up is shown in Fig. 4-2. Plexiglas columns ($L=20.5\text{ cm}$, $D=4.0\text{cm}$) with metal end pieces were equipped with a pore stone and also a Whatman filter paper ($0.7\mu\text{m}$) to prevent soil dispersion. A peristaltic pump and a high level container were used to maintain a constant flow through the column.

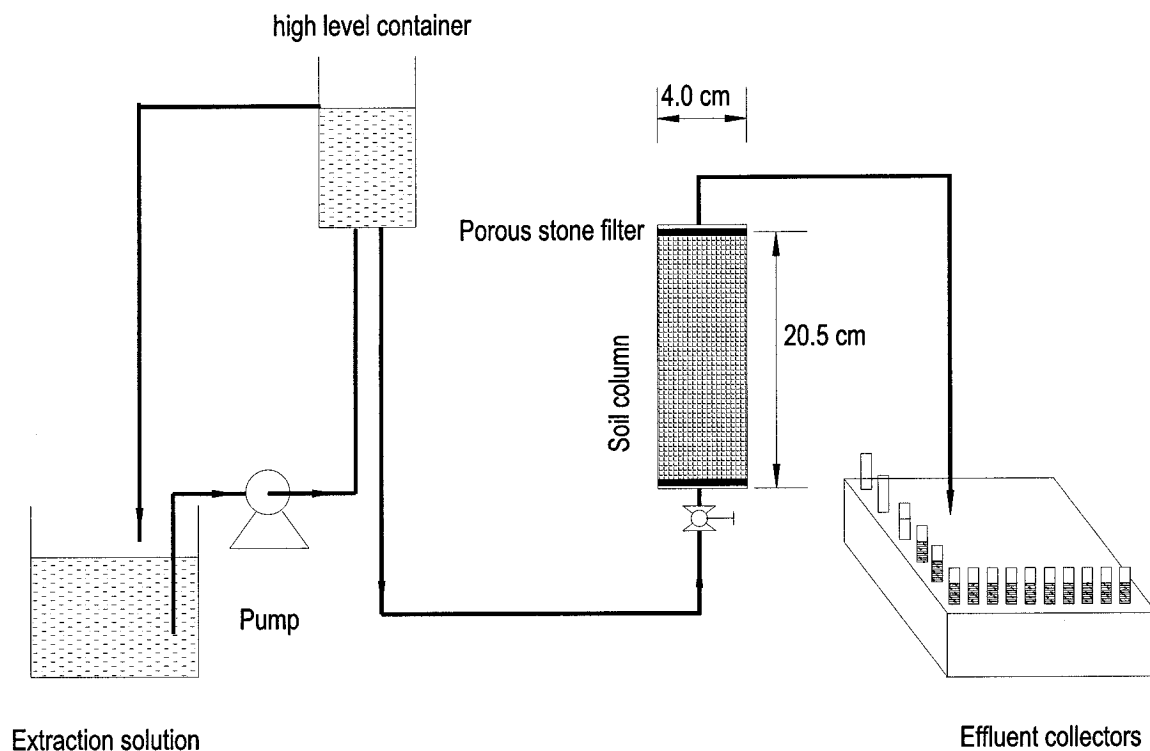


Fig. 4-2 Schematic setup of the column experiment

A series of column experiments were conducted to investigate the effect of surfactants and the complexing agent solution involved in the soil flushing technology on metal removal. The soil samples for each column test were separately prepared, by mixing 2% bentonite and 98% sand. These two ingredients were mixed thoroughly in a large plastic box using a 25mm plastic spatula. Following this, the soil mixture was shaken for nearly 20 minutes. The column was packed with the mixed dried soil by adding the soil in layers of 2 cm under continuous tapping against the Plexiglas wall to provide uniformity. The flow was maintained at the desired pore water velocity (V) by

adjusting the valve. 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}):

$$P_v = W_{sat} - W_{dry} \quad (4-1)$$

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

$$V = QL / P_v \quad (4-2)$$

Here, Q is the average flux of water through the columns (m^3/s), L is the column length (m), and P_v is the pore volume (m^3).

The surfactant solution or water was pumped through the soil column. The column effluent was manually collected for a constant time at regular intervals. All the samples of effluent were digested by HNO_3 (70%) and shaken at 60 rpm for 24 hours. Following this, AA analysis was performed to measure the metal concentration in the effluent. The amount of metal removed was calculated as the product of concentration (C_s) and the collected effluent volume. The removal efficiency was calculated based on this data and the level of initial contamination.

CHAPTER 5

DISCUSSION OF RESULTS

5.1 General remarks

In the present study, distilled water, surfactants with and without a complexing agent are used to remove Zn (II) and Cu (II) from an artificially contaminated sandy soil. SDS, AOT and Tx-100 are the surfactants used. EDTA is the complexing agent selected for soil washing. The temperature for all experiments was in the range of $25^{\circ} \pm 2^{\circ}$ C.

5.2 Batch tests

5.2.1 Effect of surfactant concentration

The results of batch extraction experiments are shown in Fig. 5-1 to Fig. 5-6. Table B-1 to Table B-3 provide the additional details such as pH data related to the tests. The initial pH values denote the pH values of surfactant solution before they were added to the soil samples. The final pH is the pH value noted after shaking the soil sample 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 mentioned before, the solid: liquid ratio is 5g: 40mL.

$$1 \text{ mg/L (metal ion)} = 1 \text{ mg/L} \times 40 \text{ mL} / 5 \text{ g} = 8 \text{ mg/kg.}$$

Surfactant concentration is an important factor influencing the removal efficiency of heavy metals. The results for Tx-100 show that the desorbed metal concentrations increase with increasing surfactant concentration C_s until $C_s = 0.5 \text{ mM} = 2.17 \text{ CMC}$

(Figs. 5-1 and 5-2). Beyond this surfactant concentration, metal removal remained nearly constant. Unlike the experiments dealing with the anionic surfactants (AOT and SDS) at higher concentrations, in tests involving nonionic Tx-100, no metal precipitation was observed. It may be added that Doong et al (1996) asserted that more Tx-100 was 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. It may thus be possible for the adsorbed surfactant on the soil particles to displace the bound metal. The stated CMCs are based on data related to CMC in water reported by Mukerjee and Mysels (1971).

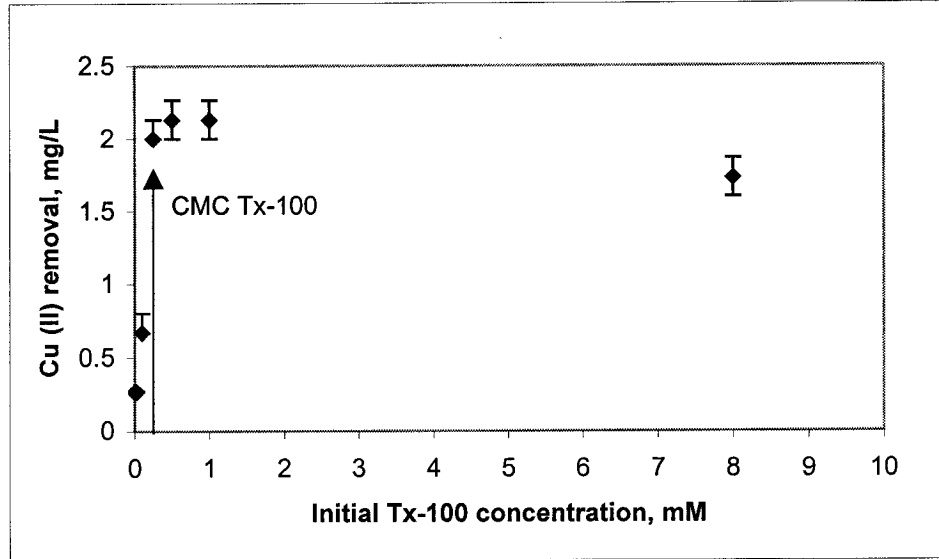


Fig. 5-1 Batch extraction of Cu (II) from contaminated soil by Tx-100
 (Soil to liquid ratio: 1g: 8 mL)

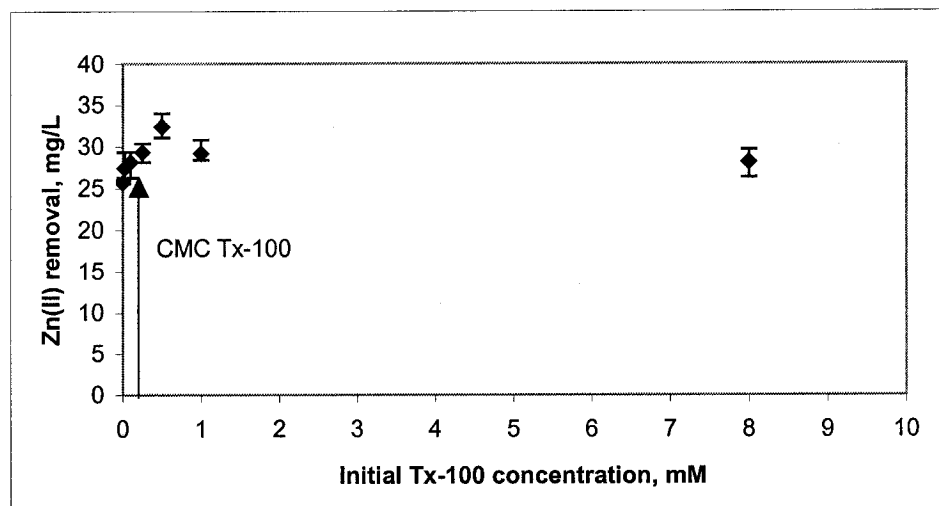


Fig. 5-2 Batch extraction of Zn (II) from contaminated soil by Tx-100
 (Soil to liquid ratio: 1g: 8 mL)

T = 25° ± 2° C, Initial pH=5.15-5.38, Final pH= 6.34-6.52

Fig.5-3 to Fig.5-6 indicate that the effect of SDS and AOT on desorption of Cu (II) and Zn (II) is not noticeable until the concentration reaches the CMC. When the concentration exceeds the CMC, metal removal tends to be high. When the surfactant concentration exceeds the CMC, the removal remains constant (Fig. 5-3 and Fig. 5-6) or decreases (Fig 5-4 and Fig. 5-5). Since both Cu (II) and Zn (II) are cations, the anionic surfactants would not directly be involved in the ion exchange process. When the surfactant concentration reaches the CMC, micelles are formed and there is a noticeable increase in metal desorption (Fig. 5-3 to 5-6). The interfacial region between the aqueous solution and the micelle containing the ionic head groups is the Stern layer of the electrical double layer (Rosen, 1979). Counter ions associated with the micelles (cation ions) in the Stern layer could exchange with the metal cations. This view is supported by the study of Gadelle et al (2001). They concluded that the most probable mechanism of metal removal by a surfactant are mainly a result of cation exchange in the electric double layer surrounding the micelles and to a lesser extent, dissolution of the soil matrix.

With an increase in concentration beyond the CMC, the micelles that trapped the metal ions appear as a precipitate and get attached to the soil particles. Especially in the case of Cu (II), blue patches of matter were clearly discernible on top of the sediment in the sampling tube. Consequently, at concentrations higher than the CMC, a further increase in metal concentration in the supernatant (Fig. 5-3 to Fig. 5-6.) should not be expected.

The exchangeable ions (monomers) will increase until the CMC is reached, and remain relatively constant above the CMC. One also notes that the negatively charged head

group of the micelles cannot exchange metal cations. However, the results obtained for two anionic surfactants in this study (Fig. 5-3 to Fig.5-6) indicate that the enhancement of heavy metal removal mainly occurs at the concentrations close to the CMC, or at concentrations a little higher than the CMC. This suggests that it is the micelle that indirectly results in the mobilization and subsequent removal of metals. Based on ultrafiltration experiments, Mulligan et al. (2001b) also found that it is the micelles that solubilize metals. They concluded that through sorption of the surfactant on to the soil surface and complexation with the metal, detachment of the metal occurs from the soil into the soil solution.

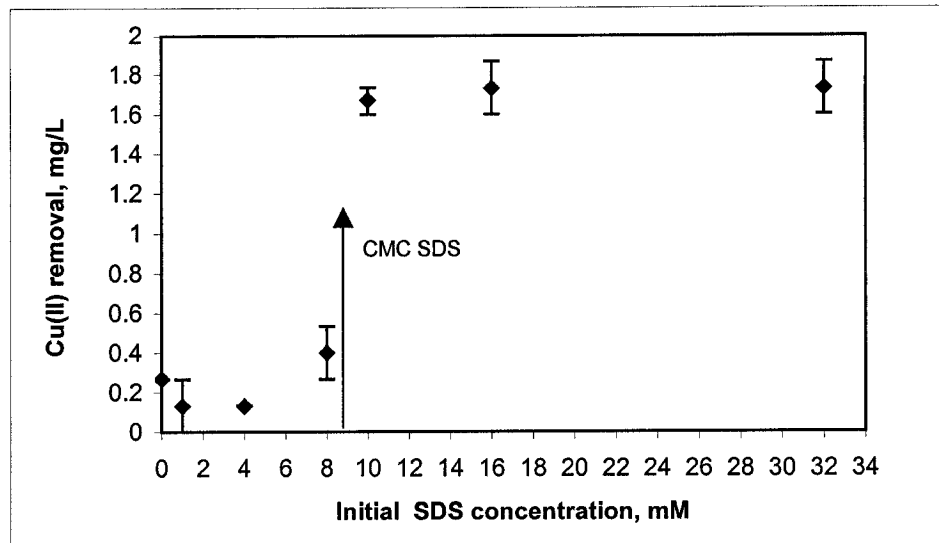


Fig. 5-3 Batch extraction of Cu (II) from contaminated soil by SDS
(Soil to liquid ratio: 1g: 8 mL)

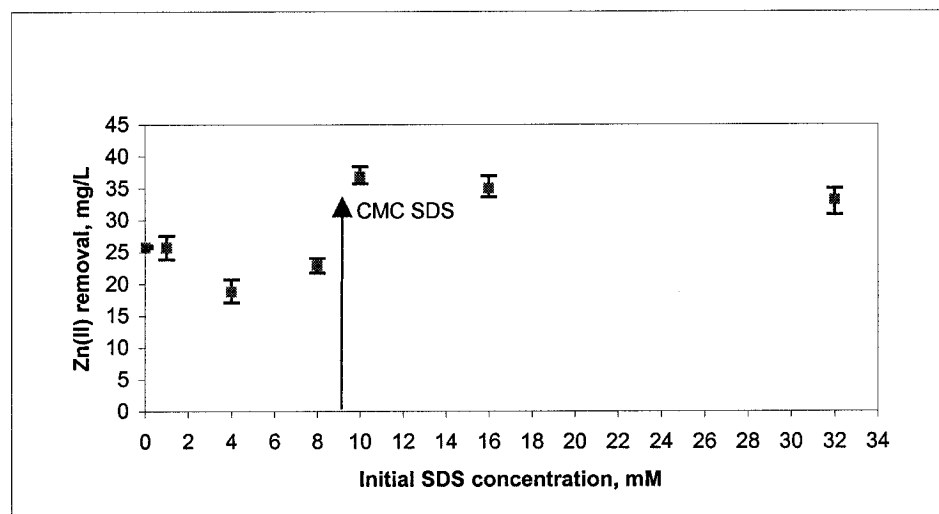


Fig. 5-4 Batch extraction of Zn (II) from contaminated soil by SDS
(Soil to liquid ratio: 1g: 8 mL)

T = 25° ± 2° C, Initial pH=4.38-3.54, Final pH= 6.32-6.76

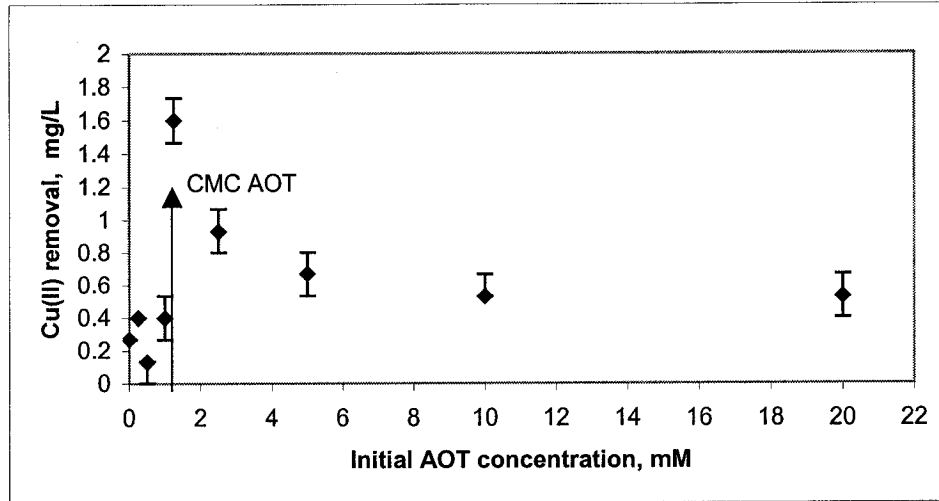


Fig. 5-5 Batch extraction of Cu (II) from contaminated soil by AOT
(Soil to liquid ratio: 1g: 8 mL)

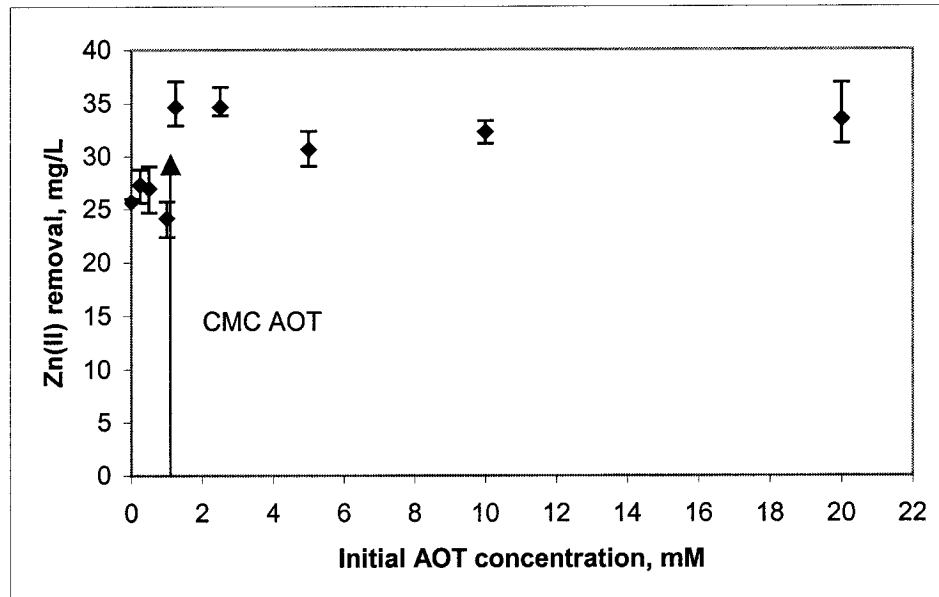


Fig. 5-6 Batch extraction of Zn (II) from contaminated soil by AOT
(Soil to liquid ratio: 1g: 8 mL)

T = 25° ± 2° C, Initial pH=5.81-7.76, Final pH= 6.21-7.39

5.2.2 Effect of surfactant type

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

Table 5-1 Results of metal extraction studies

No	Surfactant	Optimal Concentration (mM)	Ratio to CMC	Max. Cu removed (mg/L)	Ratio to Cu removed by water	Max. Zn removed (mg/L)	Ratio to Zn removed by water
1	TX-100	0.5	2.17	2.13	7.98	32.40	1.26
2	SDS	10	1.25	1.65	6.25	36.80	1.43
3	AOT	1.25	1.11	1.60	5.99	34.67	1.35

At equilibrium, distilled water removed 0.2mg/L of Cu (II) and 25.7mg/L Zn (II) through solubilization. The highest desorbed concentrations of Cu (II) were 2.17mg/L, 1.25mg/L and 1.11ppm in Tx-100 (Fig. 5-1), SDS (Fig. 5-3) and AOT (Fig. 5-5) amended system respectively. This corresponds to 7.98, 6.25 and 5.99 times greater mobilization of Cu than that mobilized by distilled water. The desorbed concentrations of Zn (II) were 32.4 mg/L, 36.8 mg/L and 34.67 mg/L respectively in Tx-100 (Fig. 5-2), SDS (Fig.5-4) and AOT (Fig. 5-6) amended systems. This corresponds to Zn (II) removal which is 1.26, 1.43, and 1.35 times greater than that by distilled water alone. The optimal concentration generally occurs at a slightly higher concentration than the standard CMC.

For the present test results, the reported CMCs are based on data related to CMC in water. However, many factors such as temperature, pH, electrolyte and other additives strongly affect the observed CMC of surfactant systems (Myers, 1999). Consequently, the

presence of the constituents of the soil may affect the CMCs of surfactant systems. Further more, loss of surfactant occurs as some of it gets adsorbed to the soil. Hence, one should expect the surfactant to attain CMC at a higher concentration. It is possible to experimentally determine the changes in CMC due to presence of the sandy soil used in the present tests.

As mentioned before, the nonionic surfactant would not be involved in the ion exchange processes and counterion binding. One would normally expect anionic surfactants to exhibit better metal removal efficiency than nonionic surfactant. However, the results indicate that there is little difference in metal extraction. This may be partly due to the fact that anionic surfactants can precipitate metal cations from the soil solution. As stated earlier, in particular, the precipitation of Cu (II) as greenish-blue color solid on top of the sediment was discernible in the sample tubes.

5.2.3. Effect of surfactants as additives to the complexing agent

Recently, studies have been conducted to know the effect of using a mixture of ligands and surfactants to enhance the solubilization of metal ions (Ellis et al. 1986; Eliot et al. 1989; Peter and Shem 1992; and Reed et al 1996). To know the effect of addition of surfactant to EDTA in removing heavy metal Cu (II) and Zn (II), a few tests were performed. To this end, the 3 surfactants were added individually to EDTA and the metal removal efficiency was determined.

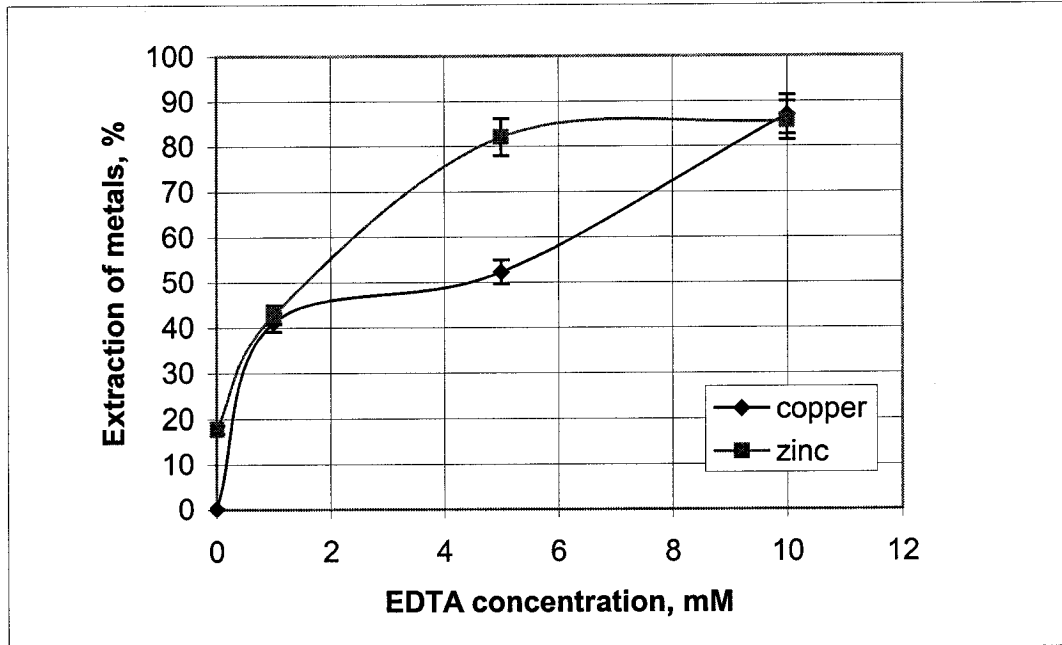


Fig. 5-7 Batch extraction of Cu (II) and Zn (II) with EDTA only

Fig. 5-7 and Table B-4 illustrate the extraction of Cu (II) and Zn (II) with EDTA only. Using EDTA does significantly enhance the removal of these metals. The extraction efficiency increased with increasing concentration of EDTA. However, the pH is also changing as the EDTA concentration increases which affects the metal ion solubility. The final pH is 5.34 when 1mM is used and pH is 2.34 when 10 mM EDTA is used. The extent of desorption differed for these two metals. Referring to the removal of metals by water alone, the enhancement of metal removal was more for Cu (II) than for Zn (II). Therefore it is difficult to determine the effect of pH and the effect of addition of the EDTA without the proper control.

Fig. 5-8 and Fig. 5-9 illustrate the extraction efficiency of Cu (II) and Zn (II) by a combination of surfactants and EDTA (5mM). Table B-5 provides additional data related to these tests. Different extraction capabilities of the surfactants and complexing agents are demonstrated. The pH is relevant and will be discussed in the section 5.3.5. Clearly, Cu (II) removal rate by combination of EDTA and SDS (10 mM) is nearly twice the removal rate of Cu (II) by EDTA alone (Fig. 5-8). 95% of Cu (II) was removed by the mixture of EDTA and SDS. The removal of Cu (II) is also improved by the addition of the other two surfactants to EDTA. However, AOT does not significantly improve Cu (II) removal compared to EDTA alone (Fig. 5-8). The Zn (II) removal rate appears to improve when EDTA is combined with surfactants (Fig. 5-9). The combination of SDS (10mM) and EDTA is extremely effective in removing all of Zn (II) in the sandy soil. 99% of Zn (II) was removed when using the mixture the SDS and EDTA. pH shown in the Fig. 5-8 and Fig. 5-9 refer to final values in the supernatant.

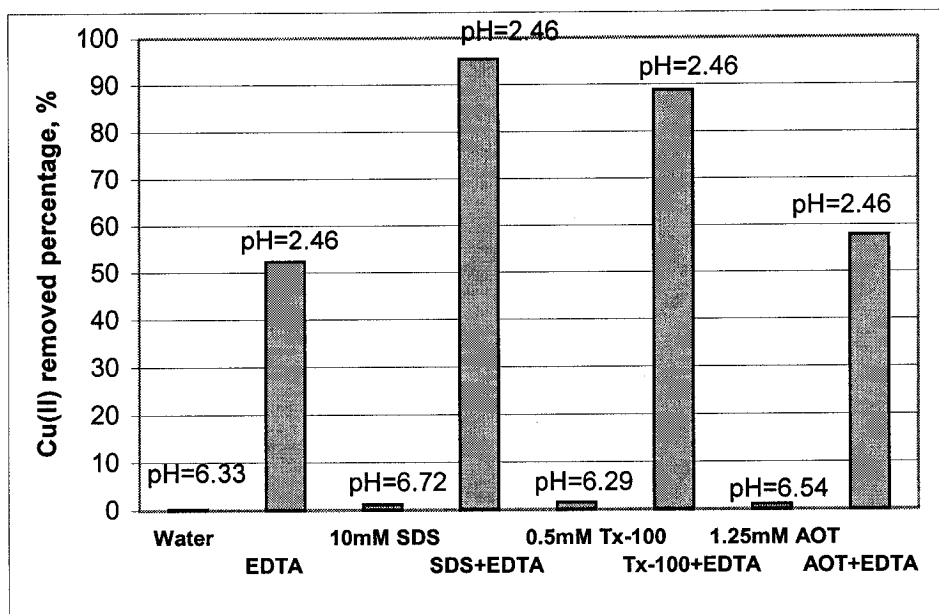


Fig. 5-8 Batch extraction of Cu (II) by surfactants and complexing agent EDTA (5mM EDTA)

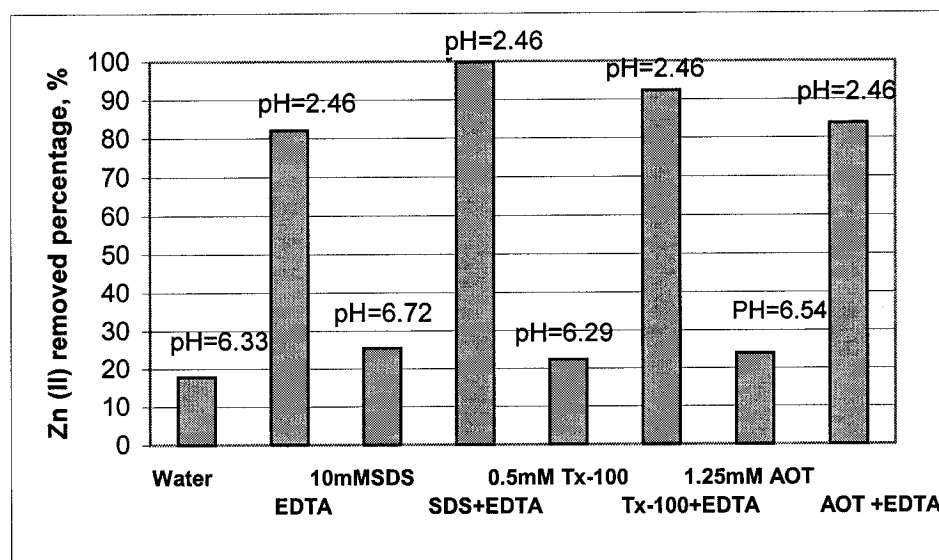


Fig. 5-9 Batch extraction of Zn (II) by surfactants and complexing agent EDTA (5mM EDTA)

5.2.4 Effect of contaminant aging

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

Batch extraction experiments were conducted to compare the mean metal removal efficiencies. The age of contaminants varied from 2 weeks to 12 weeks. Strictly speaking, the difference in age of contaminant 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. Specifically, over the study period, the extractable Zn (II) from each soil sample appears to decrease with time from 25.7 mg/L to 21.3 mg/L (Fig.5-10), and extractable Cu (II) from 0.23mg/L to 0.13mg/L (Fig.5-11). To confirm the effect of aging in removal efficiency, additional tests are required. Due to the limited scope of these experiments related to aging, the conclusions drawn are to be considered as tentative. Further additional tests should be conducted to study aging effects of soils historically contaminated with metals.

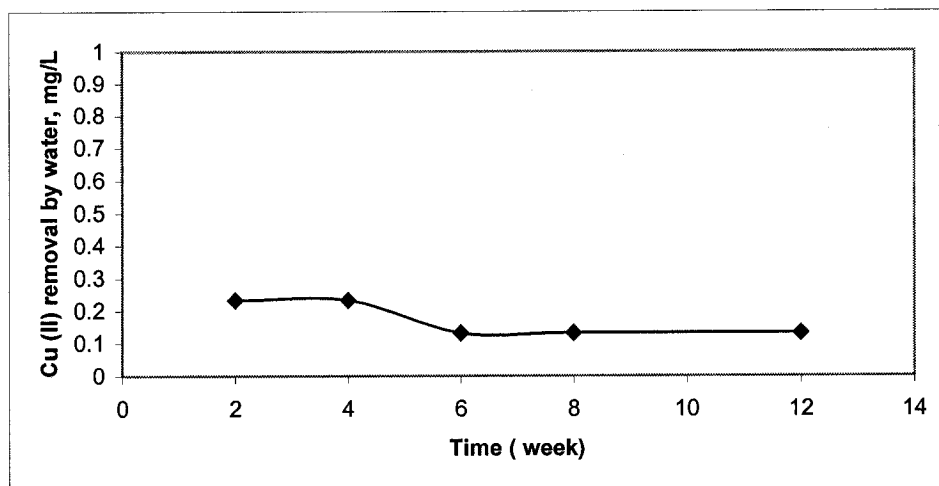


Fig. 5-10 Effect of contaminant aging on the extraction of Cu (II)

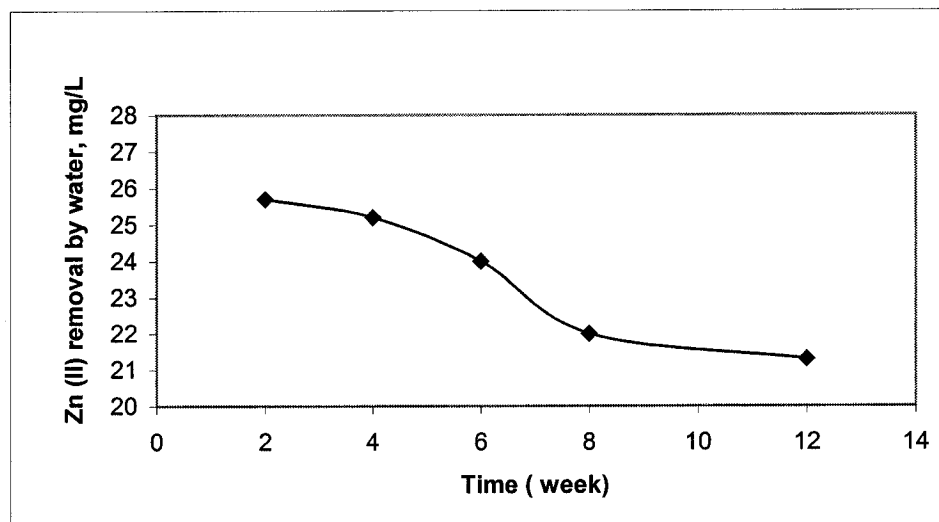


Fig. 5-11 Effect of contaminant aging on the extraction of Zn (II)

5.2.5 Effect of metal affinities and interaction

Many studies deal with heavy metal adsorption/desorption, when a single metal contaminant is present in soils. However, the presence of multiple competing heavy metal ions is more frequently encountered in nature.

Fig. 5-12 presents the results of AA analysis of metals for soil sample 1 that contains both copper and zinc salts. It shows that the amount of Cu (II) retained (1216 mg/kg) is slightly higher than the amount of Zn (II) retained (1152 mg/kg). This suggests that copper has a slightly higher affinity to the soil matrix adsorption sites than zinc.

When several heavy metals are present, synergic effects could change adsorption and desorption. In order to study the interaction between the two metals Cu (II) and Zn (II), parallel experiments were conducted to compare the results with and without metal interactions. A metal salt solution containing 4,000 mg/L of only Cu (II) was added to the sand and bentonite samples. This soil sample is termed as soil sample 2. Metal salts containing 4,000 mg/L of only Zn (II) were added to the sand and bentonite samples to form soil sample 3. The procedure to prepare soil sample 2 and soil sample 3 was identical to the procedure followed to prepare soil sample 1. Again, AA analysis was used to determine the amount of metal retained by the soil sample (Fig. 5-12).

Fig. 5-12 shows that Cu (II) retention in the presence of Zn (II) is marginally affected, while the retention of Zn (II) is significantly reduced in the presence of Cu (II). These

results confirm that Cu (II) has a higher affinity for the available adsorption sites of the soil.

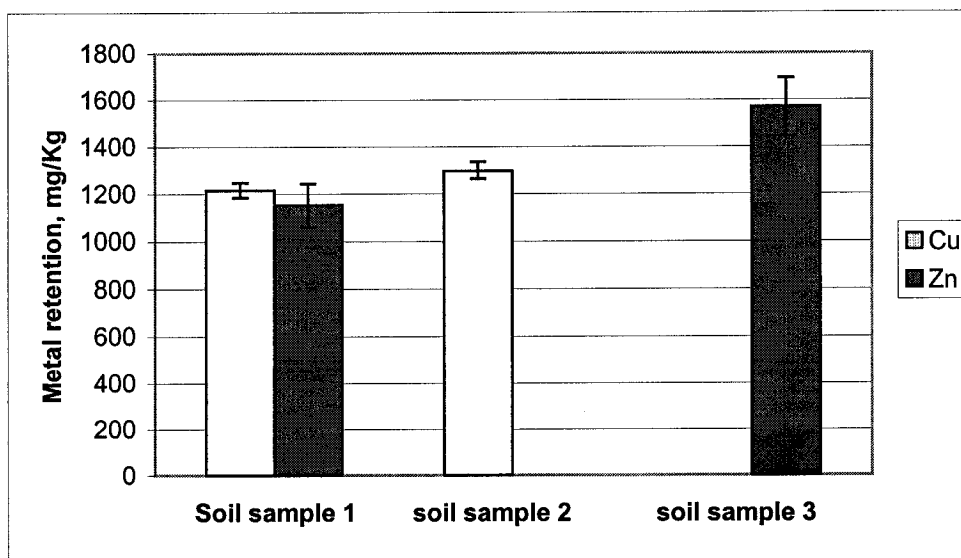


Fig. 5-12 Interaction study related to metal retention

The competition between Cu (II) and Zn (II) in the desorption mode was also studied using the same artificially formed soil samples. The extraction study for soil sample 1 (Fig. 5-13) shows that in distilled water, a large amount of Zn (II) (17.9%) gets desorbed compared to the amount of Cu (II) (0.17%) desorption. This observation holds good qualitatively for tests where the surfactant SDS was used (Fig. 5-14, soil sample 1). This behavior of Zn (II) can again be traced to the fact that Zn (II) is not as strongly bound as Cu (II) to the adsorption sites of the soil matrix.

To know more about the interaction between metals during desorption, desorption tests were conducted on soil samples 1 and sample 2 using both distilled water and surfactant

SDS (Figs. 5-13 and 5-14). The results indicate that the presence of Zn (II) in the soil significantly reduces Cu (II) desorption. Quantitatively, Cu (II) desorption decreases to 0.23% from 0.63% in water and to 1.7% from 4.3% in SDS when Zn (II) is also present. This confirms the interaction effect between these two metals. Further more, Figs. 5-13 and 5-14 indicate that a much larger amount of Zn (II) desorption occurs when Cu (II) is also present in the soil. Quantitatively, when Cu (II) is present, Zn (II) desorption increase to 17.7% from 5.3% in water and 25.4% from 7.1% in SDS (soil sample 1 and 3). A possible reason for this behavior of metals may be traced to the following facts. Cu (II) is bound to the stronger soil adsorption sites such as organic phase sites. In fact, in an earlier study (Ramos et al., 1992), it was stated that copper was associated with the organic fraction or residual fraction, and that Zn (II) was primarily associated with the oxide fraction.

When Cu (II) is absent, these sites are available for Zn (II). Hence, in this case, removal of Zn (II) is more difficult (soil sample 3). These observations hold good for both desorption test for distilled water and surfactant SDS.

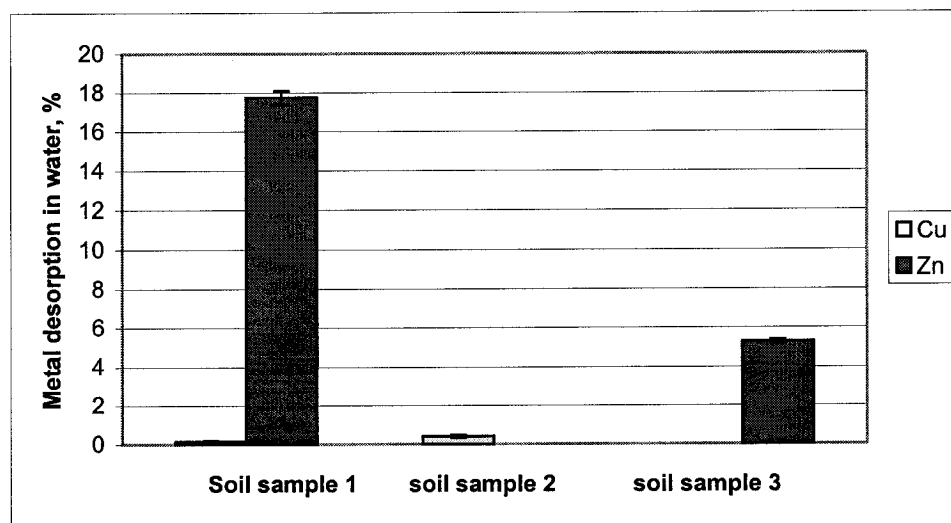
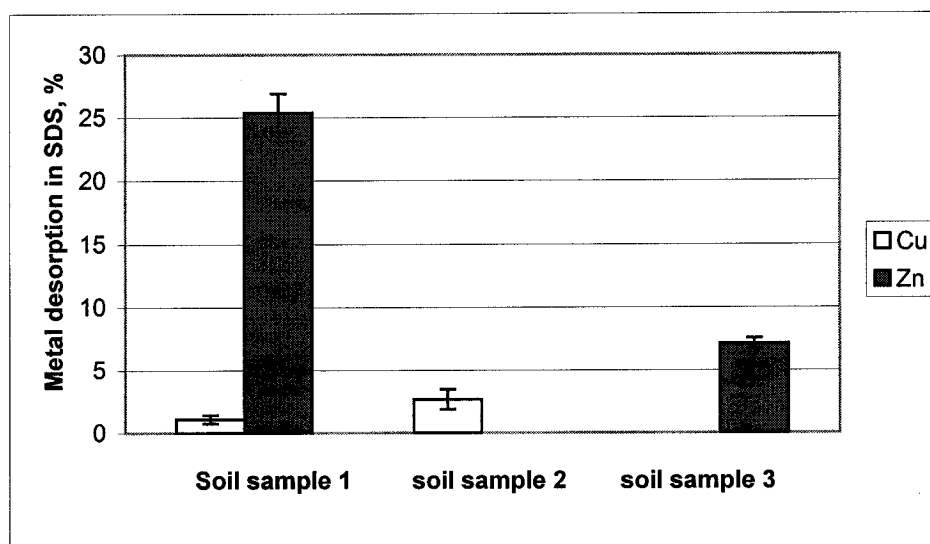


Fig. 5-13. Interaction study related to metal desorption (Solvent: water)



**Fig. 5-14. Interaction study related to metal desorption
(Solvent: 10 mM SDS solution)**

5.3 Column studies

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 (Allen et al., 1995). The column method is more realistic in simulating field conditions. In the field, the matrix is in a fixed position and the surfactant passes through it (Allen et al., 1995). As such, to reproduce field conditions, column studies were conducted.

Batch experiments indicated that surfactants could enhance the removal of copper and zinc compounds from a sandy soil. Characteristic coefficients of adsorption or desorption are usually provided by batch experiments conducted in shake flasks. Soil moisture, temperature history, contaminant concentration, age of contamination and water flow rate may change the rate and extent of chemical reaction with the soil matrix (Allen et al., 1995). For the column tests, the column was initially packed uniformly with the soil. The surfactant was continuously introduced at a fixed rate until steady state was achieved.

Metal washing from soil columns were evaluated with distilled water, surfactant, complexing agent EDTA and EDTA together with a surfactant. The batch tests established that SDS was the most effective of the 3 surfactants in removing the metal contaminants related to Zn (II) and Cu (II). Consequently, column tests were conducted using SDS as the surfactant to augment the removal of Zn (II) and Cu (II) with and

without EDTA. Table 5-2 lists some of the relevant details pertaining to the column studies. The last 3 column studies used the same extracting agent at different flow rates in order to investigate the effect of flow rates on washing efficiencies. Hydraulic conductivity is $0.00363 \pm 0.00017 \text{ cm/s}$ (See appendix A) and one pore volume is 92 mL.

Table 5-2 Column properties

Extracting Agent	Mass of soil (g)	Soil density (g/cm³)	Flow rate (mL/min)	Pore water velocity (cm/min)
Distilled water	392.5	1.52	12	2.7
SDS (10 mM)	393.2	1.53	12	2.7
EDTA (5mM)	392.6	1.52	12	2.7
SDS (10 mM) With EDTA (5mM)	392.8	1.53	12	2.7
SDS (10 mM) With EDTA (5mM)	393.2	1.53	4	0.9
SDS(10 mM) With EDTA (5mM)	393.0	1.53	40	8.9

5.3.1 Column test results

Column results using distilled water and 10 mM SDS are shown in Fig. 5-15 to Fig. 5-17. Table C-1 and Table C-2 provide more detailed data related to these tests. These results indicated that Cu (II) removed by water alone is quite small. In fact, 50 pore volumes of water appear to remove only 2 % of Cu (II). On the other hand, the amount of Zn (II) removed by water is relatively high (17 %) at 50 pore volumes. Results (Fig. 5-17) indicate that metal removal is insignificant after 20 pore volumes. The same tests also indicate that SDS removes 13 % of Cu (II) and 21 % of Zn (II) at 50 pore volumes.

Fig. 5-17 shows the amount of metal removal plotted as a function of the pore volume. Compared to metal removal by distilled water (2 %), SDS appears to be quite effective in removing Cu (II) (13 %). However, SDS shows only a marginal improvement in the removal of Zn (II), since even distilled water itself can remove nearly 17 % of Zn (II) at 50 pore volumes. This may be traced to the earlier stated fact that Zn (II) is less strongly bound than Cu (II) to the soil matrix and gets removed more easily.

In this study, the metal concentrations were very high in the effluent, when the first 3 pore volumes passed through the column. This may partly be due to the fact that the contaminant's age is not large. The escape of some fine particles through the filters may also have contributed to this fact.

Batch experimental results indicate that the addition of anionic and nonionic surfactants enhance desorption of heavy metals from the contaminated soil. Based on the

concentration ratio of heavy metals extracted from the SDS system to those extracted from the blank control system, the enhancement ratios were found to be 6.25 for Cu (II) and 1.43 for Zn (II) respectively. In column studies, for 50 pore volumes, the enhancement ratios were 6.06 for Cu (II) and 1.21 for Zn (II). In terms of removal percentages, the quantities were 13.5 % for Cu (II) and 21.1 % for Zn (II) can be removed after 50 pore volumes. We notice a reasonable agreement between column and batch tests.

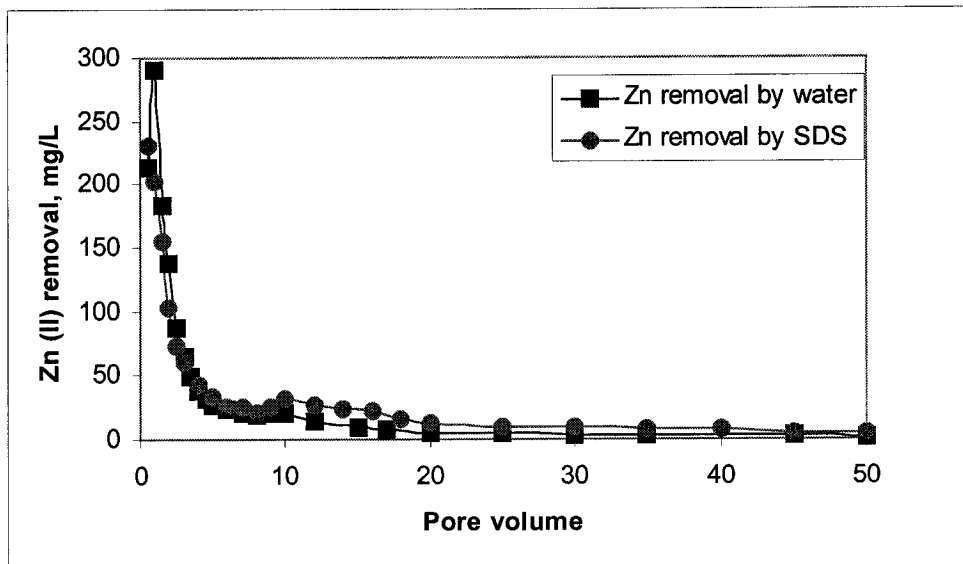


Fig. 5-15 Zn (II) removal from column by distilled water and 10mM SDS

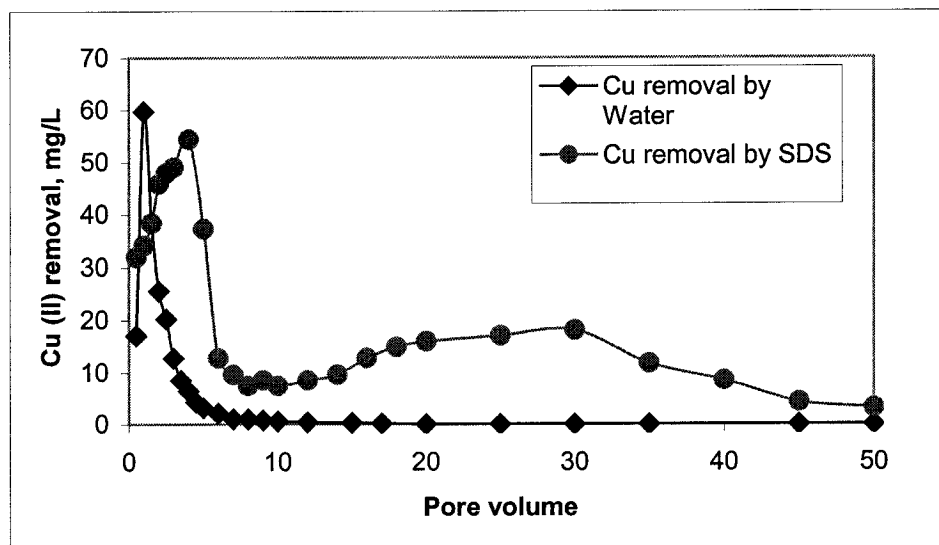


Fig. 5-16 Cu (II) removal from column by distilled water and 10mM SDS

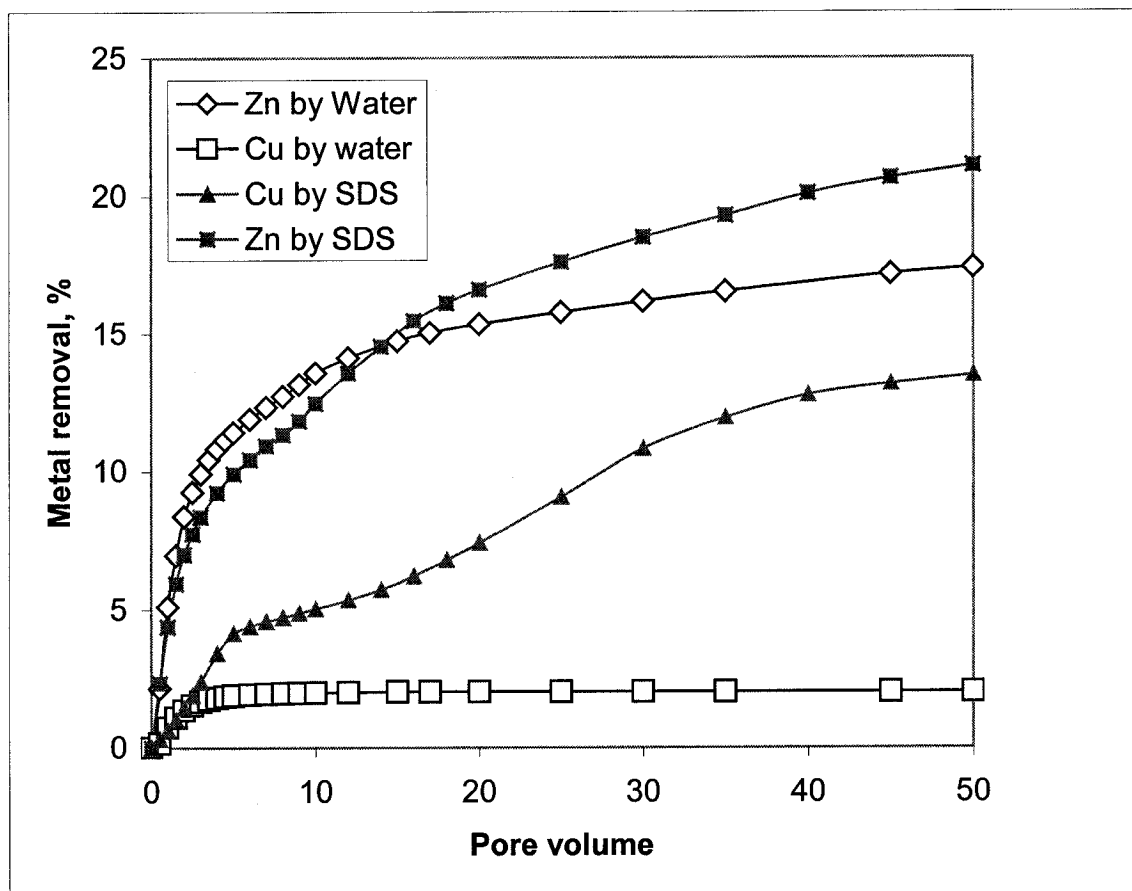


Fig. 5-17 Metal removal efficiencies by distilled water and 10mM SDS

5.3.2 Column studies using complexing agent EDTA

Column test results using 5 mM EDTA only and 10 mM SDS with 5 mM EDTA are shown in Figs. 5-18 to 5-20 respectively. Table C-3 and Table C-4 also provide additional data related to these tests. Fig. 5-19 indicates that the addition of SDS to EDTA improves the removal of Cu (II). The highest effluent concentration of Cu (II) occurs at about 35th pore volumes for the case where only EDTA is used. With the addition of SDS to EDTA, the highest effluent concentration of Cu (II) occurs at about the 18th pore volume. The highest effluent concentration of Zn (II) occurs at about 20th pore volume for the case where only EDTA is used. With the addition of SDS to EDTA, the highest effluent concentration of Zn (II) occurs at about the 10th pore volume (Fig. 5-18). In fact, at about 11 pore volumes, the total Zn (II) removal is the same as the removal of Zn (II) by EDTA alone at 20 pore volumes.

Fig. 5-20 is derived from Fig. 5-18 and Fig. 15-19. It indicates that the addition of SDS to EDTA does improve metal removal rate, as expected. For instance, for 60 pore volumes, Cu (II) removal rate increases from 50.5% to 59.1%, when SDS is added to EDTA. Similarly, Zn (II) removal rate increases from 61.0% to 70.4%, when SDS is added to EDTA. In the batch systems, addition of SDS enhanced the extraction by 1.82 times for Cu (II) removal and 1.21 times for Zn (II) removal. The enhancement in removal efficiency is clearly less than that in the batch systems. This is probably due to the fact that equilibrium was not achieved, even after 60 pore volumes in column tests.

When using SDS alone as the solvent, the highest effluent concentration of Cu (II) occurs at $P_v = 35$ (Fig. 5-18). The highest effluent concentration of Zn (II) occurs at about $P_v = 20$ (Fig. 5-19). Cu (II) can be strongly bound to the clay mineral. Copper can also occur in soil as crystal lattice-bound Cu (II) (Alloway, 1990). This fraction of Cu (II) can be released through solvent diffusion. Wu et al. (1999) also assert that high energy binding of copper associated with organics and the layered silicate makes it difficult to release the metal during desorption. Part of the delay in the occurrence of the peak concentration of Cu (II) may hence be attributed to the process of the solvent diffusion that is required for the release of Cu (II). Diffusion is a slow process and that may be the cause of delay in peaking.

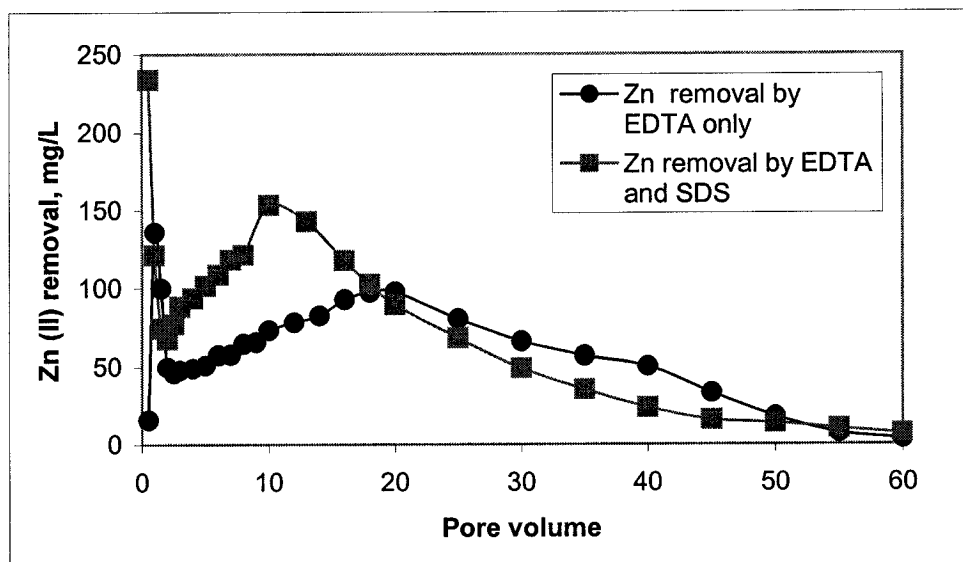


Fig. 5-18 Zn (II) removal from column by 5 mM EDTA
(With and without 10 mM SDS)

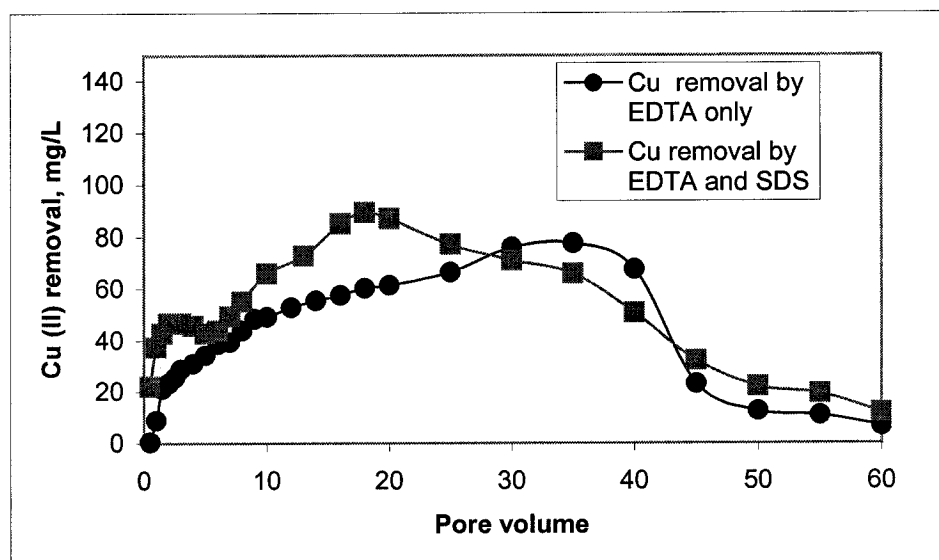


Fig. 5-19 Cu (II) removal from column by 5 mM EDTA
(With and without 10 mM SDS)

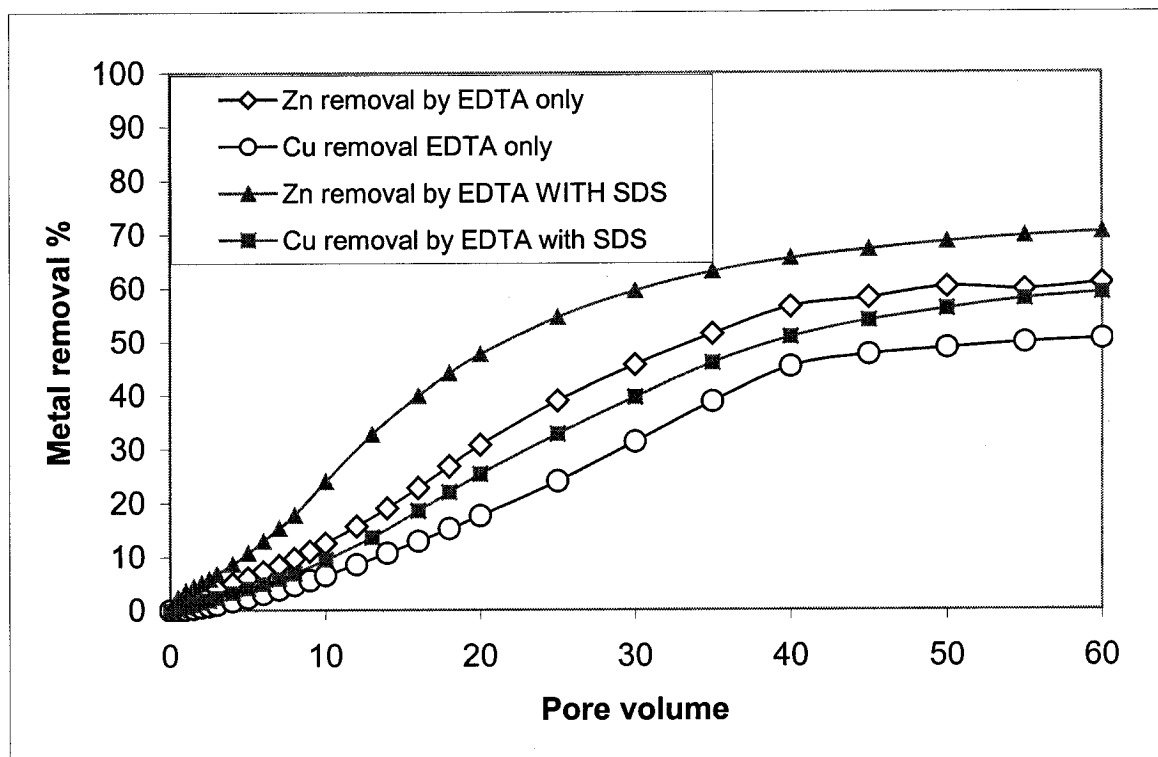


Fig. 5-20 Metal removal efficiencies by 5 mM EDTA
(With and without 10 mM SDS)

5.3.3 Effect of flow rate

The flow rate through the column was varied over a range of 4 to 40 ml/min using SDS (10 mM) together with EDTA (5 mM). The time of washing using a fixed solution volume varied from 26 hours to 2.6 hours.

Fig. 5-21 and Fig. 5-22 illustrate the metal removal result at different flow rates. Table C-4, Table C-5 and Table C-6 provide the data related to the tests. The general trend of metal washing curves is the same for all flow rates in this study. Even when the flow rates were very different, both Zn (II) and Cu (II) removal were best correlated with the volume of the extraction solution. Therefore, the metal removal is primarily related to the volume of the washing solution. It is not very dependent on the reaction rate. Yet, for metal removal, flow rate is slightly influential although it is not a dominant factor.

From Fig. 5-21 and Fig. 5-22, one can see that the highest flow rate is desirable for removal of Zn (II). Generally, removal of Zn (II) appears to slightly increase at the higher flow rate of 40 ml/min compared to the removal at lower flow rate. Approximately 93 % of Zn (II) was removed at the highest flow rate of 40ml/min after 60 pore volumes. This may be attributed to the higher fluid shear and increased dispersion of the solute in the soil media for removal of Zn (II). Furthermore, it is noted that Zn (II) is less strongly bound and does not require a long residence time to be removed.

A lower flow rate appears to be more desirable for Cu (II) removal (Fig. 5-22). At the lowest flow rate of 4 ml/min, the total Cu (II) removal increased to 66 % from 59 %

(flow rate 12 ml/min) after 60 pore volumes. This may be partly due to the longer contact and reaction time needed to release the strongly bound Cu (II).

In general, the results demonstrated that little gain in washing efficiency is achieved by employing the lower flow rate. The fastest flow rate produces washing efficiencies near that of the slower rates, while requiring a much shorter wash time. Operation at highest possible flow rate is recommended to extract the readily removable contamination, so that treatment time is minimized. Lower flow rate subsequently may be employed for more efficient removal of the persistent metal. The column tests related to flow rate changes may be further verified by repeating the tests to ensure that the trends seen in figs 5-21 and 5-22 are achieved consistently.

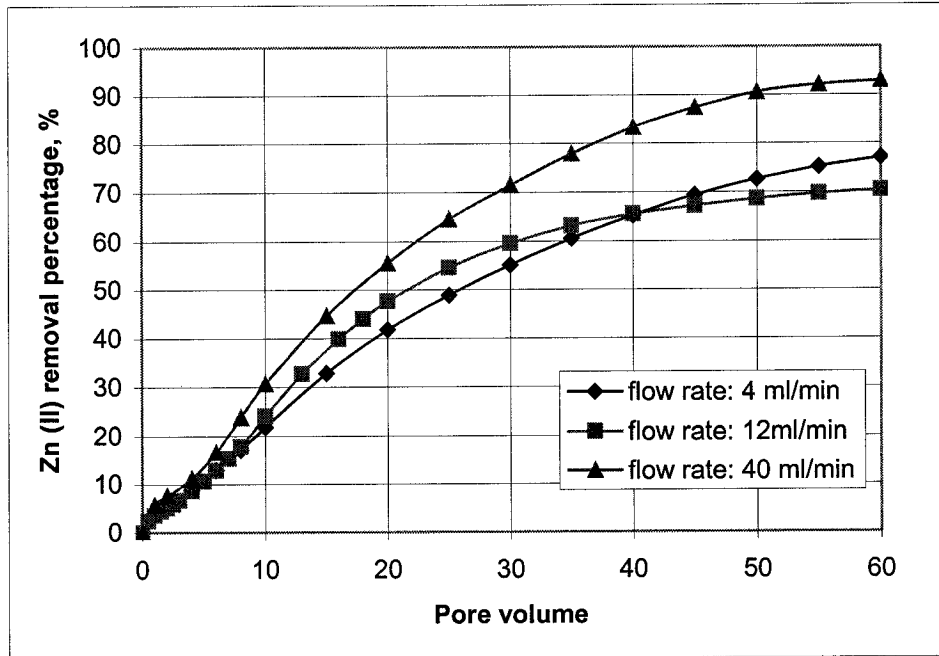


Fig. 5-21 Zn (II) removal by different flow rates
 (Solvent: mixture of 5 mM EDTA and 10mM SDS)

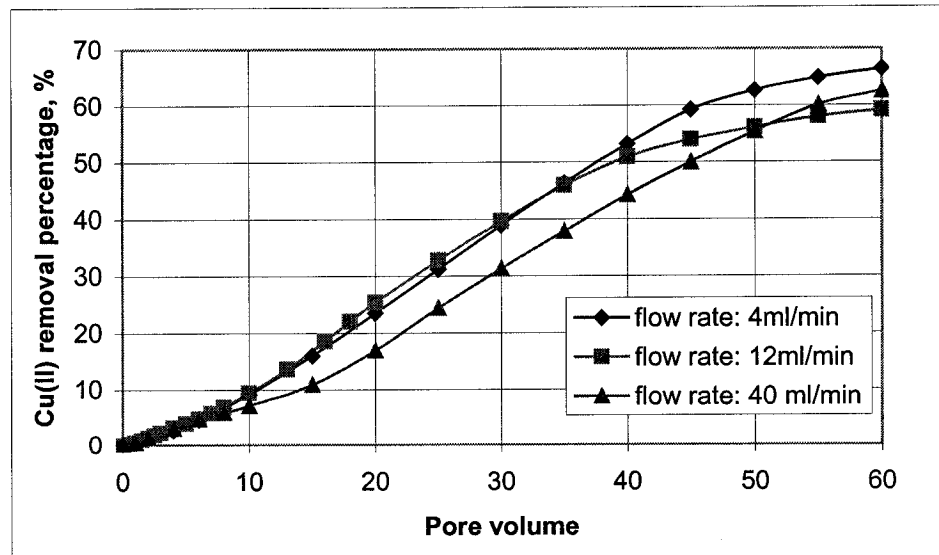


Fig. 5-22 Cu (II) removal by different flow rates
 (Solvent: mixture of 5 mM EDTA and 10mM SDS)

5.3.4 Effect of interruption in applying the washing solution

After 60 pore volumes, the solution injection was stopped for 2 weeks (Fig. 5-23, Fig. 5-24 and Table C-4). Following this interruption, feeding of EDTA with SDS was resumed. Fig. 5-23 and Fig. 5-24 show that effluent concentration and pH increase drastically when the test was resumed after 60 pore volumes. The Cu (II) concentration in the column effluent that was originally flushed increased from 11mg/L to 73mg/L and the Zn (II) concentration increased from 7.3mg/L to 77.3mg/L. After 10 more pore volumes, 6 % more Cu (II) and 9 % more Zn (II) were removed. The increased residence time permitted the solvent to diffuse and reach the crystal lattice-bound metals and release them.

The above suggests that for more efficient metal removal, one could use intermittent washing system to get higher removal results, if time is not a significant factor. Since these tests are not extensive, the conclusions are to be treated as tentative.

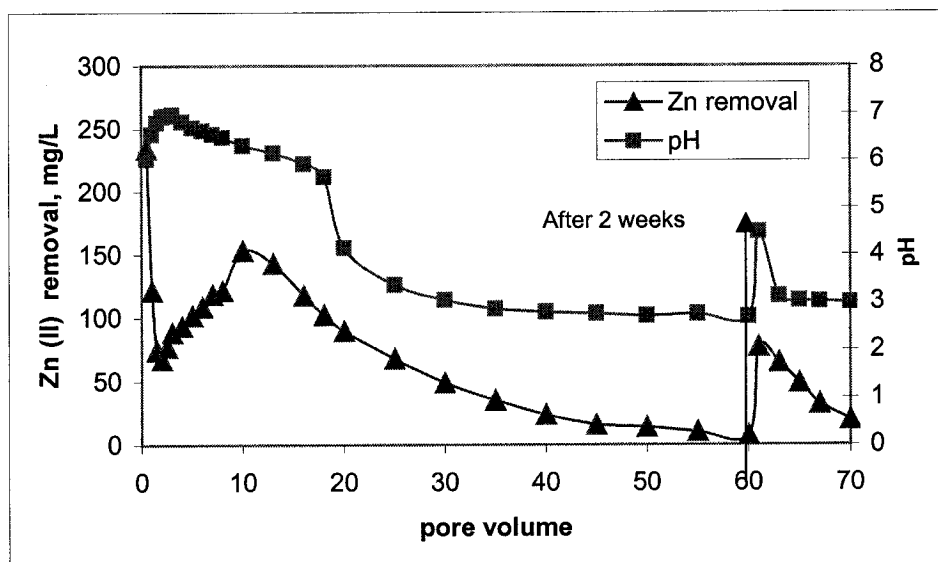


Fig. 5-23 Zn (II) removal after flow is interrupted for 2 weeks

(Solvent: mixture of 5 mM EDTA and 10mM SDS. Flow rate: 12 ml/min)

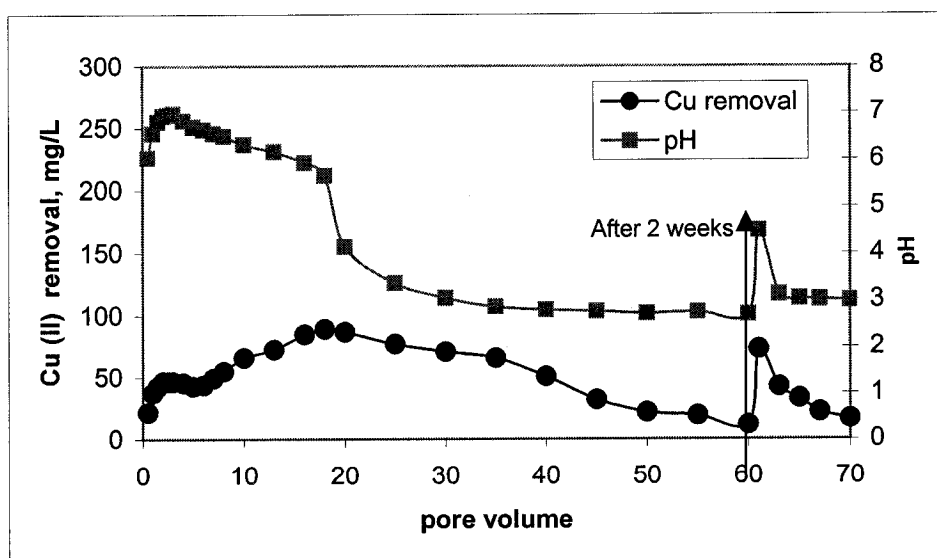


Fig. 5-24 Cu (II) removal after flow is interrupted for 2 weeks

(Solvent: mixture of 5 mM EDTA and 10mM SDS. Flow rate: 12 ml/min)

5.3.5 Effect of pH

Following Alloway (1990), one notes that hydrogen ions can replace most the metal cations that are bound to the soil particles and that pH affects the content of metals that are present in the soil. For pH less than 7.7, Zn (II) is the dominant species and its activity is given by the following equation (Alloway, 1990).

$$\text{Log Zn (II)} = 5.8 - 2\text{pH} \quad (5-1)$$

For copper, the activity of Cu (II) in soil can be estimated from the following equation (Alloway, 1990).

$$\text{Log Cu (II)} = 2.8 - 2 \text{ pH}. \quad (5-2)$$

The above equations indicate that the activity of both Zn (II) and Cu (II) increase with decreasing pH and hence pH value significantly affects the solubility of Cu (II) and Zn (II) in the soil. Recall that at low concentrations, activity is equal to the concentration.

In the batch experiments, the final pH was noted after shaking the contaminated soil with either water or a surfactant for 24 hours before conducting AA analysis of the supernatant. Desorption of metal is affected strongly by the final pH for batch tests. When SDS alone is used (Fig. 5-8, Fig. 5-9 and Table B-5), the removal rate of Cu (II) is only 1.1 % and that for Zn (II) is 26 % at the final pH of 6.72. When EDTA alone is used (Fig. 5-8, Fig. 5-9), the removal rate of Cu (II) is 52 % and that for Zn (II) is 82 % at the final pH of 2.46. The mixture of EDTA and SDS can remove 95 % of Cu (II) and 99 % of Zn (II) at the final pH of 2.46. For Cu (II), the removal rate of 95 % is much more than the sum of the metal removal rates using EDTA alone and SDS alone. This synergic effect is possibly due to the low final pH of 2.46 that is attained, when a combination of

EDTA and SDS is used. For the case of Zn (II), the same argument is applicable, when one uses the water-soluble fraction (17.9 %) of Zn (II) as the reference point. This change in reference was not necessary for Cu (II), since Cu (II) removed by water alone was very insignificant (0.18 %). It may be added that the synergic effects are generally present for the two other surfactants Tx-100 and AOT, as the final pH is lowered to 2.46 in these cases also (Fig. 5-8, Fig. 5-9). In view of the above, it will be interesting to study the effect of systematically varying pH of the surfactants on the removal of Cu (II) and Zn (II).

In column tests, as the pore volume increases, pH generally drops after 3 pore volumes (Figs. 5-23 and 5-24). For pore volume (Pv) less than 3, although the pH is nearly 7, the rate of removal of metals (Figs. 5-23 and 5-24) from the soil is quite high. This corresponds to the loosely bound metal fractions that appear initially in the effluents. Following this, the pH monotonically drops till $Pv = 60$ and the strongly bound metal fractions are released slowly. For Zn (II), these fractions include the ions bound to soil particles by electric charges, the fraction bound to the organic and inorganic ligands and the fraction associated with primary minerals and insoluble metal oxides (Alloway, 1990). For Cu (II), these fractions include inorganic and organic complexes in the soil solution, exchangeable fraction adsorbed on the clay-humus colloidal complex and the metal hydrous oxides, and the crystal lattice-bound Cu in the soil minerals (Alloway, 1990). Fig. 5-23 and Fig. 5-24 denote the metal concentrations in the effluents. As stated earlier, the delay in the occurrence of the peak for Cu (II) compared to the peak for Zn (II) can be traced to the fact that Cu (II) is more strongly bound than Zn (II).

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 General remarks

The present study attempts to evaluate the potential of surfactants to enhance the remediation of sandy soils contaminated by Cu (II) and Zn (II). To this end, both batch and column experiments were conducted to investigate the sorption/desorption and transport behavior of Cu (II) and Zn (II). Both the effects of competition as well as interaction associated with sorption/desorption of these metals were investigated. Anionic surfactants (SDS and AOT), a nonionic surfactant (Tx-100) and a complexing agent (EDTA) were used in this study.

6.2 Conclusions

1) Batch tests indicate that surfactants can enhance metal removal from the soil. The three surfactants (AOT, SDS and Tx-100) were able to remove Cu (II) nearly 6 times more than that by distilled water alone. The removal of Zn (II) by surfactants was 30 % higher than the removal of Zn (II) by distilled water.

2) Batch tests also show that the combination of SDS (10 mM) and EDTA (5mM) was the optimal system for the removal of Cu (II) and Zn (II). The combination of these two solvents can remove nearly 95% of Cu (II) and 99% of Zn (II). The final pH of the mixture of surfactant and EDTA is very low and this may be the reason for the higher

efficiency of metal removal. It should be noted that addition of surfactant to EDTA also results in the reduction of toxicity besides enhancing metal removal.

3) Batch tests demonstrate that competition and interaction between Cu (II) and Zn (II) can affect the metal retention pattern in the soil. Specifically, retention of Zn (II) in soil gets decreased by about 30% in the presence of Cu (II). The effect of Zn (II) on the retention of Cu (II) in soil is marginal.

4) Column tests indicate that the pH generally drops with increasing pore volumes of the surfactant used.

5) For a more efficient metal removal with a mixture of EDTA and SDS, one could use the intermittent washing method to get a higher metal removal result, if the constraint of time is not a significant factor.

6) Pore volume rather than the flow rate determines the total metal removal.

6.3 Recommendations for future work

- 1) Removal efficiency of contaminants associated with heavy metals other than Cu (II) and Zn (II) are to be studied for the effective use of surfactant.
- 2) The use of surfactant to remove heavy metal from naturally contaminated soils should be investigated.

- 3) Future research should include the studies related to the cost effectiveness of surfactant in the removal of soil contaminants. These studies should also include surfactant loss in the soil and the effect of surfactant on the environment.
- 4) It is desirable to develop a predictive mathematical model for use in surfactant enhanced field remediation efforts.
- 5) The column tests related to metal removal by the combination of EDTA and SDS may be further verified by repeating the tests to ensure that nearly 20% higher metal removal rate is achieved consistently (Fig. 5-20).
- 6) It is useful to study the removal of metals from soils containing higher concentrations of bentonite, as more clayey soils are getting contaminated with heavy metals.

REFERENCES

- Abdul, A.S. and Gibson, T.L., 1991. *Laboratory studies of surfactant-enhanced washing of polychlorinated Biphenyl from sandy material*, Environ. Sci. Technol. 25, pp. 665-671.
- Alloway, B.J., 1990. *Heavy metals in soils*. John Wiley & Sons. Inc. New York.
- Allen, D., and Inderbir, S., 1995. *Washing Zinc (II) from a contaminated soil column*. J.Environ.Eng, 121, No.2
- Allen, Herbert. E., Chen, Yu-tung., Li, Yimin and Huang, C.P., 1995. *Soil partition coefficients for Cd by column desorption and comparison to batch adsorption measurements* Environ. Sci. Technol, 29, No.8.
- Allen, J.P. and Torres, I.G. 1991. *Physical separation techniques for contaminated sediments*, in *recent developments in separation science*. Li, N.N., Ed., CRC press, West Palm Beach, FL(V).
- Atanasaova, I.D., 1995. *Adsorption and desorption of Cu at high equilibrium concentrations by soil and clay samples from Bulgaria*. Environ. Pollut. 87, pp.17-21.
- Bedient, P.B., Rifai, H.S., and Newell, R.C., 1994. *Ground water contamination: transport and remediation*. Prentice Hall, U.S.A.

Beveridge, A. and Pickering, W.F., 1983. *The influence of surfactants on the adsorption of heavy metal ions by clays*. Water research, (17), pp. 215-225.

Cameron, R.E., 1992. *Guide to Site and Soil Description for Hazardous Waste Site Characterization (1): Metals*. Environmental Protection Agency EPA/600/4-91/029.

Cheah, E., Reible, D.D., Valsaraj, K.T., Constant, W.D., Walsh, B.W., and Thibodeaux, L.J., 1998. *Simulation of soil washing with surfactants*. Journal of 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*. Environ. Sci. TR. Technol. 21, pp.1231-1245.

Christophi, C. A. and Axe, L., 2000, *Competition of Cd, Cu, and Pb Adsorption on Goethite*. J. Environ. Eng. 154, pp.245-267.

Cline, S.R., and Reed, B.R., 1995. *Lead removal from soils via bench-scale soil washing techniques*, J. Environ. Eng. 121, (10), pp. 700-705.

Deshpande, S., Shiau, B.J., Wade, D., Sabatini, A.D and Harwell, J.H, 1999. *Surfactant selection for enhancing ex situ soil washing*. Water Research. 33, No. 2, pp. 351-360.

Deuren, Julie Van., Lloyd, Teresa., Chhetry, Shobha., Liou, Raycharn. and Pec, James., 2002. *Remediation Technologies Screening Matrix and Reference Guide*, 4th Edition. (<http://www.fitr.gov/matrix2/section4/4-3.html>)

Doong, Rue-an., Lei W.G., Chen, T.F., Lee, C.Y., Chen, J.H., and Chang, W.H., 1996. *Effect of anionic and nonionic surfactants on sorption and micellar solubilization of monocyclic aromatic compounds*. Wat. Sci.Tech. 34, (7-8), pp. 327-334.

Doong, Rue-an., WU Y.W., Lei W.G., 1998. *Surfactant Enhanced Remediation of Cadmium contaminated soils*. Wat. Sci.Tech. 37, (8), pp. 65-71

Duffield, A.R., Ramurmathy, A.S. and Campanelli, J.R. 2003. *Surfactant enhanced mobilization of mineral oil with porous media*. Water, Air and Soil Pollution, 143 pp.111-122.

Dupont, Ruan., Marve Hyman R., 2001. *Groundwater and soil remediation process design and cost estimating of proven technologies*. ASCE Press.

Edwards, D.A., Adeel.Z., and luthy, R.G., 1994. *Distribution of Nonionic surfactant and phenanthrene in a sediment/aqueouse system*. Environ, Sci. Technol. 28, pp.1550-1560.

Elliot, H.A.and Brown, G.A., 1989. *Comparative Evaluation of NTA and EDTA for Extractive Decontamination of Pb-Polluted soils*. Water, Air and soil pollution, 45, pp.361-369.

Ellis W.d., Fogg, T.R., and Tafuri, A.N., 1986, *Treatment of soils contaminated with heavy metals, land disposal, remedial action, Incineration and treatment of Hazardouse waste*. 12th Annu. Res. Sympos., EPA 600/9-86/022. Cincinnati, OH, pp. 201-207.

Erwin J.M., Temminghoff, Sjoern E.A.T.M, and Meindert G.Keizer., 1994, *The influence of pH on the desorption and speciation of copper in a sandy soil*. Soil science, 158, (6), pp. 398-408.

Evanko, C.R., and Davia, A., D., 1997. *Remediation of Metals-contaminated soils and groundwater*. Report of Ground-water remediation technologies analysis center.

Gadelle, F., Wan, jiamin., and Tokunaga, T.K., 2001, *Removal of Uranium (VI) from contaminated sediments by surfactants*, J. Environ. Qual. 30, pp. 470-478.

Harwell, J.H, 1992. *Factors affecting surfactant performance in Groundwater Remediation Application*, Chap.10, *Transport and Remediation of Subsurface Contaminants* (Sabatini, D.A.and Knox, R.C., Eds). ACS symposium Series 491. Washington, DC: American Chemical Society, pp.124-132.

Hong, A., Chen, T.C., and Okey, R.W., 1995. *Chelating extraction of copper from Soil Using S-carboxy methycystein*. Water Environment Research, 67, pp. 971-979

Hong, A., Li, C., Banerji, S.K. and Regmi, T., 1999. *Extraction, Recovery, and Biostability of EDTA for remediation of heavy metal-contaminated soil*. Journal of soil contamination. 8, (1), pp. 81-103.

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*. Journal of soil contamination, 6, (5), pp. 537-556.

Kile, D.E., Chiou, C.T., 1989, *Water solubility enhancements of DDT and Trichlorobenzene by some surfactants below and above the critical micelle concentration*. Environ. Sci.Technol. 23, pp. 832-840.

Kinniburgh, D.G., 1986. *Multipurpose sorption isotherms*. Environ.Sci.Technol. 20, pp 895-904.

Kornechi, T.D., Brown, G.O. and Basta, N., 1998, *Cationic surfactant feasibility for use in removal of lead from sandy soil*, Environ. Geosci. 5, (1), pp. 29-38.

Li, Qiao, 2000. *Effect of surfactants on the sorption and transport of Cu (II) in a sandy soil: batch, column experiments and modeling*. M.A.Sc thesis. Concordia University. Montreal, Canada.

Mathewson, C.H., 1964. *Zinc: The science and technology of the metal, its alloys and compounds*. Reinhold.

Miller, D.M., Summer, M.E. and Miller, W.P., 1989. *A comparison of Batch- and Flow-generated anion adsorption isotherms*. Soil Sci. Soc Am. J. 53, pp. 373-380.

Mohammad, A., and Jabeen, N., 2003. *TLC studies and separation of heavy metal cation on soil amend silica gel layers developed with surfactant- mediated solvent systems*. Indian Journal of Chemical Technology, 10, pp. 79-86.

Myers, D., 1999. *Surfaces, interfaces, and colloids: principles and applications*. Second Edition, Wiley-Vch.

Mukerjee P, Mysels KJ., 1971. *Critical micelle concentrations of aqueous surfactant systems*. National Standard Data Series. 36, National bureau of standards, Washington DC.

Mulligan, C.N., Yong, R.N. and Gibbs, B.F., 1999a. *On the use of biosurfactants for the removal of heavy metals from oil-contaminated soil*. Environ. Prog. 18, (1), pp. 50–54.

Mulligan, C.N., Yong, R.N. and Gibbs, B.F., 1999b. *Removal of heavy metals from contaminated soil and sediments using the biosurfactant surfactin*. J. Soil Contam. 8, pp. 231–254.

Mulligan, C.N., Yong, R.N. and Gibbs, B.F., 2001a. *Surfactant- enhanced remediation of contaminated soil: a review*. Engineering Geology, 60, pp. 371-380.

Mulligan, C.N., Yong, R.N. and Gibbs, B.F., 2001b. *Heavy metal removal from sediments by biosurfactant*. Journal of Hazardous Materials, 85, pp. 111-125.

Nivas, B.T., Sabatini, D.A., Shiao, B.J., and Harwell, J.H., 1996, *Surfactant enhanced remediation of subsurface chromium contamination*. Water research, 30, pp. 511-520.

Nriagu, Jerome. O., 1979, *The biogeochemistry of lead in the environment*, Topics in Environmental Health, (1A. A). Ecological Cycles, Elsevier /North –Holland Biomedical press.

Pagilla, K. R. and Canter Larry W., 1999. *Laboratory studies on remediation of Chromium-contaminated soils*. J.Environ.Eng, 125,(3), pp. 243-248.

Peters, R.M. and Shem, L., 1992. *Use of chelating agents for remediation of heavy metal contaminated soil, in removing organics and metal ion pollutants* (G.f. Vandegrift, D.T. Reed, and I. R. Tasher, Eds). ACS Symp, 509, Am.Chem.Soc., Washington D.C, pp. 70-84.

Peters, R.M. and Shem, L., 1992. *Adsorption / desorption characteristics of lead on various types of soil. Environ. Prog.* 11, (3), pp. 234-240.

Peters, R.W., 1999. *Chelant extraction of Heavy metals from contamination soils. J. Hazardous materials*, 66, pp. 151-210.

Pump, H.H and Krist, H., 1998. *Laboratory manual for the examination of water, wastewater and soil. VCH Publishers*, pp.154.

Rampley, C.G., and Ogden, K.L., 1998. Preliminary studies for removal of lead from surrogate and real soils using a water soluble chelator: adsorption and batch extraction, *Environ. Sci. Technol.* 32, (7), pp. 987-993.

Reed, B.E., Carriere, P.C., and Moore, R., 1996. *Flushing of a Pb (II) contaminated soil using HCl, EDTA, and CaCl₂*. *J. Environ. Eng.* 1221, pp. 48-50.

Rosen, M.J., 1989. *Surfactants and interfacial phenomena*.. Wiley-Interscience, 2nd Edition, New York.

Sabatini, D.A. and Knox, R.C., 1992. *Transport and remediation of subsurface contaminants*.(Chapter 10 , In *Transport and remediation of subsurface contaminants*) ACS symposium (491). Washington.DC: American Chemical Society, pp.124-132.

Selim, H.M. and Amacher, M.C., 1996. *Reactivity and transport of heavy metals in soils*, CRC press, Inc, U.S.A.

Selim, H.M., Ma, Liwang, and Zhu, Hongxia., 1999, *Predicting solute transport in soils: second-order two-site models*, Soil Sci. soc. Am. J. 63, pp. 768-777.

Sigma, 1993, *sigma production information sheet* www.sigmaaldrich.com/cgi-bin/hsrun/Suite7/Suite/HAHTpage.

Sinex, Scott A. 2004. *EDTA- A Molecule with a complex story*.
<http://www.chm.bris.ac.uk/motm/edta/edtah.htm>

Tran, Y.T., Barry, D.A., Bajracharya, K., 2002. *Cadmium desorption in sand*. Environment international, 28, pp. 493-502

Wu, J., Laird, D.A., and Thompson, M.L., 1999. *Sorption and desorption of Copper on soil clays components*. J .Environ. Qual. 28, pp.334-338.

Yaron, B., Dagan, G., Goldshmid , J., 1984. *Pollutants in porous media : the unsaturated zone between soil surface and groundwater*. Berlin, New York.

Yin, Yujun., Allen, Herbert E., Huang C.p and Paul F. sanders., 1997. *Adsorption/desorption isotherm of Hg(II) by soil*. Soil science. 162, (1), pp.35-40

Wilson, D.J., and Clarke, A.N., 1994 *Soil surfactant flushing /washing*. in: *Hazardous waste site soil remediation: Theory and application of innovative technologies* (Davis J. Wilson and Ann, N. Clake, Eds). pp. 493-550. Marcel Dekker, Inc. U.S.A.

APPENDIX A

Measurement of soil hydraulic conductivity

1. Procedure

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 in small steps of 2 cm layers.
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).
3. Collect the outflow in a graduated cylinder. Record the outflow vs. time (at 10 ml intervals) until the time interval for 10 ml outflow remains constant for five consecutive samples.
4. Calculate the hydraulic conductivity K by the following equations:
$$q=Q/t \quad (A-1) \quad \quad \quad v=q/F \quad (A-2)$$
$$i=H/L \quad (A-3) \quad \quad \quad K=v/I \quad (A-4)$$
5. Reload the column, repeat steps 1-4, and triplicate the experiments. Calculate hydraulic conductivity as the average value.

2. Experimental results and calculations

Diameter (D) = 4.0 cm, Section Area F= 12.56 cm²

H= 84 cm

L=20.5 cm

Table A-1 Calculations for soil hydraulic conductivity

Reading	Q (mL)	Time T (s)	q=Q/T (mL/s)	V=q/F (cm/s)	i=H/L	Hydraulic Conductivity K=V/i (cm/s)
1	400	2260	0.194	0.0154	4.1	0.00376
2	300	1630	0.184	0.0147		0.00359
3	200	1030	0.177	0.0141		0.00353

The hydraulic conductivity was calculated as the average of the three values.

$$K = (0.00376 + 0.00359 + 0.00353) / 3 = 0.00363 \text{ cm/s}$$

Standard deviation

STDEV

$$= (((0.00376 - 0.00363)^2 + (0.00359 - 0.00363)^2 + (0.00353 - 0.00363)^2) / 2)^{1/2} = 0.00017$$

cm/s

The range of the hydraulic conductivity can be expect estimated to be 0.00363 ± 0.00017

cm/s

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

APPENDIX B

RESULTS OF BATCH STUDIES

B.1 Results of extraction studies with different surfactant concentrations

Table B-1 Extraction of metals by surfactant Tx-100

Soil(5g)/Solution (40ml)

No	Surfactant Concentration mM	Ratio to CMC	Cu removed mg/L	Ratio to Cu removed by water	Zn removed mg/L	Ratio to Zn removed by water	Initial pH	Final pH
1	0	0.00	0.267	1.00	25.7	1.00	5.6	6.33
2	0.025	0.11	0.267	1.00	27.46	1.07	5.15	6.34
3	0.1	0.43	0.67	2.51	28.13	1.09	5.15	6.35
4	0.25	1.09	2	7.49	29.33	1.14	5.16	6.28
5	0.5	2.17	2.13	7.98	32.4	1.26	5.22	6.29
6	1	4.35	2.13	8.61	29.2	1.14	5.24	6.46
7	8	34.78	1.73	6.48	28.13	1.09	5.38	6.52

Table B-2 Extraction of metals by surfactant SDS

Soil (5g)/Solution (40ml)

No	Surfactant Concentration mM	Surfactant Concentration CMC	Cu removed mg/L	Ratio to Cu removed by water	Zn removed mg/L	Ratio to Zn removed by water	Initial pH	Final pH
1	0	0	0.27	1.01	25.7	1.00	5.6	6.33
2	1	0.125	0.13	0.49	25.7	1.00	4.38	6.32
3	4	0.5	0.13	0.49	18.8	0.73	4.25	6.4
4	8	1	0.4	1.50	22.9	0.89	3.97	6.65
5	10	1.25	1.67	6.25	36.8	1.43	3.81	6.72
6	16	2	1.73	6.48	35	1.36	3.63	6.8
7	32	4	1.7	9.36	33.1	0.77	3.54	6.76

Table B-3 Extraction of metals by surfactant AOT

Soil (5g)/Solution (40ml)

No	Surfactant Concentration mM	Surfactant Concentration CMC	Cu removed mg/L	Ratio to Cu removed by water	Zn removed mg/L	Ratio to Zn removed by water	Initial pH	Final pH
1	0	0	0.27	1.01	25.7	1.00	5.6	6.33
2	0.25	0.22	0.40	1.50	27.33	1.06	5.81	6.21
3	0.5	0.44	0.13	0.49	27.00	1.05	5.92	6.22
4	1	0.89	0.40	1.50	24.17	0.94	5.99	6.47
5	1.25	1.11	1.60	5.99	34.67	1.35	6.1	6.54
6	2.5	2.22	0.93	3.48	34.67	1.35	6.45	6.69
7	5	4.45	0.67	2.51	30.67	1.19	6.87	7.07
8	10	8.90	0.53	1.99	32.33	1.26	7.13	7.32
9	20	17.79	0.53	1.99	33.50	1.30	7.76	7.39

B.2 Results of complexing agent studies

Table B-4 Extraction of metals by EDTA

Soil (5g)/Solution (40ml)

No	EDTA Concentration mM	Cu removed mg/L	removed percentage	Zn removed mg/L	removed percentage	Initial pH	Final pH
1	0	0.27	0.18	25.73	17.86	5.6	6.33
2	1	62.53	41.14	61.70	42.85	4.56	5.34
3	5	79.47	52.28	118.25	82.11	2.15	2.46
4	10	132.27	87.02	123.41	85.70	2.15	2.34

Table B-5 Extraction of metals by EDTA

Soil (5g)/Solution (40ml)

No	Surfactant Concentration mM	Cu removed mg/L	Cu removed percentage	Zn removed mg/L	Zn removed percentage	Initial pH	Final pH
1	0	<u>0.27*</u>	<u>0.18**</u>	<u>25.73***</u>	<u>17.86****</u>	5.6	6.33
2	5mM EDTA	79.47	52.28	118.25	82.11	2.15	2.46
4	10mM SDS	1.67	1.10	36.8	25.56	3.54	6.72
4	5mM EDTA + 10mM SDS	145.07	95.44	143.27	99.49	3.81	2.46
5	0.5mM TX-100	2.13	1.40	32.4	22.5	5.22	6.29
6	5mM EDTA + 0.5mM TX-100	134.93	88.77	132.95	92.32	4.25	2.46
7	1.25mM AOT	1.60	1.05	34.67	24.08	6.1	6.54
8	5mM EDTA + 0.5mM TX-100	131.60	86.58	130.43	90.57	3.81	2.46

Calculation details for rows 1:

Cu removal percentage = $(0.27 \text{ mg/L} \times 40 \text{ mL} / 5 \text{ g}) / 1216 \text{ mg/Kg} = 0.18\% **$

Zn removal percentage = $(25.73 \text{ mg/L} \times 40 \text{ mL} / 5 \text{ g}) / 1512 \text{ mg/Kg} = 17.86\% ****$

APPENDIX C

RESULTS OF COLUMN STUDIES

(One Pore volume = 92 mL*)

Table C-1 Removal of metals from column by distilled water (Flow rate: 12mL/min)

Total Cu (II) = 392.5Kg x 1216 mg/kg = 477 ** mg Total Zn (II) = 392.5Kg x 1152 mg/kg = 452mg

o	Pore volumes	Cu (II) concentration in effluent solution mg/L	Cu (II) removal percentage %	Zn (II) concentration in effluent solution mg/L	Zn (II) removal percentage %	pH
1	0	0	0.00	0	0.00	
2	<u>0.5***</u>	<u>17.07****</u>	<u>0.16*****</u>	213.52	2.17	6.35
3	<u>1@</u>	<u>59.73@@</u>	<u>0.74@@@</u>	289.87	5.12	6.29
4	1.5	38.40	1.11	183.61	6.99	6.53
5	2	25.60	1.36	136.73	8.38	6.7
6	2.5	20.27	1.55	86.34	9.26	6.81
7	3	12.80	1.68	64.85	9.92	6.82
8	3.5	8.53	1.76	49.61	10.42	6.89
9	4	6.40	1.82	38.29	10.81	6.85
10	4.5	4.27	1.86	30.86	11.13	6.9
11	5	3.20	1.89	27.35	11.41	6.93
12	6	2.13	1.93	24.22	11.90	6.91
13	7	1.07	1.95	21.10	12.33	7.02
14	8	1.07	1.97	19.53	12.73	6.94
15	9	0.80	1.99	20.71	13.15	7.03
16	10	0.60	2.00	20.71	13.57	7.12
17	12	0.40	2.02	13.67	14.13	7.06
18	15	0.30	2.03	10.16	14.75	7.11
19	17	0.20	2.04	7.42	15.05	7.27
20	20	0.00	2.04	5.08	15.36	7.34
21	25	0.00	2.04	4.30	15.80	7.32
22	30	0.00	2.04	3.91	16.19	7.36
23	35	0.00	2.04	3.52	16.55	7.38
24	45	0.00	2.04	3.13	17.19	7.4
25	50	0.00	2.04	2.34	17.43	7.38

Calculation details for rows 2 & 3:

$$92\text{mL} * x 0.5*** x 17.07**** \text{mg/L} / 477** \text{mg} = 0.16\% *****$$

$$0.16\% ***** + 59.73@@ \text{mg/L} x (1@ - 0.5***) x 92 * \text{mL} / 477** = 0.74\% @@@$$

Table C-2 Removal of metals from column by SDS (10mM)**Flow rate: 12mL/min**

No	Pore volumes	Cu (II) concentration in effluent solution mg/L	Cu (II) removal percentage %	Zn (II) concentration in effluent solution mg/L	Zn (II) removal percentage %	pH
1	0	0	0.00	0	0.00	
2	0.5	32.00	0.31	231.20	2.35	6.35
3	1	34.13	0.64	201.73	4.40	6.14
4	1.5	38.40	1.01	154.13	5.96	5.79
5	2	45.87	1.45	103.36	7.01	6.28
6	2.5	48.00	1.91	72.53	7.75	6.65
7	3	49.07	2.39	60.07	8.36	7
9	4	54.40	3.43	42.84	9.23	7.12
11	5	37.33	4.15	33.55	9.91	7.17
13	6	12.80	4.40	25.39	10.42	7.28
14	7	9.60	4.59	24.48	10.92	7.16
15	8	7.47	4.73	19.95	11.32	7.26
16	9	8.53	4.89	24.93	11.83	7.21
17	10	7.47	5.04	31.28	12.47	7.3
18	12	8.53	5.37	26.97	13.56	7.25
19	14	9.60	5.74	24.25	14.55	7.34
20	16	12.80	6.23	22.89	15.48	7.36
21	18	14.93	6.81	15.87	16.12	7.33
22	20	16.00	7.42	12.01	16.61	7.36
23	25	17.07	9.07	9.97	17.62	7.36
24	30	18.13	10.82	8.84	18.52	7.38
25	35	11.73	11.95	7.71	19.30	7.4
26	40	8.53	12.77	7.93	20.11	7.38
27	45	4.27	13.18	5.44	20.66	7.39
28	50	3.20	13.49	4.31	21.09	7.42

Table C-3 Removal of metals from column by EDTA alone (5mM)**(Flow rate: 12mL/min)**

No	Pore volumes	Cu (II) concentration in effluent solution mg/L	Cu (II) removal percentage %	Zn (II) concentratio n in effluent solution mg/L	Zn (II) removal percentage %	pH
1	0	0	0.00	0	0.00	
2	0.5	0.56	0.01	16.00	0.16	5.72
3	1	8.89	0.09	136.00	1.55	5.99
4	1.5	21.11	0.29	100.00	2.56	6.36
5	2	23.33	0.52	50.00	3.07	6.45
6	2.5	25.56	0.77	46.00	3.54	6.51
7	3	28.89	1.04	48.00	4.03	6.53
8	4	31.11	1.64	49.10	5.03	6.45
9	5	34.22	2.30	50.90	6.07	6.47
10	6	38.56	3.05	57.60	7.24	6.48
11	7	39.44	3.81	57.90	8.42	6.41
12	8	43.89	4.65	64.80	9.74	6.34
13	9	48.33	5.59	65.70	11.07	6.29
14	10	49.11	6.53	73.30	12.56	6.25
15	12	52.89	8.57	78.30	15.75	6.21
16	14	55.44	10.71	82.50	19.11	6.14
17	16	57.56	12.93	92.80	22.89	6.09
18	18	60.22	15.25	97.50	26.86	6.06
19	20	61.33	17.61	97.80	30.84	5.94
20	25	66.44	24.02	80.60	39.04	5.8
21	30	76.00	31.34	66.10	45.77	5.64
22	35	77.56	38.82	57.20	51.59	5.48
23	40	67.56	45.33	40.30	55.69	5.12
24	45	23.11	47.56	22.60	57.99	4.57
25	50	12.56	48.77	18.10	59.83	4.57
26	55	10.89	49.82	7.50	60.60	4.49
27	60	6.67	50.46	3.60	60.96	4.51

Table C-4 Removal of metals from column by EDTA (5mM) with SDS (10mM)**(Flow rate: 12mL/min)**

No	Pore volumes	Cu(II) concentration in effluent solution mg/L	Cu (II) removal percentage %	Zn (II) concentration in effluent solution mg/L	Zn (II) removal percentage %	pH
1	0	0	0.00	0	0.00	
2	0.5	22.00	0.21	234.00	2.38	6.03
3	1	37.33	0.57	121.33	3.61	6.55
4	1.5	42.67	0.98	74.53	4.36	6.8
5	2	46.67	1.43	67.60	5.05	6.92
6	2.5	46.67	1.88	77.31	5.84	6.94
7	3	46.67	2.33	88.40	6.73	6.97
8	4	45.73	3.21	93.60	8.63	6.82
9	5	42.80	4.04	101.75	10.70	6.69
10	6	43.87	4.88	108.68	12.91	6.63
11	7	49.20	5.83	118.39	15.31	6.55
12	8	55.07	6.89	121.33	17.77	6.49
13	10	66.00	9.44	153.23	24.00	6.31
14	13	72.80	13.65	142.83	32.70	6.16
15	16	85.07	18.57	117.69	39.86	5.93
16	18	89.33	22.01	102.44	44.02	5.65
18	20	87.07	25.37	89.61	47.66	4.14
19	25	77.07	32.80	68.12	54.58	3.36
20	30	71.07	39.65	49.05	59.56	3.04
21	35	65.87	46.00	35.36	63.15	2.86
22	40	50.80	50.89	23.92	65.58	2.79
23	45	32.13	53.99	15.95	67.20	2.76
24	50	22.00	56.11	14.04	68.62	2.71
25	55	19.33	57.97	10.40	69.68	2.75
26	60	11.87	59.12	7.28	70.42	2.69
27	61	73.07	60.53	77.31	71.99	4.48
28	63	42.53	62.17	65.00	74.63	3.12
29	65	33.07	63.44	49.05	76.62	3.03
30	67	22.27	64.30	32.59	77.94	3.01
31	70	16.80	65.27	20.11	79.17	2.99

Table C-5 Removal of metals from column by EDTA (5mM) with SDS (10mM)**Flow rate: 4mL/min**

No	Pore volumes	Cu (II) concentration in effluent solution mg/L	Cu (II) removal percentage %	Zn (II) concentration in effluent solution mg/L	Zn (II) removal percentage %	pH
1	0	0	0.00	0	0.00	
2	1	21.47	0.41	189.28	3.84	4.98
3	2	38.67	1.16	71.07	5.29	5.97
4	4	42.53	2.80	88.92	8.90	6.29
5	6	49.20	4.70	98.80	12.91	6.21
6	8	56.67	6.88	104.35	17.15	6.1
7	10	59.47	9.17	115.09	21.82	6.08
8	15	71.07	16.02	108.51	32.84	5.94
9	20	77.87	23.53	88.40	41.81	4.87
10	25	79.73	31.21	70.03	48.92	4.56
11	30	80.67	38.99	61.01	55.11	4.03
12	35	76.93	46.40	53.91	60.59	3.73
13	40	70.53	53.20	46.11	65.27	3.49
14	45	62.40	59.22	40.58	69.39	3.33
15	50	35.47	62.64	32.07	72.64	3.21
16	55	23.60	64.91	25.13	75.19	3.15
17	60	16.40	66.49	18.89	77.11	3.03

Table C-6 Removal of metals from column by EDTA (5mM) with SDS (10mM)**(Flow rate: 40mL/min)**

No	Pore volumes	Cu (II) concentration in effluent solution mg/L	Cu (II) removal percentage %	Zn (II) concentration in effluent solution mg/L	Zn (II) removal percentage %	pH
1	0	0	0.00	0	0.00	
2	1	22.53	0.43	282.36	5.73	3.7
3	2	46.93	1.34	93.95	7.64	5.23
4	4	46.40	3.13	86.49	11.15	5.42
5	6	43.87	4.82	133.12	16.56	5.76
6	8	28.80	5.93	176.97	23.75	5.86
7	10	32.60	7.19	170.91	30.69	5.9
8	15	38.93	10.94	137.63	44.66	5.53
9	20	62.40	16.95	107.29	55.55	5.27
10	25	77.07	24.38	88.92	64.58	4.02
11	30	71.87	31.31	68.12	71.49	3.53
12	35	68.27	37.89	63.09	77.90	3.38
13	40	66.27	44.28	53.73	83.35	3.26
14	45	59.30	49.99	40.04	87.42	3.15
15	50	55.87	55.38	31.37	90.60	3.1
16	55	48.93	60.09	15.08	92.14	2.98
17	60	25.20	62.52	7.80	92.93	2.88