SURFACTANT ENHANCED REMOVAL OF Zn(II), Cu(II) AND HOCs

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ABSTRACT

SURFACTANT ENHANCED REMOVAL OF Zn(II), Cu(II) AND HOCs

Zeenat Aman

In recent years, heavy metals and hydrophobic organic compounds have frequently been found together in contaminated soils. Soil Washing is one of the promising treatment methods for contaminated site remediation. The simultaneous desorption of heavy metals such as Zn(II) and Cu(II) and hydrophobic organic compounds such as Xylene and Ethylbenzene from an artificially contaminated sandy soil were investigated. SDS (sodium dodecyl sulfate), AOT (Sodium dioctyl sulfosuccinate) and Triton X – 100 were the surfactants selected as the washing liquids. The effect of complexing agent EDTA (ethylenediaminetetraacetic acid) on the removal of heavy metals and HOCs was also studied briefly.

Artificial soil was formed by a mixture of clean sand and bentonite. Surfactants were used at concentrations below and above the critical micelle concentrations (CMC). Removal efficiencies varied with surfactant concentration and with the surfactant type. Distilled water was used as the control. Results were based on both batch and column tests. Tests were conducted to see the interference effects of Zn(II) in the presence of Xylene. Column tests related to interference effects between Xylene, Cu(II) and Zn(II) were performed. Also, a few column tests linked to flow rate effects were conducted. Maximum desorption of Xylene (97%) occurred in the soil column when it was flushed with SDS at the flow rate of 4ml/min. Maximum desorption of Zn(II), and Cu(II) occurred when the soil column was flushed with SDS in combination with EDTA respectively.

ACKNOWLEDGMENTS

I would like to thank everyone who made this thesis possible. It was challenging experience for me. I wish to thank my supervisor Dr. A. S. Ramamurthy, who suggested research study. Also, I would like to thank Miss. Claire Therrien and Mr. Lang Vo for their assistance and support in the laboratory.

Finally I would like to express my deepest gratitude for the constant support, understanding and encouragement that I received from faculty and staff of the Department of Building , Civil , and Environmental Engineering at Concordia University during my graduate studies.

DEDICATION

I dedicate this thesis to my family, for their continuous support and encouragements not only for my academic career, but my entire life;
to my father who taught me the value of patience and hard work;
to my mother who encouraged me to be self-reliant and independent;
My gratitude to you is impossible to fully express.

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LIST OF ABBREVIATIONS

AA	Atomic Absorption
AOT	Sodium dioctyl sulfosuccinate
BTEX	Benzene, Toluene, Ethyl benzene , Xylene
CMC	Critical Micelle Concentration
Cu	Copper
DNAPL	Dense Non -Aqueous Phase Liquid
EDTA	Ethylenediaminetetraacetic acid
EPA	Environmental Protection Agency
FID	Flame Ionization Detector
GC	Gas Chromatography
HOCs	Hydrophobic organic compounds
K_{ow}	Octanol- water partition Coefficient
LNAPL	Light Non- Aqueous Phase Liquid
NPL	National Priority List
PAH	Poly Aromatic Hydrocarbon
SDS	Sodium Dodecyl Sulfate
SVOC	Semi Volatile Organic Compounds
SVE	Soil Vapor Extraction
Tx-100	Triton X – 100
VOC	Volatile Organic Compound
Zn	Zinc

CHAPTER 1

INTRODUCTION

1.1 Background

Soil contamination is related to mixing of either solid or liquid hazardous substances with the natural soil. Usually contaminants in the soil are physically or chemically attached to the soil particles or are trapped in small spaces between soil particles. This can occur by human activities such as accidental spills of chemicals or waste materials, leakage from septic tanks or buried storage tanks, improper injection of liquid wastes into the unmanaged dump sites, land application of agricultural pesticides etc. The most common chemicals involved are petroleum hydrocarbons, solvents, pesticides, lead and other heavy metals. Most of the national priority list (NPL) sites contain three contaminant groups such as volatile organic carbons (VOCs), metals and semi-volatile organic carbons (SVOCs) (Khodadust et al., 2005). Currently, one of the biggest environmental problems in developed nations is the contamination of soil and groundwater caused by accidental releases of hazardous chemicals and petroleum hydrocarbons. Hutchins et al. (1991) reported that approximately 6 million tons of petroleum products spill and leak into soil each year in US alone. According to EPA reports (1990, 1990a), as of 1989, 1224 contaminated sites were on EPA's National Priorities List (Liu and Roy, 1992). Organic compounds and inorganic compounds are considered as targets for treatment of soil contamination because they are the most common health threatening materials detected in soil. Nonaqueous phase liquids (NAPLs) are hydrocarbons that exist as a separate, immiscible phase when in contact with water and/or air. Nonaqueous phase liquids are typically classified as either light nonaqueous phase liquids (LNAPLs) which have densities less than that of water, or dense nonaqueous phase liquids (DNAPLs) which have densities greater than that of water. Drinking water limits for NAPLs have been set at very low levels, which are more than three orders of magnitude lower than their solubility's in ground water, suggesting that relatively small quantities of NAPLs can contaminate a large area (Feenstra *et al.*, 1991). Examples of LNAPL are BTEX. BTEX are hydrophobic organic compound (HOCs). The components of BTEX are Benzene, Toluene, Ethyl benzene and Xylene. Xylene and Ethyl benzene are typical HOCs. BTEX display high pollution potential owing to their relatively high concentration in gasoline and solubility in water and chronic toxicity. Migration of BTEX from gasoline to groundwater or other potential drinking water resources is therefore an issue of major environmental concern. (Rosanna et al., 2001).

BTEX are widely used in industry and exert serious adverse effects on environmental air quality (Pohl et al., 2003). In general, BTEX are frequently produced not only from industrial sources, including printing and laminating facilities, foundries, electronics, and paint manufacturing units, but also occur at hazardous waste sites (ATSDR, 2001) .

Heavy Metals like Zinc and Copper are essential trace elements for plants and animals but excessive concentrations can damage overall soil fertility (Alloway 1990). Road ways and automobiles now are considered to be one of the largest sources of heavymetals. Brakes release copper and tire wear releases zinc. The Superfund Amendments and Reauthorization act requires the use of remedial technologies that permanently and significantly reduce the volume, toxicity or mobility of contaminated materials at affected sites. (Mark et al., 1998).

Recently, the use of surface-active agents (surfactants) has found a use in enhancing remediation of contaminants from soils in-situ or during soil washing. Chemical washing technology using surfactants and co solvents is known to be one of the fastest, the most economical and the most built-in for treating the soil contaminants provided with some proper techniques for recovery of surfactants or solvents [Fountain et al., 1996; Rao et al., 1997; Lee 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 PAHs and chlorinated hydrocarbons by increasing the solubility of the contaminants via micellar solubilization (Edward et.al 1994).

1.2 Objectives of the research

1. One of the major aims of the research is to identify the removal efficiency of heavy metals and hydrophobic organic compounds by individual extracting agents. The desorption efficiencies of heavy metals [Zn(II) and CuII)] and HOCs [Xylene, Ethyl benzene] from an artificially contaminated sandy soil was studied using several surfactants and a typical chelating agent. Surfactants that are used included two anionic surfactants sodium dodecyl sulfate (SDS) and sodium dioctyl sulfoscuccinate (AOT) and a non-ionic surfactant Triton X-100. The chelating agent EDTA (ethylenediaminetetraaceticacid) was used as extracting agent.

2. Another aim of the study is to investigate the effects of interaction and competition between Cu (II) and Zn (II) during site remediation.

3. The other objectives of the study are listed below

a. To investigate the effects of interaction between Xylene and Zn (II) during site remediation.

b. To study the interaction between Xylene and Ethyl benzene

c. To study the effect of flow rate on desorption characteristics of sandy soil containing Cu (II), Zn (II) and Xylene.

d. Study of the effect of flow rate on the desorption characteristics of a sandy soil containing a mixture of Cu (II) and Zn (II).

1.3 Thesis Outline

Chapter 1 gives the introduction of the problem and the objectives of the thesis.

Chapter 2 presents the background information and a brief literature related to site remediation.

Chapter 3 provides brief information on the fate and transport of heavy metals and organics.

Chapter 4 includes the materials and methodology used in this study.

Chapter 5 provides the results of both batch and column tests.

Chapter 6 gives the conclusions and provides recommendations for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Remediation technologies for contaminated soils

Remediation is considered to be the treatment, containment, removal or management of chemical substances or wastes so that they no longer represent an actual or potential risk to human health or the environment, taking into account the current and intended use of the site (EPA, 2006). Soil Washing, Soil Flushing, Soil Vapor Extraction, Phyto-remediation and Electro kinetics are a few technologies used for treating contaminated sites.

2.1.1 Soil washing

Soil washing as a physico-chemical process in which contaminated soil is excavated, screened to remove undesirable contaminants. For soil washing, contaminants sorbed onto fine soil particles are separated from bulk soil in water based system on the basis of the particle size. The washing solutions may be mineral acids or organic acids, chelating agents such as EDTA (Reed et al., 1996, Hong et al., 1999). Soil and washing solutions are then mixed ex-situ in a tank or other treatment unit. The washing solution and various soil fractions are usually separated using gravity settling. The ex-situ type of soil washing is both cumbersome and more expensive (Davis and Singh 1995).

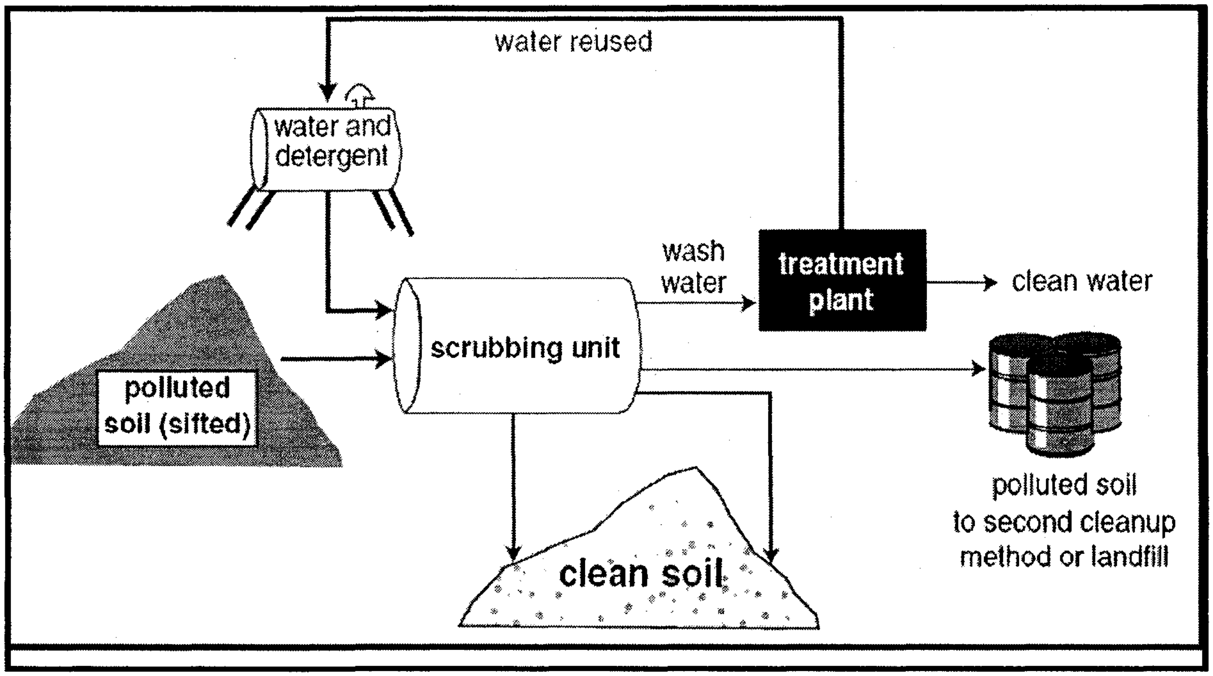


Fig 2.1 Soil Washing$^{(1)}$

2.1.2 Soil Flushing

Water or water containing an additive to enhance contaminant solubility is applied to the soil or injected into ground water to raise the water table of the contaminated soil zone. This causes the contaminants to be leached into the ground water. Soil flushing in columns of sandy loam artificially polluted by Pb was investigated using HCl, EDTA and CaCl2 as flushing solutions (Reed, 1996). Most of the past and current research efforts have been focused on surfactant- enhanced solubilization of DNAPL, PCB and PAHs (West, 1992, Abdul et al., 1991, Fountain, 1995, Edwards 1994).

The In Situ Soil Flushing Process (Using Vertical Wells)

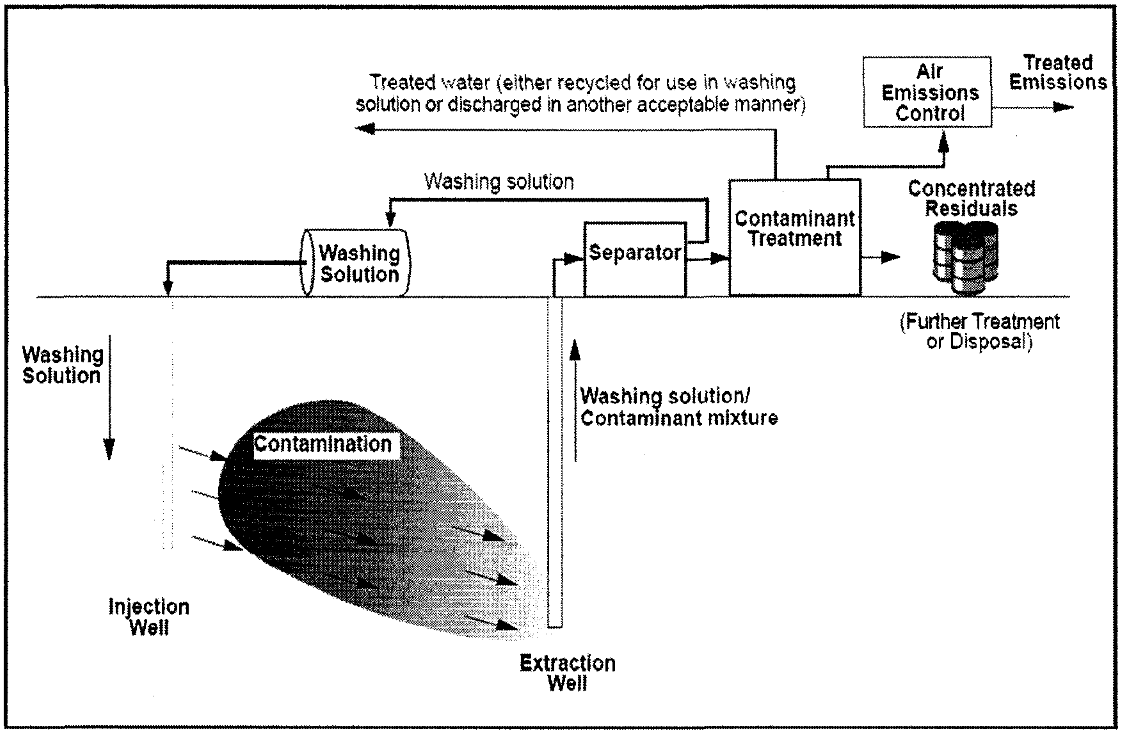


Fig 2.2 Soil Flushing$^{(2)}$

2.1.2.1 Chelating agent-enhanced soil washing/flushing

EDTA (ethylenediaminetetraacetic acid) is a popular chelating agent that has been widely studied for removing heavy metals from soils because of its high chelating ability

(Lo and Yang, 1999; Lee and Kao, 2004; Zhang and Lo, 2006). The effects of the operating conditions, the initial concentrations of heavy metals in soils, and the competition among heavy metals during ethylenediaminetetraacetic acid (EDTA)-enhanced soil washing were extensively investigated by Weihua et al., 2007). Biodegradable, synthetic organic chelate ethylenediaminedisuccinic acid (EDDS), and commonly used ethylenedimanetetraacetic acid (EDTA) were used for induced phytoextraction with a test plant Brassica rapa and in situ washing of soil contaminated with 1350 mg/kg of Pb (Bostjan et al., 2003). EDTA and Hcl were used to wash two urban soils from Montreal contaminated with high levels of trace metals (Tejowulan, 1998).

2.1.3 Soil Vapor Extraction (SVE)

SVE is used to remediate unsaturated (vadose) zone soil. A vacuum is applied to the soil to induce the controlled flow of air and remove volatile and some semi volatile organic contaminants from the soil. This technology has been proven effective in reducing concentrations of volatile organic compounds (VOCs) and certain semi-volatile organic compounds (SVOCs) found in petroleum products. soil vapor extraction (SVE) is an in-situ remedial technique for cleaning up saturated soil and ground water contaminated with volatile organic compounds (VOCs) both in the no aqueous liquid (NAPL) phase and dissolved aqueous phase by enhanced volatilization (Waduge. 2007).

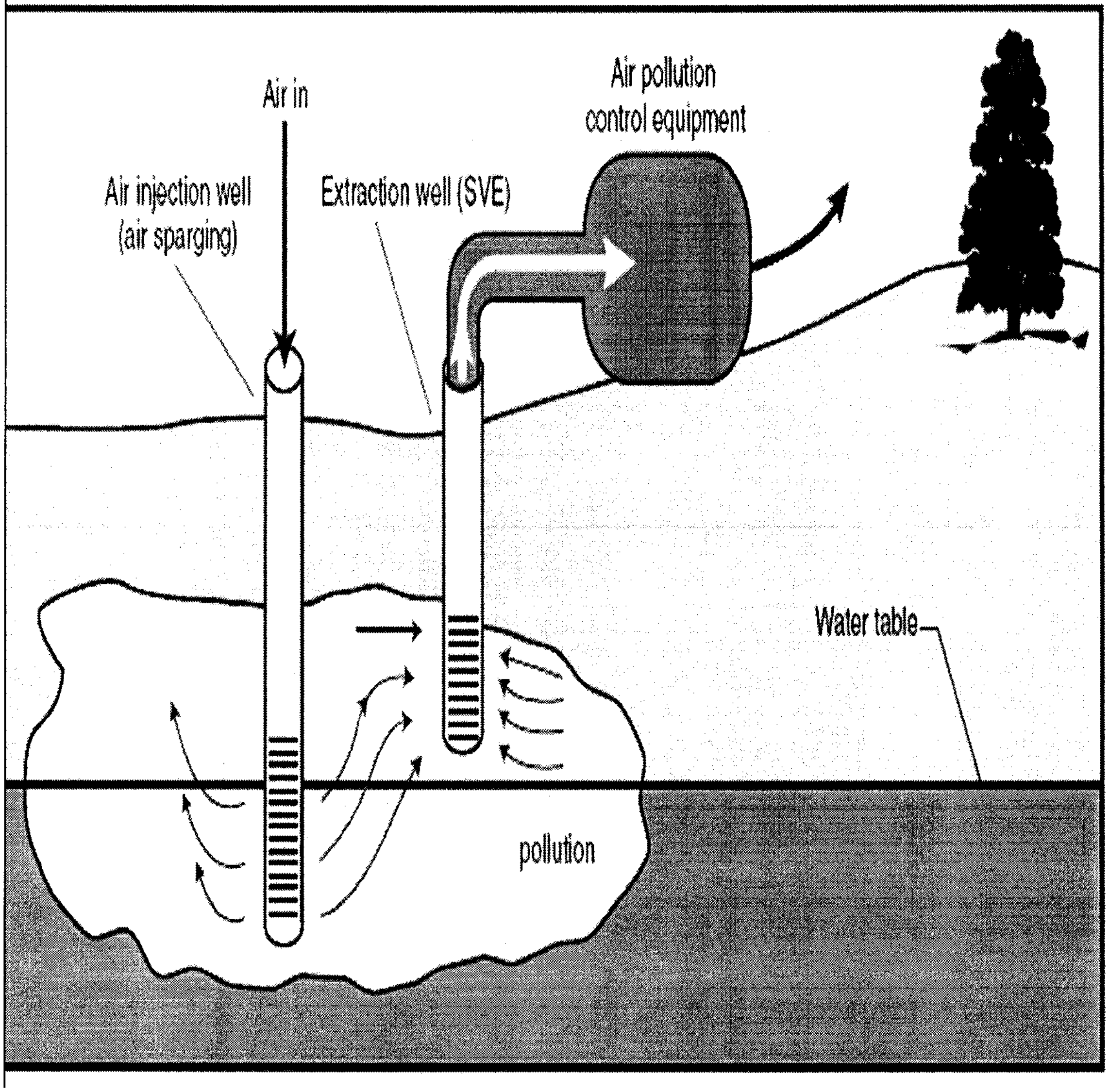


Fig 2.3 Soil Vapor Extraction[3]

2.1.4 Phytoremediation

It is a process that uses plants to remove, transfer, stabilize or destroy contaminants in soil, sediment and ground water. Plants remove harmful chemicals from the ground when their roots take in water and nutrients from polluted soil, streams and groundwater. Plants can clean up chemicals as deep as their roots can grow. These polluted plants will be harvested. Examples of such plant species are Helianthus sp, Brassica etc.

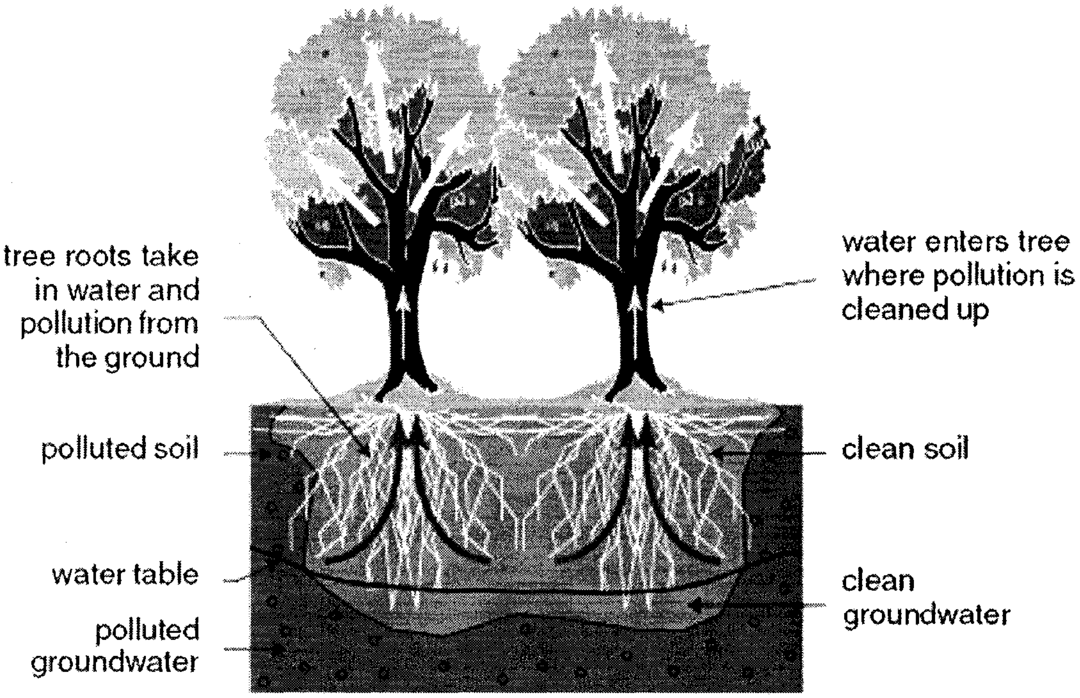


Fig 2.4 Phyto- remediation(4)

2.1.5 Electro Kinetics

It relies upon application of a low intensity direct current through the soil between ceramic electrodes that are divided into a cathode array and an anode array. This mobilizes charged species, causing ions used water to move towards the electrode. The removal of DNAPL using electro-kinetic remediation method to treat a simulated pool of DNAPL (tetrachloroethylene or PCE) in a low permeability environment (fine sand) in a small scale laboratory was investigated by (Keong et al., 2005)

2.2 Surfactants Background

Surfactants can lower the surface and interfacial tension, and thus facilitate the transport of organic contaminants from soils into a washing solution. They are used as flocculating wetting and foaming agents (Mulligan 1999a et al.). Surfactants are usually organic compounds that are amphilhilic. They contain both hydrophobic groups (their tails) and hydrophilic groups (their heads). They are soluble in both organic solvents and water. Previous studies show that surfactants could remove both heavy metals and hydrophobic organic compounds from soil successfully.

Recently, the use of surfactants for the extraction of heavy metals and organics from contaminated sites has attracted a great deal of research interest. Recent studies have been conducted on surfactant assisted removal of Copper (II), Cadmium (II), and Lead (II) from a Sandy Soil (Shalchian, 2006). Allen et al conducted several chemical column- washing experiments and concluded that efficient washing occurred while using organic chelating agents at the lowest flow rate. Numerous studies have also been conducted on the surfactant enhanced remediation of organics (Harwell 1992). Column studies were conducted to investigate the relative flushing efficiencies of very dilute Triton X-100 solutions delivered through Ottawa sand spiked with light white mineral oil (Duffield, 2003). Chelating agent such as EDTA is quite effective in removing heavy metals, but can potentially affect the permeability of the treated soil (Abumaizar and Khan, 1996). Surfactants can extract heavy metals without changing the soil pH, when coupled with ligand that forms a micelle solubilized complex (Barrington and Shin, 2004). For the last several decades, surfactant- enhanced oil recovery has been developed and used in oil production. This technology is called tertiary oil recovery (Reed and Healy, 1977). Shiau et al (2000) used food grade surfactants in column studies to remove chlorinated solvents through enhanced mobilization

2.2.1 Classification of surfactants

The common classification of surfactants given below is based on the nature of the hydrophilic part. The following is a brief summary of surfactant characteristics (Myers, D., 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.

Anionic surfactants are used in petroleum recovery due to their high aqueous solubility and repulsion from soils that possess a negative surface charge. Head groups of anionic surfactants include sulfonates, Sulfates and phosphates. EDTA- and SDS-enhanced soil washing can be employed either sequentially or concurrently to remediate soils contaminated with heavy metals and hydrophobic organics together (Khodadoust et al., 2005).

Cationic surfactants head groups are usually compressed with an amino or quaternary nitrogen group and do not perform well in soils possessing a negative surface charge due to strong adsorption of the soil particles. Nonionic surfactants are uncharged and soluble through hydrogen bonding at oxygen or hydroxyl groups (Ouyang 2002).The water solubility of non-ionic surfactants is contingent upon the length of the ethoxylated chain that is the longer it is, the greater its solubility(Rosen 1989).

2.3 Surfactant Mechanisms

2.3.1 Micellar Solubilization

Critical Micelle concentration (CMC) is defined as the concentration of surfactant above which micelles are spontaneously formed. CMC is different for every surfactant. The formation of surfactant micelles can be very sensitive to temperature. Below a critical temperature called the Krafft point (Rose, 1989). In a micelle, the individual monomers are oriented with their hydrophilic moieties in contact with aqueous phase while their hydrophobic moieties get tucked into the interior of the micelle (Harwell, 1992). Non-ionic surfactants generally have lower CMC than anionic surfactants (Rosen 1989). Typical CMC values range from 0.1 to 10mM (West and Harwell 1992). Hydrophobic compounds like PAHs, partition into the hydrophobic core of micelles.

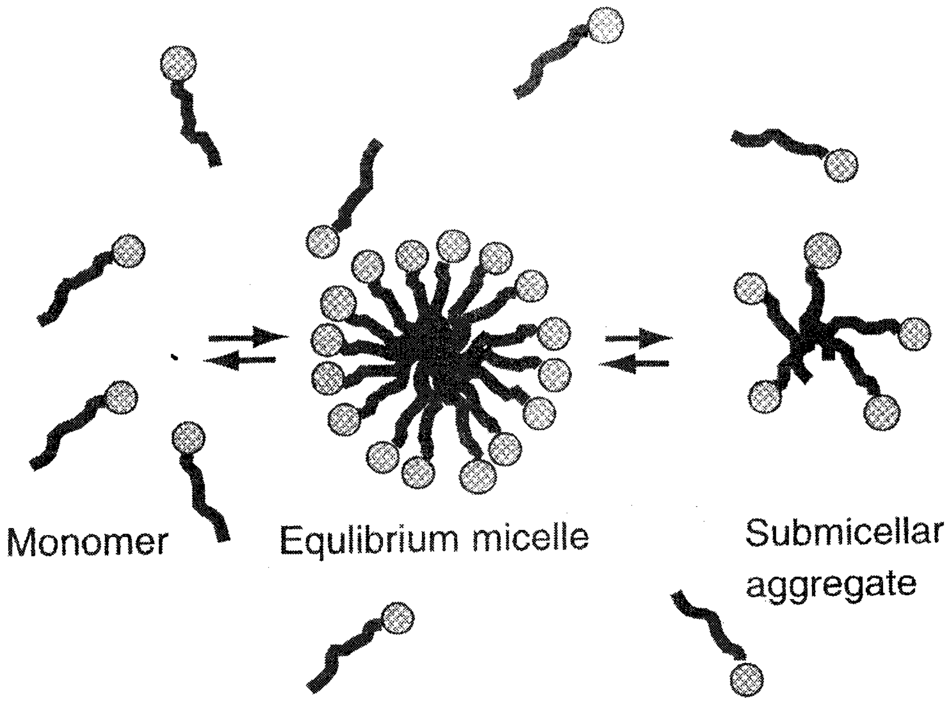


Fig 2.5 Surfactant micellization (Myers 1999)

2.3.2 Mobilization

Aqueous surfactant solutions also have the capacity to displace or mobilize residual NAPL (non-aqueous phase liquids) from porous media. NapL movement through the subsurface is governed by capillary forces (Han 2000). 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.

2.4 Surfactant Assisted NAPL removal from contaminated soils.

Surfactants increases the mobility of contaminants by combination of following three mechanisms (Fountain 1995)

1. Increasing contaminant solubilization.
2. Reducing contaminant sorption.

3. Lowering interfacial tension between water and NAPLs.

Abdul et.al (1992) examined the efficiency of surfactants in removing automatic transmission fluid from batch samples of a sandy textured soil. Results showed that surfactants removed 56 to 84% of contaminants where as water alone removed 23% of contamination. Column studies were conducted to assess the suitability of a non-ionic surfactant for washing pentachlorophenol (PCP) from soil and non-aqueous phase liquids (Sung et al., 2005**)**. Dense nonaqueous phase liquids (DNAPLs) prevent remediation of contaminated aquifers by preventing the solubilization and mobilization of residual NAPL. A new method that increases the efficiency of NAPL removal and surfactant recovery involves the use of nonionic surfactants such as Triton X-100 (Miller et al., 1996).

2.5 Surfactant assisted metal removal from contaminated soil

Some surfactants have been found to remove heavy metals from soils, under acidic conditions (Herman et.al 1995) without changing the soil pH. Surfactants can extract heavy metals when coupled with a ligand that forms a micelle solubilized complex. Doong et al., (1996) 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. According to them below critical micelle concentration (CMC), the desorption efficiency increased linearly with the increasing surfactant concentration. However, they reported that 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 like surfactin, rhamnolipids and sophorolipds have also been used to remove Cu (II) and Zn (II) from a hydrocarbon–contaminated soil by Mulligan et.al (1999a). Their analysis indicated that the carbonate and oxide fractions accounted for over 90% of Zn (II) present in the soil while organic fraction constituted over 70% of Cu (II).

2.6 Surfactant Selection

Surfactants should be selected to remove the contaminant and to minimize environmental damage. They also should be non-toxic and be easily removed from the subsurface by anthropogenic or natural means. Surfactants should be biodegradable. Cationic surfactants are toxic to many aquatic organisms at mg/l concentration; the toxicity is moderated by their reactivity to solids (West 1992). Most soils are negatively charged and would attract cationic surfactants to their surfaces. This reduces the amount of surfactant available in solution with the consequent reduction in the level of contaminant removal. Also unsuitable surfactants may clog soil pores by precipitation, hydrolyzation that forms flocs, formation of very large micelles and dispersion of soil colloids (Lee, 2001).

2.7 Limitations of surfactants within contaminated soils

1. Surfactants can adhere to soil and reduce effective soil porosity.
2. Sorption reduces the efficiency of the surfactant system and increases costs.
3. Surfactant sorption is generally greater for non-ionic than for anionic surfactants but non-ionic tend to have greater solubilization capacities (Allred 2001).

CHAPTER 3

Fate and Transport of Contaminants

3.1 Fate and Transport of BTEX

The BTEX are monoaromatic hydrocarbons which are found in petroleum products like gasoline. These compounds are hazardous to public health and environment. They have acute long term toxic effects. 18% of BTEX are present in Gasoline.

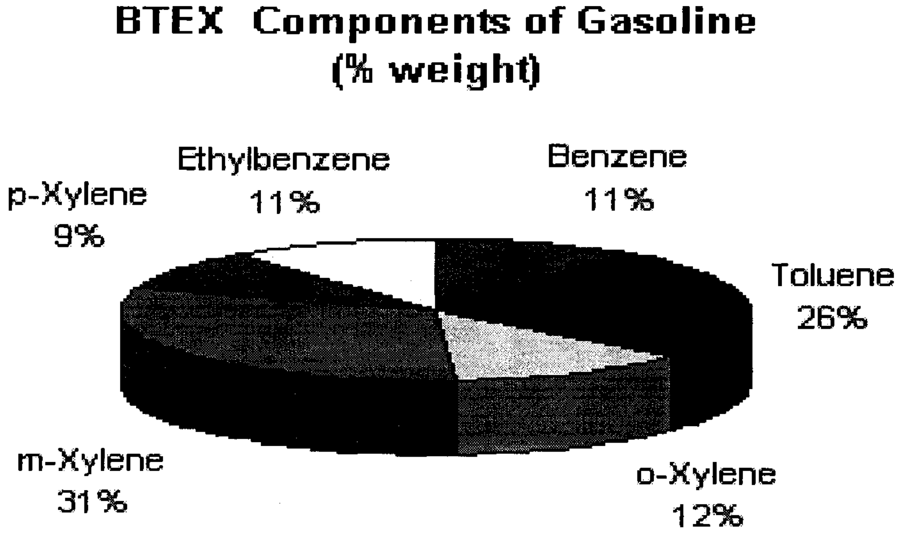


Fig 3.1 BTEX Components of Gasoline (Jasper, 1996).

The release of BTEX in to the environment depends on their fate and transport mechanisms (Charles et al., 1995). The fate and transport mechanism is of four phases. They are Volatilization, Sorption, Dissolution and Biodegradation.

Volatilization is a process in which an organic compound partitions between aqueous phase and gaseous phase. The escaping tendency of the solute molecules from the water phase to the air phase is proportional to the concentration in the water.

Sorption: Sorption is a process in which organic compounds stick to soil particles. When LNAPL is released into the subsurface, components will dissolve into the aqueous phase, then partition onto aquifer material. The sorption is controlled by contaminant characteristics such as solubility, polarity and octanol-water partition coefficient (K_{ow}). Octanol-Water Partitioning Coefficient is a measure of the distribution of the chemical between water and an organic (octanol) phase with which it is in contact (Han 2000). K_{ow} can be determined by measuring the concentration of a particular compound in both the water and the octanol phases after a period of mixing.

Dissolution: Dissolution is the process in which the LNAPL, when comes in contact with water it dissolves in it. The solubility represents the maximum concentration of that compound in water. The solubilities of the compounds most commonly found at superfund sites range over several orders of magnitude. Several parameters affecting solubility include temperature, pH, and co solvents, dissolved organic matter, and dissolved inorganic compounds, salinity.

Biodegradation: LNAPL can be biodegraded by natural micro-organisms present in subsurface. A study was conducted to evaluate the effect of viscosity of nonaqueous-phase liquids (NAPLs) on biodegradation of phenanthrene in soil slurries and to find means to enhance the process in viscous NAPLs. The rate and extent of biodegradation decreased with increasing viscosity of nontoxic NAPLs. (Birman et al., 1996).

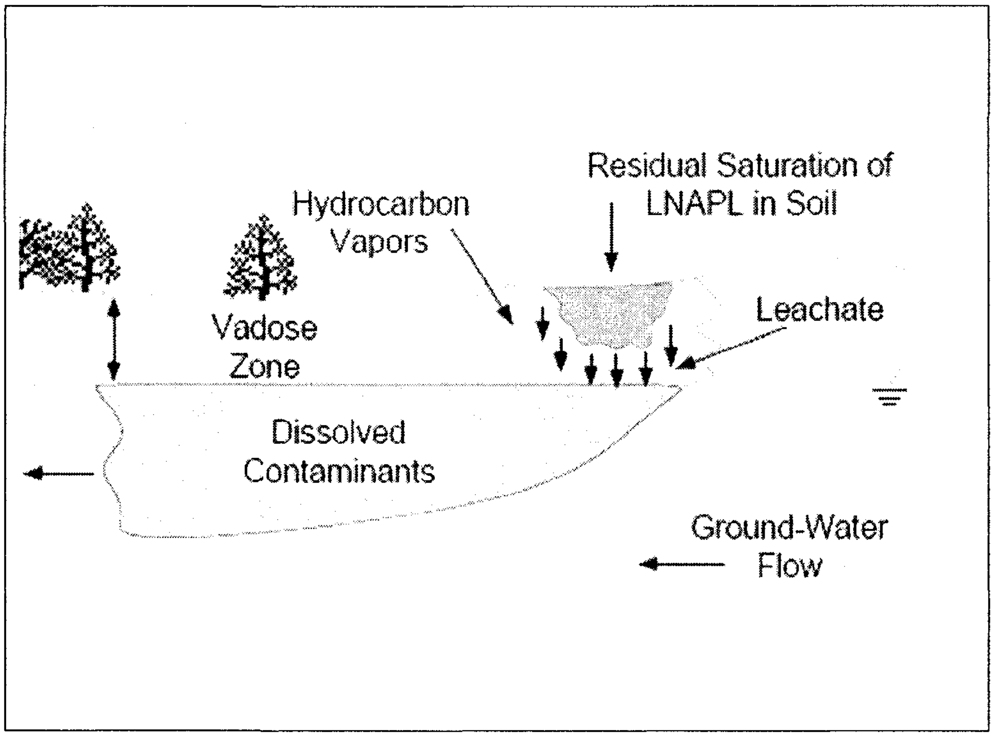


Fig. 3.2 LNAPL retained in soil

3.2 Heavy Metals

Heavy metals are metals with densities generally larger than 5g/cm3. Cadmium, Copper, Lead, and Zinc are the most hazardous heavy metals. They are in EPA's list of priority pollutants (Mulligan 2001 et.al). Heavy metal pollution arises commonly from purification of metals eg.the smelting of ores, preparation of nuclear fuels, electroplating, automobiles etc.Most of the heavy metals are cations means they carry positive charge. Most clay minerals have a net negative charge. Soil organic matter tends to have variety of charged sites on their charged surfaces, some positive and some negative. The negative charges of these various soil particles tend to attract and bind the metal cations and prevent them from becoming soluble and dissolved in water. The most important chemical processes affecting the behavior and bioavailability of metals in soils due to adsorption of metals from the liquid phase on to the solid phase.(Han 2000).

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 electro neutrality, 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 complication: 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).

3.3 Zinc in the environment

Zinc is a lustrous bluish white metal. It is brittle and crystalline at ordinary temperatures, it becomes ductile and malleable when heated between 110 and 150 degrees centigrade it is a very common substance that occurs naturally in air, water and soil. It is the 23rd most abundant element in earth's crust. The main zinc mining areas are in Canada, Russia, Australia, USA and Peru. World production of zinc exceeds 7million tones a year. More than 30% of the world's needs for zinc met by recycling.

3.3.1 Health effects of zinc

Zinc is a trace element that is essential for human health. Its deficiency causes loss of apetite, decreased sense of taste and smell, slow wound healing and skin sores, birth defects, skin lesions and sexual immaturity (Alloway, 1990). High concentrations of zinc can cause skin irritations, vomiting, nausea; anemia. Very high levels of zinc can damage the pancreas and disturb the protein metabolism.

3.3.2 Effects of zinc on the Environment

Water can be polluted with zinc due to presence of large quantities of zinc in wastewater of industrial plants. Some fish can accumulate zinc in bodies, when they live in zinc-contaminated water ways. When zinc enters bodies of fish it is able to biomagnify up in the food chain. Zinc can interrupt the activity of micro-organisms .The breakdown of organic matter may seriously be slowed down because of these adverse effects of zinc on soil microbial processes have been reported to start at added concentrations as low as 10 mg Zn/kg of soil, (McLaughlin and Smolders, 2001).

3.4 Copper in the soil

Copper is a reddish metal with a face-centered cubic crystalline structure. It is malleable and ductile and a good conductor of both heat and electricity. Copper has low chemical reactivity. In moist air, it slowly forms a greenish Surface film called patina, this coating protects the metal from further attack.

3.4.1 Copper in the environment

Copper is very common substance that occurs naturally in the environment and spreads in the environment through natural phenomena. Natural sources include windblown dust, decaying vegetation, forest fires etc. and human activities include mining, metal production, wood production and fertilizer production.

3.4.2 Health effects of Copper

Long term exposure to copper can cause irritation of the nose, mouth, eyes and it causes headaches, dizziness, vomiting . Intentionally high uptakes of copper may cause liver and kidney damage and even death. Chronic copper poisoning results in wilson's disease, characterized by hepatic cirrhosis, brain damage, renal disease and copper desorption in cornea. Alloway (1990) states that normal human diet provides 1-5 mg of Cu /day.

3.4.3 Effects of copper on environment

When copper is deposited in soil it attaches to organic matter and minerals. Copper does not breakdown so it accumulates in plants and animals when it is found in soils. Copper accumulated in soils can be responsible for phytotoxicity above a threshold which depends on both plant species and soil properties.(Brun et al., 2001). According to

(Thornton,1999) bioavailability of copper is that portion of soil copper that is available for intake into a given organism. Plants can alter the chemical mobility and thereby, the bioavailability of metals in the root environment. (McLaughlin et al., 1998)

The most important chemical processes affecting the behavior and bioavailability of metals in soils due to adsorption of metals from the liquid phase on to the solid phase.(Han 2000). Copper forms complexes with organic matter in the soil and is strongly held on inorganic and organic exchange sites present on soil particles. Hence, it is relatively more difficult to remove copper from the soil (Alloway 1990).

CHAPTER 4

Experimental: Materials and Procedure

4.1 Materials

The materials used mainly consisted of soil samples, target contaminants and surfactants.Cu(II) and Zn (II) in the form of copper chloride and zinc chloride. Nitric acid (70%) was used for digestion. Analytical-reagent grade chemicals were obtained from Fisher scientific (Canada). Distilled water was used as a control, for washing and diluting. Analytical-reagent grade SDS (sodium dodecyl sulfate), AOT (dioctyl sulfosuccinate) and Tx-100 (Triton X-100) are the surfactants used to represent anionic and non-ionic surfactants. EDTA is the complexing agent used. Surfactants and EDTA was obtained from Sigma chemicals Co.USA. The contaminants Xylene and Ethyl benzene (99.9% pure) were purchased from Fisher Scientific. Hexane is used as extractor.

4.2 Soil sample preparation

Soil sample preparation described below is similar to the procedure described in an earlier study (Li ,Ramamurthy, 2008). The soil used in this investigation contained 98% of Ottawa sand and 2% bentonite by weight. Sand was obtained from Geneq Inc., Canada and bentonite was purchased from Givesco., Canada. Bentonite has particle size which passes through the 200 mesh. The Ottawa sand used in this study corresponds to clean sand passing through 20 mesh. The specific surface area of sand was reported as 0.007m2/g (Lee et al.,2002). Hydraulic conductivity of soil sample (98% sand and 2% bentonite) was experimentally found from permeameter tests to be 3.63×10−3cm/s (Li, 2004). The properties of these three surfactants are shown in the tables 4.1 and 4.2

Table 4.1 Properties of Tx-100 and EDTA (Edwards et al, 1994)

	Tx-100	EDTA
Product name	Triton X-100 (99%)	Disodium ethylenediamine tetra acetate
Surfactant Type	Nonionic surfactant	Chelating agent
Molecular formula	$C_8H_{17}C_6(OC_2H_4)_nOH$ (n = 9-10)	$Na_2C_{10}H_{14}O_8N_2.2H_2O$
Molecular weight (g)	625	372.24
Appearance	Viscous colorless liquid	white crystalline powder
CMC	0.22-0.24 mM$^{(1)}$	-

Table 4.2 Properties of SDS and AOT

	SDS	AOT
Product name	Sodium dodecyl sulfate (>96%)	Sodium dioctyl sulfosuccinate (96%)
Surfactant Type	Anionic surfactant	Anionic surfactant
Molecular formula	$C_{12}H_{25}OSO_3Na$	$(C_9H_{17}O_2)_2CH_2CHSO_3Na$
Molecular weight (g)	288.38	444.57
Appearance	White powder	White powder
CMC	8.20mM$^{(2)}$	1.124 mM$^{(3)}$

4.3 Soil pH

Soil pH was measured using a soil to water ratio of 1:10.In this procedure 20g of soil was placed in a 400ml beaker and 200ml of distilled water added. The solution was placed on an orbital shaker for 30min and left for one hour to ensure equilibrium was reached prior to measurements.

4.4 Organic matter content

The organic matter content of the soil was determined by the weight loss on ignition method. The method is as follows: A porcelain dish was washed and weighed. 3g of air-dried soil was weighed into the pre-weighed porcelain dish. The dish was placed in a furnace set to 550°C for 1.5h. The porcelain dish was left overnight in the desiccator.The dish was then weighed and the difference in weight was divided by the initial soil weight and multiplied by 100 to give the percentage organic matter. The organic matter was 0.3%.

4.5 Soil contamination

In these experiments two general types of contaminants were identified for the study: They were heavy metals and hydrophobic organic compounds. Atomic Absorption Spectrophotometer and Gas Chromatography were used to analyze heavy metals and hydrocarbons respectively.

4.5.1 Procedure for soil contamination with heavy metals

Metal salt solution containing 4000 mg/L of copper chloride and 4000 mg/L of zinc chloride were added to bentonite 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 at 60 Oscillations/min for 24 hours at a room temperature of 25°C ± 2°C. After centrifugation at 3000 prm 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 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 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% (± 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, Perkin Elmer 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 extreme values and the average results are presented in table 4.3

Table 4.3 Soil contamination levels of metals

Cu (II) Concentration mg/kg Soil	Zn (II) Concentration mg/kg Soil
850	760

4. 5. 2 Batch experiments

Batch extraction experiments were conducted at a room temperature of 25° ±2°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 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 of contaminated soil (4.9 g of sand + 0.10 g of bentonite) samples were weighed out into the reactor formed of 40 ml amber glass centrifuge tubes. For each tests involving a washing solution, the volume of the solution chosen was 30 ml, because the tube size was 40 ml. 30 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 were done in triplicate and the reported values denote average metal concentrations.

4.6 Procedure for soil contamination with hydrocarbons

The procedure for soil contamination with Xylene and Ethyl benzene followed the method suggested by Liu and Roy (1992). To contaminate the soil 50mg of either Xylene or Ethyl benzene is dissolved in 20ml hexane and added to 100g of bentonite. After mixing on a shaker table for 10 min, the wet soil was placed in a hood at room temperature. The mixture is agitated several times during this process. Because of the higher vapor pressure of hexane, this evaporation step effectively removes hexane without significant loss of contaminants (Liu and Roy,1992).The initial contamination level is determined by simple extraction with hexane as an extractant. The results are presented in the table 4.4

Table 4.4 Soil contamination levels of HOCs

Xylene concentration, mg/kg	Ethyl benzene concentration, mg/kg
100.2 mg/kg	143.7 mg/kg

4.6.1 Batch Experiments

Five grams of soil was placed in 30ml amber glass vials. To this 30 ml of surfactant solutions of different concentrations were added. Samples were sealed with teflon screw caps and tumbled for 24 h. Previous research has shown that 24 h was sufficient for surfactant and hydrocarbons to reach equilibrium. (Rouse et.al., 1993).After equilibration, samples were allowed to settle and filtered with a filter paper. The filtrate then was analyzed for Xylene and Ethyl-Benzene concentration. Each test was performed in triplicate.

4.6.2 Gas Chromatography conditions

All GC experiments were performed with Varian CP-3800 gas chromatography with flame ionization detector (FID). The column flow was 1ml/min and the injection port temperature was 250^0 C. The column oven temperature was programmed as shown in table 4.5

Table 4.5 GC conditions:

Temp C	Rate c/min	Hold min	Total min
40		3.00	3.00
150	10	8.00	22.00
250	20.0	5.00	32.00

4.7 Column experiments

4.7.1 Column Design

Column experiments were performed to simulate surfactant flushing in soil (Lee et., al, 2001). Column experiments were conducted at the room temperature of $22^{\circ}\mathrm{C} \pm 2^{\circ}\mathrm{C}$. the experiment set up is illustrated in Fig 4.1 Plexiglas columns (L = 20.5 cm, D = 4.0 cm) were designed to conduct column tests. The columns were equipped with two pore stone filters and two plastic gaskets to prevent soil dispersion and ensure uniform flow distribution. A small electric pump and a constant head reservoir were used to provide steady flow through the column. Column experiments simulated an ex-situ soil flushing technology for removal of heavy metals and HOC from contaminated sites.

4.7.2 Test Procedures

Each column contains nearly 565g of contaminated soil sample which were prepared by mixing 98% sand and 2% bentonite in a large glassware using a plastic spatula. Following this, the soil mixture was shaken for nearly 20 minutes to ensure uniform mixing of sand and bentonite. The column was filled with mixed dried soil in the layers of 2 cm. the column was given controlled shocks by tapping with a thin wooden rod after placing each layer and tapping was performed to provide the uniform packing of the soil in the column. The pore volume P_v of the packed column

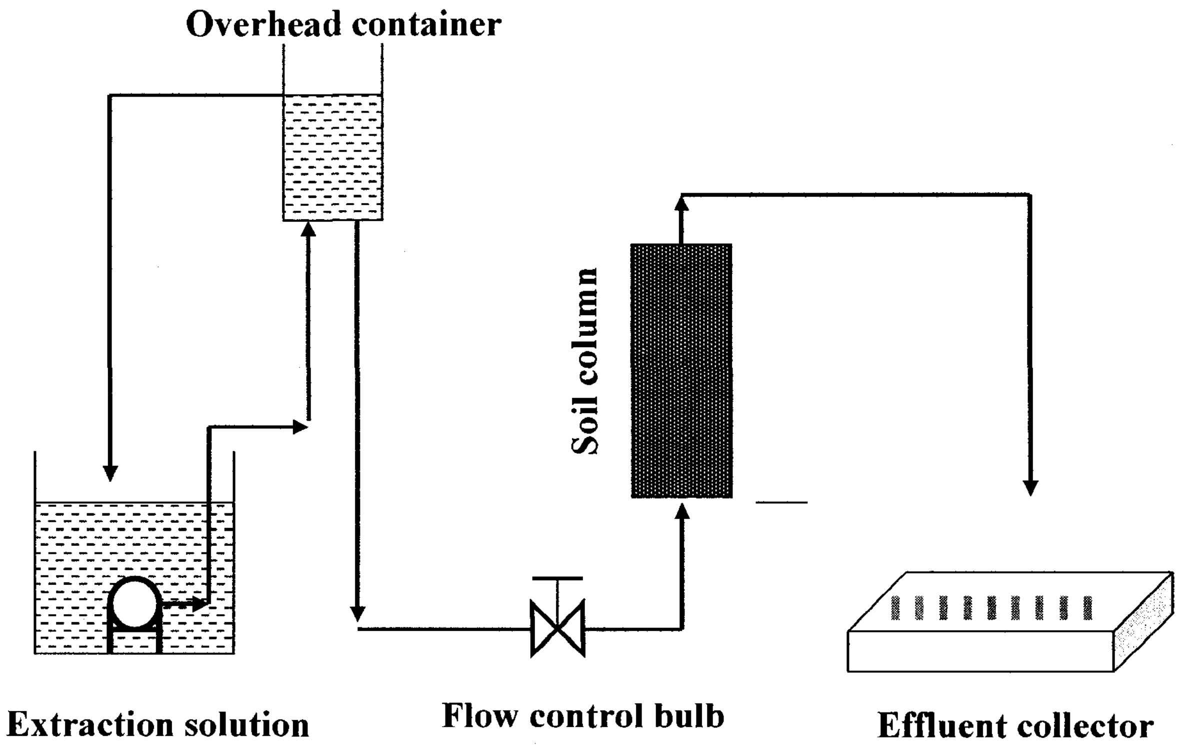


Fig. 4.1 Schematic setup of column experiment

was determined by the weight difference between water-saturated column (W_{sat}) and dried soil column (W_{dried}) with the following equation:

$$P_v = (W_{sat} - W_{dried})\ \rho_w^{-1}$$

where ρ_w (Kg / m^3) is the density of the water.

The surfactant was pumped through the soil columns. The effluent is collected manually at specific intervals. All the effluent samples were filtered and prepared for AA and GC analysis. Finally, the removal efficiency was calculated using the results of AA and GC analysis and initial amount of contamination.

CHAPTER 5

Discussion of results

5.1 General Remarks

Distilled water, one nonionic surfactant and two anionic surfactants were used in this study to investigate their removal efficiency related to heavy metals, Zn(II) and Cu(II) and organics Xylene and Ethyl benzene. Further addition of the EDTA as a chelating agent to improve removal efficiencies was also explored. The results of batch and column experiments, related graphs, and interpretation of the results are described in the following sections. All the experiments were conducted at a room temperature of $22^\circ C \pm 2^\circ C$. Soil to liquid ratio was set as 5g: 30ml.

5.2 Batch Test Results of Heavy Metals

5.2.1 Preliminary Batch tests to remove Cu(II) and Zn(II) from soil samples using surfactants

Batch tests involved the removal of Cu(II) and Zn(II) from a sandy soil. Previous test results related to removal of only Zn(II) and Cu(II) from sandy soil were available (Li, 2004). Hence comprehensive tests related to removal of Zn(II) and Cu(II) were not conducted. Only a few typical tests were conducted and the results were used to compliment detailed tests involving both metals and organics. Some results are reported in the Figs 5.1and 5.2. Table A.1 provides the additional details such as pH data related to the experiments. Some differences between the results of the previous tests (Li, 2004) and present tests can be traced in part to the differences in ageing of the contaminant and the errors that are inherent in the experimental procedures (Figs 5.1 and 5.2).

The results in the Figs 5.1 and 5.2 show that the removal efficiency increases with increasing concentration. From soil sample SDS removed 1.36% of Cu(II) and it removed 32% of Zn(II). Beyond this concentration of SDS the removal rate remained almost constant. The initial pH range during batch tests was 5.63 – 6.89 and final pH range was 6.32 – 7.01.

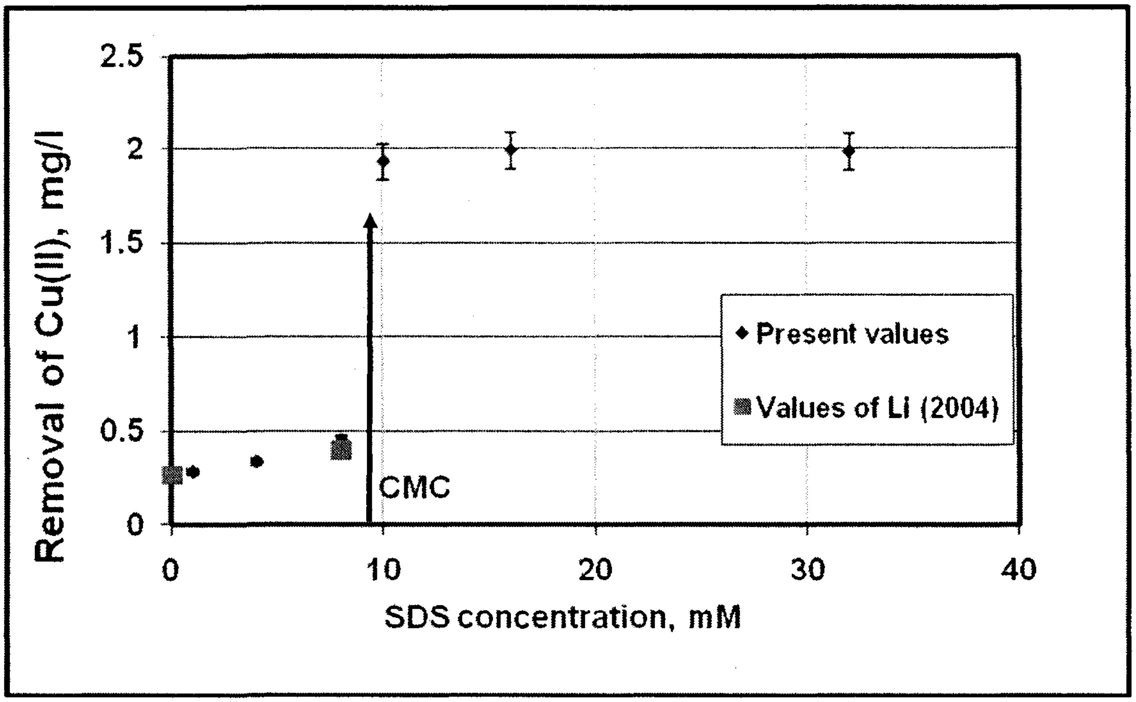


Fig 5.1 Extraction of Cu(II) from contaminated soil by SDS

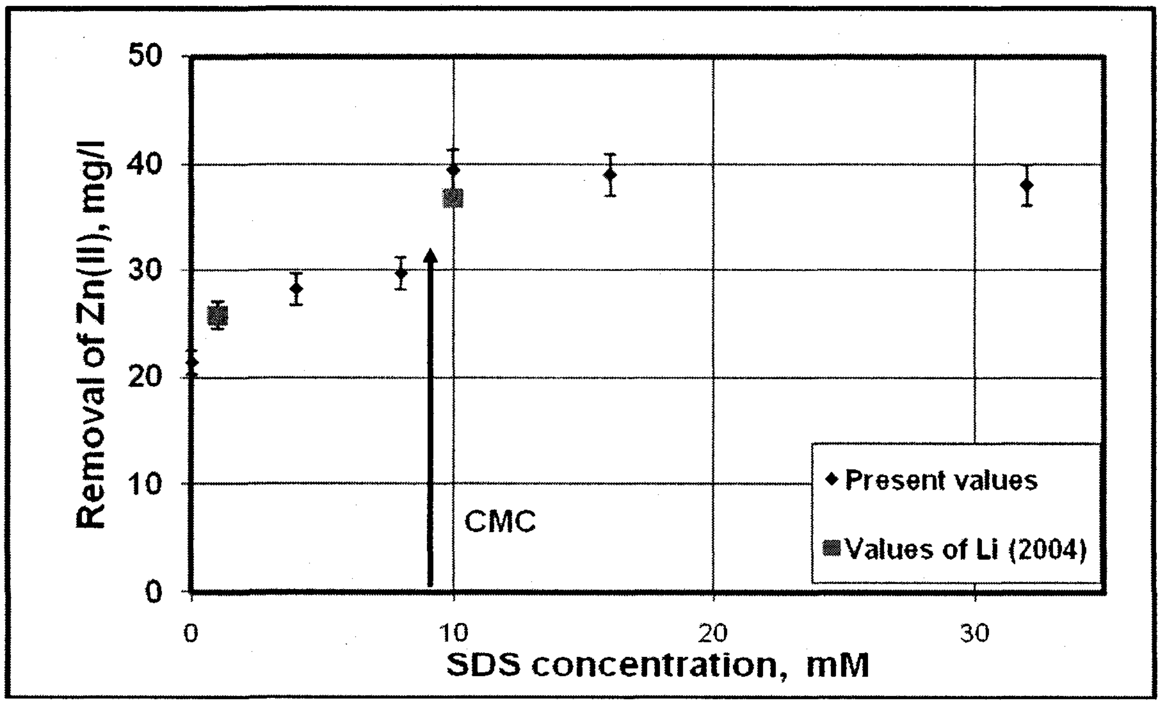


Fig 5.2 Extraction of Zn(II) from contaminated soil by SDS

5.2.2 Preliminary Batch tests to remove heavy metals [Cu(II) and Zn(II)] using EDTA

Figure 5.3 illustrates the results of extraction of Cu(II) and Zn(II) with EDTA only. The removal efficiency increased with EDTA. 57.88% of Cu(II) and 77.36% of Zn(II) were removed with EDTA alone. The removal efficiency of EDTA is more compared to surfactants. However, one prefers to use surfactants, because of their low toxicity and favorable biodegradability (Deshpande et al. 1999).

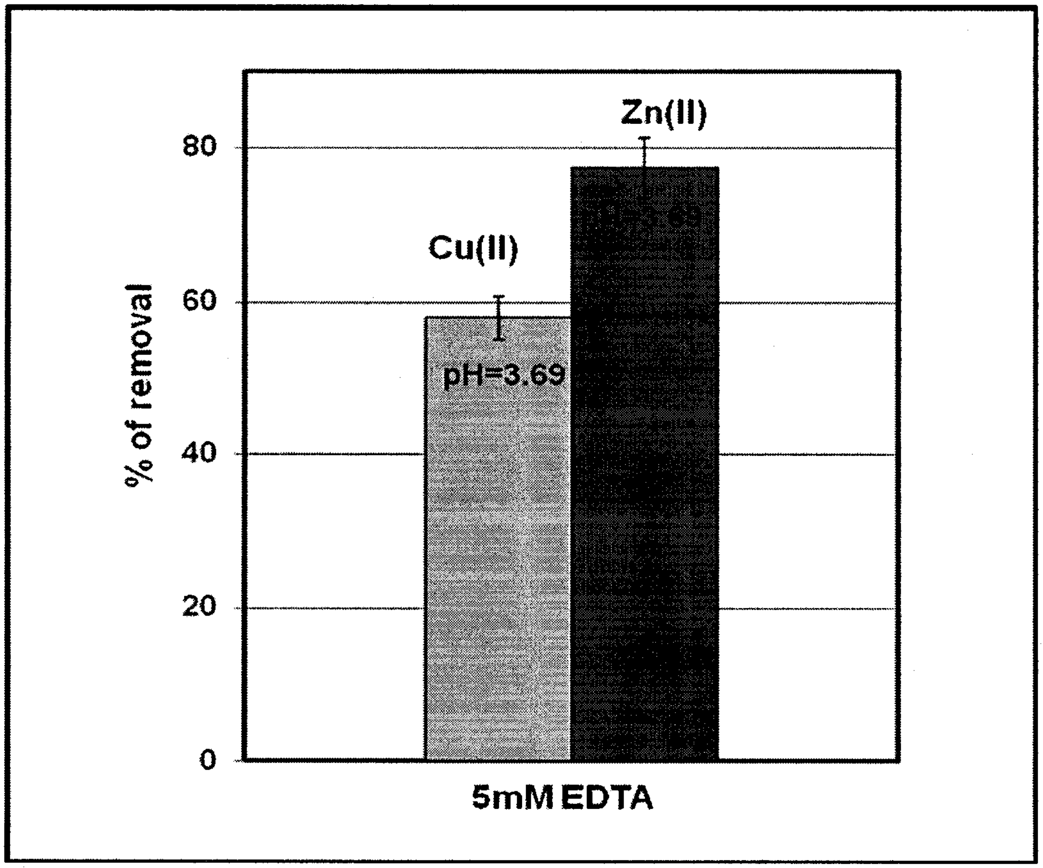


Fig 5.3 Batch extraction of Cu(II) and Zn(II) by 5mM EDTA

5.3 Preliminary Column test results of Cu(II) and Zn(II) removal by SDS and EDTA

Column tests are preferred to batch tests because 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. Column experiments (Fig 5.4 and 5.5), were conducted to compare the removal efficiencies at different flow rates (4ml/min, 12ml/min, and 40ml/min). Tables B.7 – B.12 show the detailed results of this tests. 10mM SDS and 5mM EDTA were used as washing solutions. The results in Figs 5.4 and 5.5 show that varying the flow rate influenced the removal rate of Zn(II) and Cu(II). Zn(II) removal rate is high at 40ml/min compared to flow rates of 12ml/min and 4ml/min. 96.6% of Zn(II) was removed at the flow rate of 40ml/min in 60 pore volumes (Fig 5.4). At larger flow rate, higher boundary shears are present and hence the loosely attached Zn(II) gets removed. 74.39% of Cu(II) was removed at the flow rate of 4ml/min in 60 pore volumes (Fig 5.5). At lower flow rates, more Cu(II) is removed. This is consistent with the fact that Cu(II) is more strongly bound to the soil particles and the desorption is controlled more by diffusion. At lower flow rates, there is more time for larger diffusion as residence time is higher.

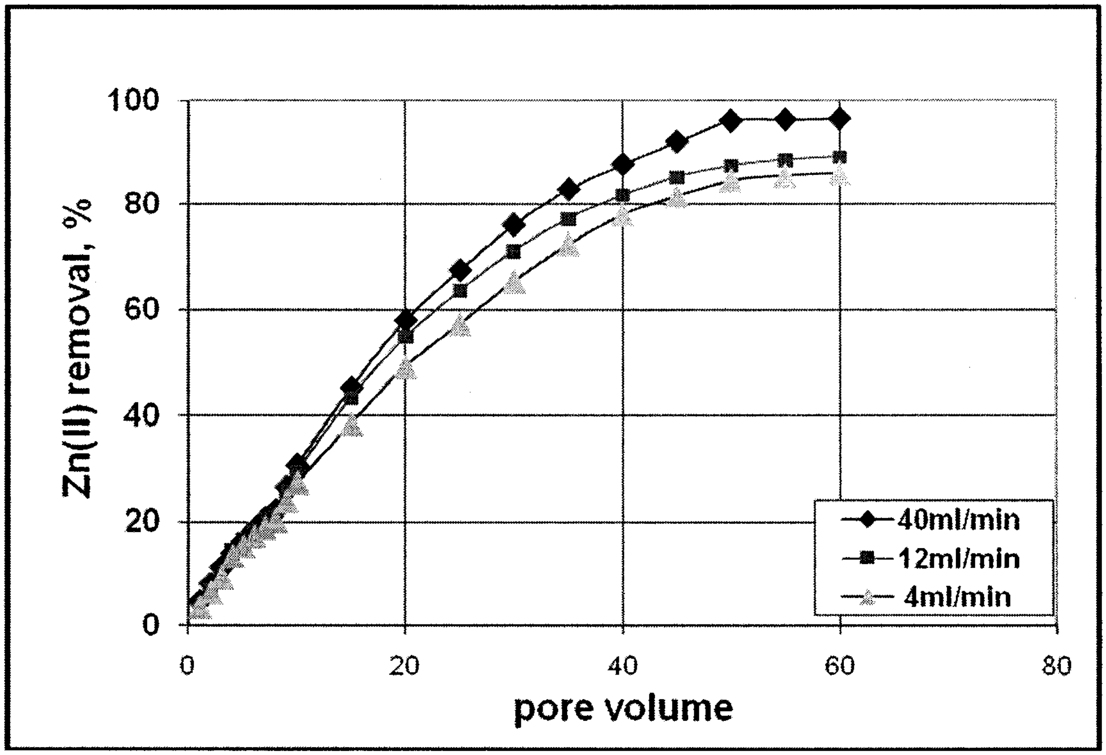


Fig 5.4 Zn(II) removal by different flow rates with10mM SDS and 5mM EDTA

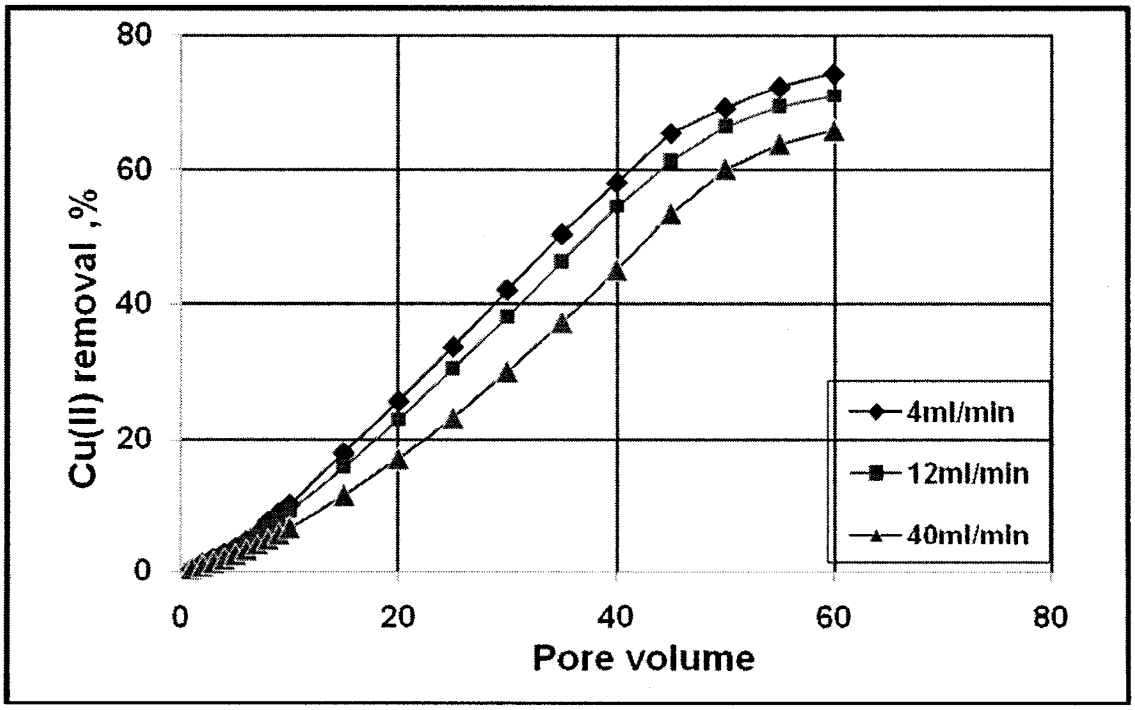


Fig 5.5 Cu(II) removal by different flow rates with 10mM SDS and5mM EDTA

5.4 Batch Test Results for Xylene and Ethyl benzene

5.4.1 Desorption of Xylene and Ethyl benzene using SDS

The solubilities of hydrophobic compounds such as Xylene and Ethyl benzene are very low in water. Solubility of such compounds can be increased by addition of surfactants (Liu and Roy 92). Batch experiments, (Fig 5.6-5.11) show that water can remove 9% to 11% of these hydrocarbons. Table A.2 shows the detailed results of the experiment such as percentage of removal of Xylene and Ethyl benzene at different concentration for SDS. Surfactants on the other hand remove 12 to 25% of these HOCs. Out of the three surfactants used in the batch tests, SDS was found to be most effective in removing hydrocarbons from the soil (Fig 5.6 and 5.7). For SDS, the removal increased drastically at the concentration of 10mM which is close to its CMC, which is 8.20mM. At this concentration, 22.9% of Xylene is removed and its solubility appears to be increased in the surfactant micelles. Anionic surfactants like SDS are less adsorbed onto the soil than non-ionic surfactants. (Han, 2000). Hence the highest removal occurred close to the CMC.

According to previous studies Chu (2003), the washing mechanisms are of 2 types: At low concentrations, the removal of HOCs is less due to the adsorption of the surfactant to the soil. Further, HOCs that are present in the soil have the affinity to be retained in the soil particles and the remaining HOCs in the liquid phase get more easily trapped in the hydrophobic cores of surfactant micelles.

At high concentrations, the HOCs completely dissolve in the micellar phase and fixed HOCs have the chance to come in contact with unoccupied micelles. Hence extraction of HOCs fixed to the soil increases there by reducing HOC in the soil media. The initial pH range was 6.13 – 6.38 and final pH range was 7.11 – 7.95 in this tests.

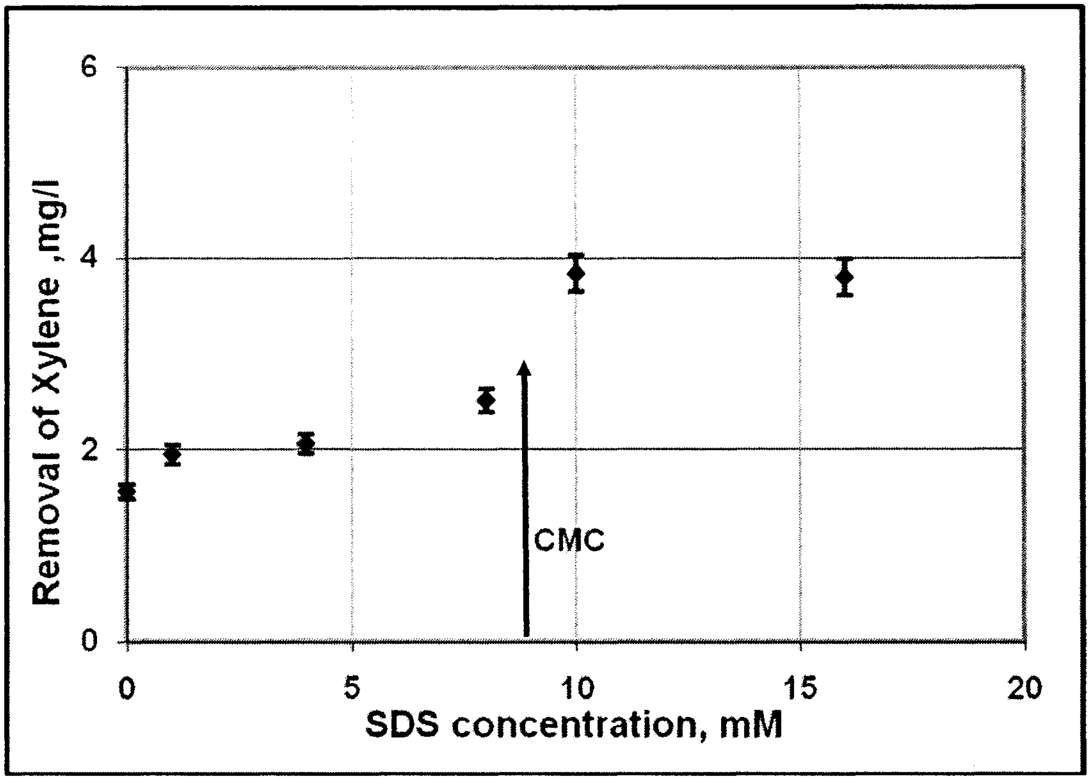


Fig. 5.6 Batch Extraction of Xylene from contaminated soil by SDS

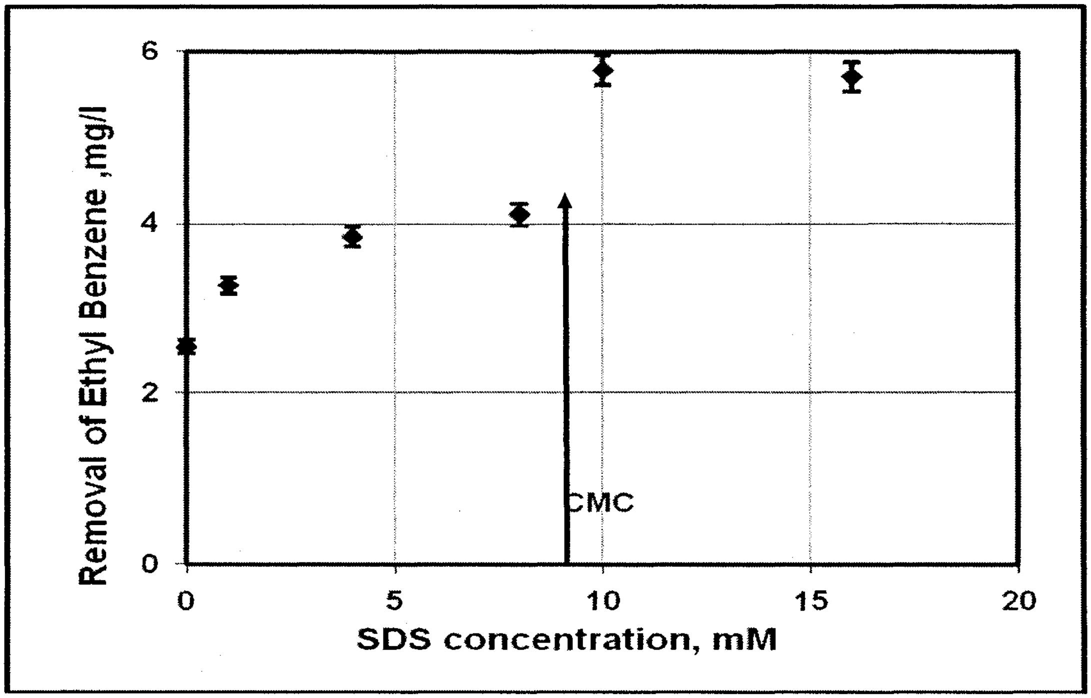


Fig 5.7 Batch Extraction of Ethyl benzene from contaminated soil by SDS

5.4.2 Desorption of Xylene and Ethyl benzene using Tx-100

Figs 5.8 and 5.9 show the results of Xylene and Ethyl benzene removal by Tx-100 respectively in batch tests. Table A.3 shows the detailed values for these batch tests. 18.50% of Xylene and 20.7% of Ethyl benzene are removed at 0.5mM of Tx-100. The CMC for Tx-100 is 0.22mM. In case of Tx-100, there is loss of surfactant to the soil and the maximum removal occurs at concentration much higher than CMC. The desorption rates of Tx-100 were 1.98 and 1.94 times greater than that with distilled water alone.

The initial pH range was 6.17 – 6.85 and final pH range was 7.11 – 7.94 in this tests. The initial pH values denote the pH values of surfactant solution before they were added to the soil samples. The final pH range is the pH range value noted after shaking the soil sample for 24 hours.

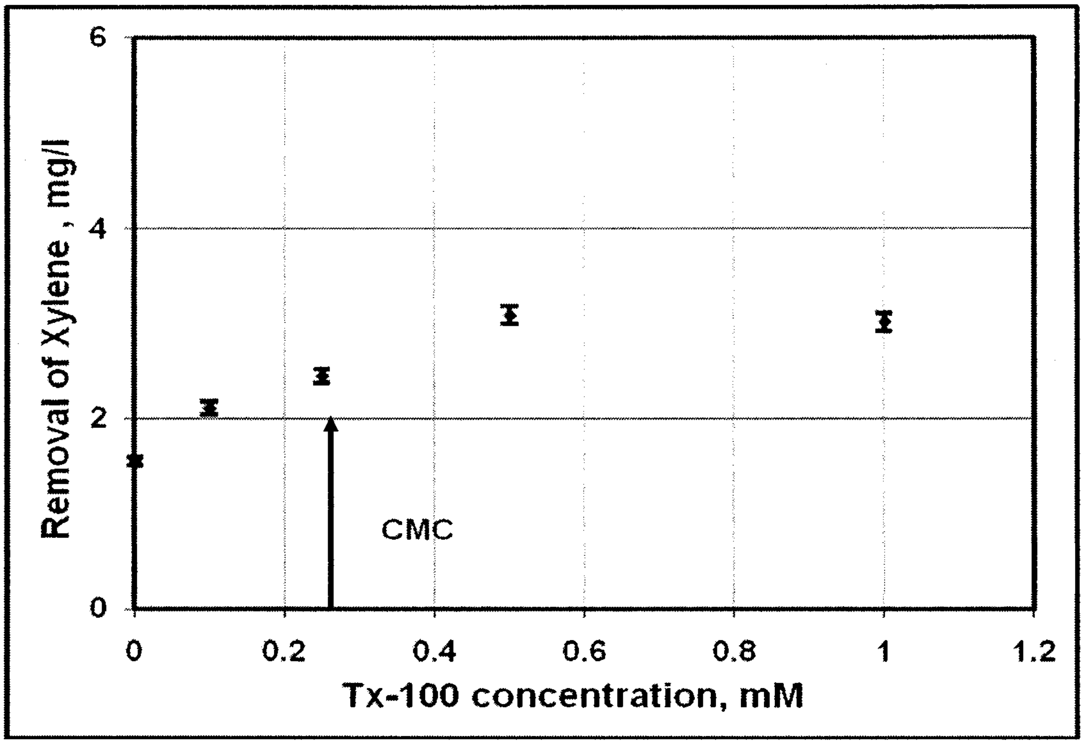


Fig 5.8 Batch Extraction of Xylene from contaminated soil by Tx-100

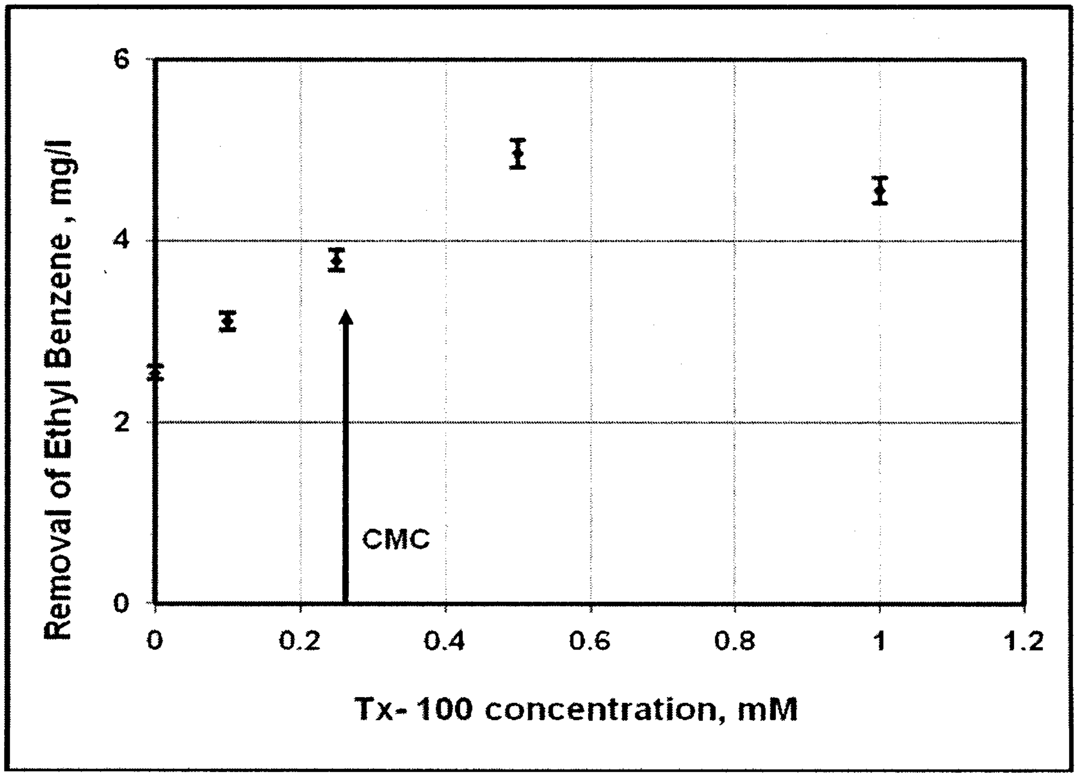


Fig 5.9 Batch Extraction of Ethyl benzene from contaminated soil by Tx-100

5.4.3 Desorption of Xylene and Ethyl benzene using AOT

Figs 5.10 and 5.11 show the removal efficiency of Xylene and Ethyl benzene by AOT respectively in batch tests. Table A.4 shows the detailed results of these batch tests. 13.41% and 15.99% of Xylene and Ethyl benzene were removed at 1.25mM respectively. The desorption rates of AOT were 1.43 and 1.5 times greater than that with distilled water alone for Xylene and Ethyl benzene respectively. In case of anionic surfactants SDS and AOT, the maximum removal rate is close to CMC and beyond this point the removal of HOCs is not significant. Further Figs 5.10 and 5.11 show that there is a slight decrease in the removal of Xylene and Ethyl benzene after CMC is reached. Figs 5.6 to 5.11 also indicate that the removal percentage is high for Ethyl benzene compared to Xylene.

Based on results of these batch tests, we would expect SDS to be a good candidate for surfactant-assisted soil remediation. It has good solubilizing abilities for Xylene and Ethyl benzene. SDS has carbon chain length of 12 and according to Rosen(1989) if the surfactants have more carbons, generally they have high solubilizing abilities for hydrophobic substances.

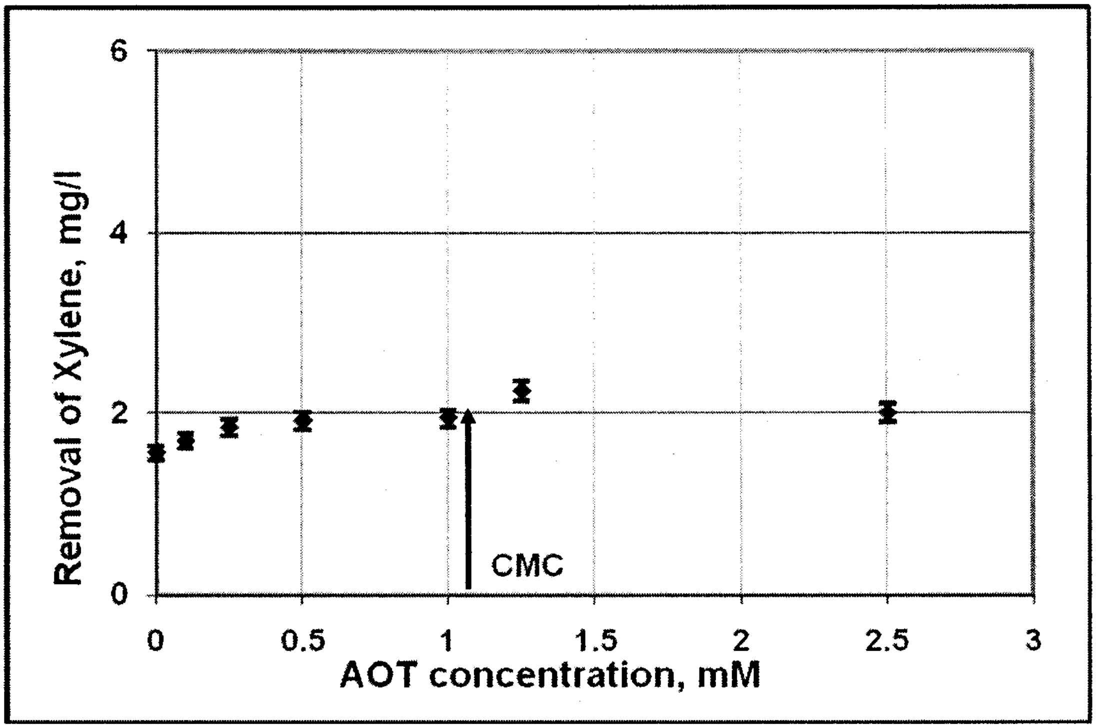


Fig 5.10 Batch Extraction of Xylene from contaminated soil by AOT

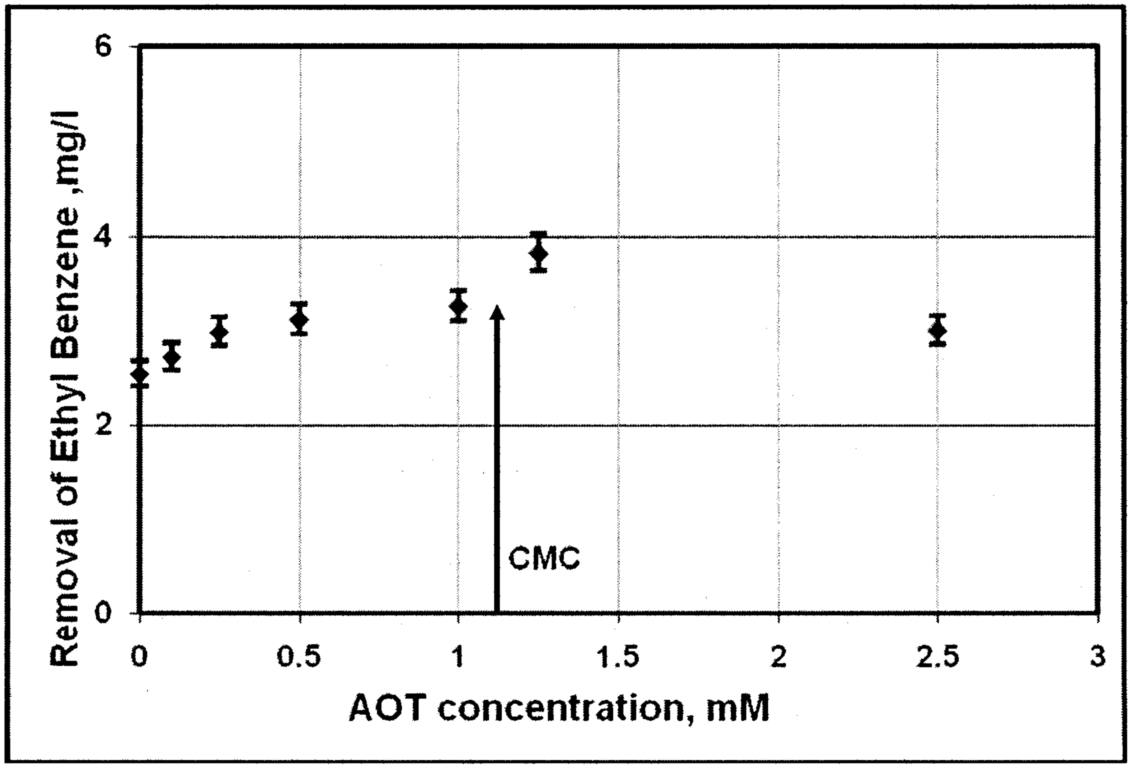


Fig 5.11 Batch Extraction of Ethyl benzene from contaminated soil by AOT

5.5 Interaction between Zn(II) and Xylene retention in soil samples 1, 2 and 3

A few tests were conducted to observe the interactions between Xylene and Zn(II) in batch tests. For the batch studies related to retain of heavy metal and HOC in the soil samples 1,2 and 3, Zn(II) and Xylene were selected. Three different soil samples were selected. Soil sample 1 was contaminated with both Xylene and Zn(II). Soil sample 2 was contaminated with Xylene alone and soil sample 3 was contaminated with Zn(II). The preparation of samples similar to the preparation of samples described in section 4.6

For soil sample 1, which contained both Xylene and Zn(II), Xylene retained in the soil was 80 mg/kg and Zn(II) retained was 696 mg/kg, (Fig 5.12). In soil sample 2, containing only Xylene, Xylene retained in soil was 120mg/kg and in soil sample 3, containing only Zn(II), Zn(II) retained in soil was 1320mg/kg.

Table 5.1 Retention capacities of Xylene and Zn(II)

Sample no.	Compounds	Retention in soil, mg/kg
1	Xylene and Zn(II)	80 mg/kg and 696 mg/kg
2	Xylene	120mg/kg
3	Zn(II)	1320 mg/kg

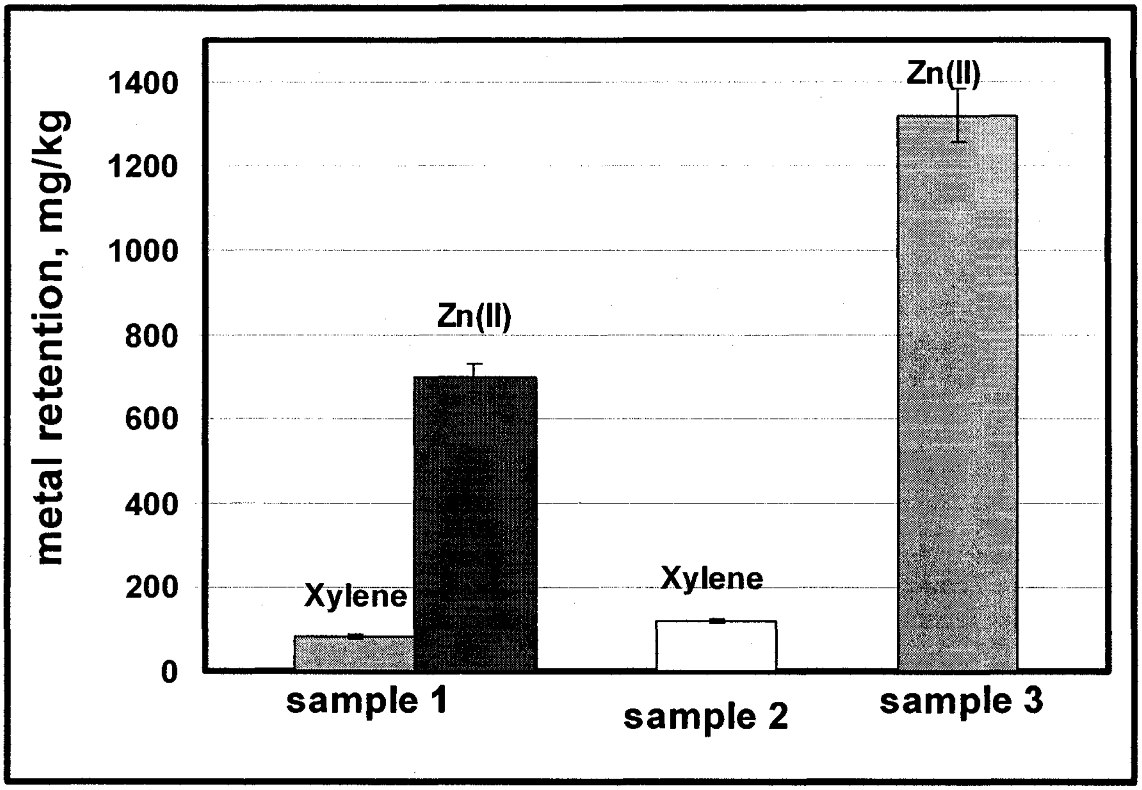


Fig 5.12 Interaction study related to Zn(II) and Xylene retention

5.5.1 Desorption of Xylene and Zn(II) using distilled water

(Interference Effects)

The results of extraction batch studies also show (Fig 5.13) that distilled water removed 1.1% of Xylene and 2.7% of Zn(II) from sample 1, containing Xylene and Zn(II). From sample 2, containing only Xylene, distilled water removed 11% of Xylene. From sample 3, which contained only Zn(II), it removed 18% of Zn(II). There is large drop in the removal efficiency of Zn(II) in soil sample 1 compared to soil sample 3 (Fig 5.13). Removal efficiency of Zn(II) is inhibited in the presence of Xylene. There was also a significant drop in the removal of Xylene from sample 1, compared to removal from sample 2 due to presence of Zn(II). The presence of Zn(II) appears to suppress the adsorption of Xylene and the presence of Xylene appears to suppress the absorption of Zn(II) indicating strong interference effects.

5.5.2 Desorption of Xylene and Zn(II) using SDS (Interference Effects)

The result of extraction batch studies in Fig 5.14 also show that SDS removed 3.12% and 3.08% of Xylene and Zn(II) respectively in soil sample 1, which contained both Zn(II) and Xylene. From sample 2,containing only Xylene SDS removed 26% of Xylene and from sample 3, containing only Zn(II), it removed 22% of Zn(II). There is again a significant drop in the removal of Zn(II) from sample 1compared to removal of Zn(II) from sample 3. Xylene removal rate from sample 1 also was reduced drastically compared to sample 2. Previous studies (Zheng and obbard et.al 2002), show that less effective SDS washing occurred because there is a decrease in the amount of SDS available in solution to form micelles that could solubilize hydrophobic organic compounds , as part of SDS is used to remove Zn(II).

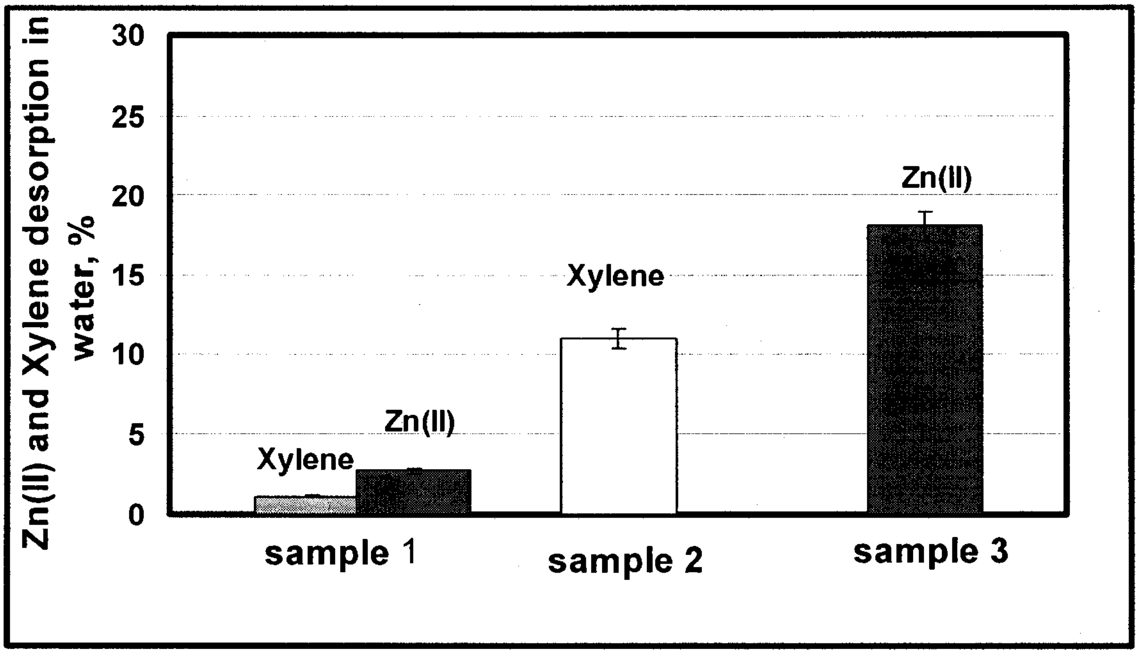


Fig 5.13 Interaction study related to Zn(II) and Xylene desorption in water

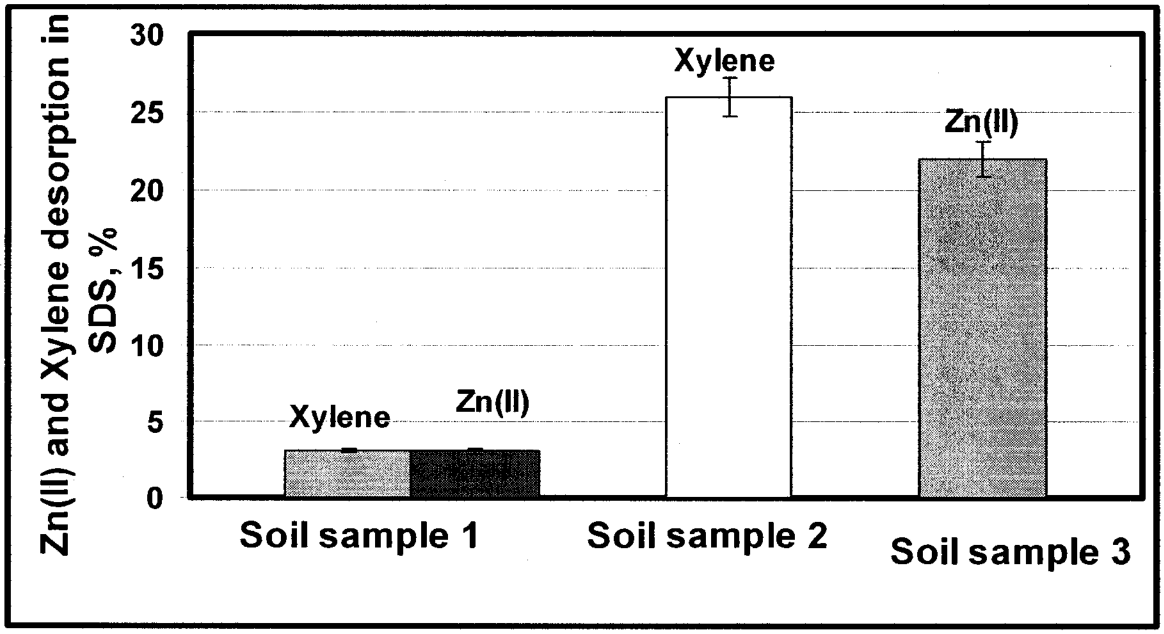
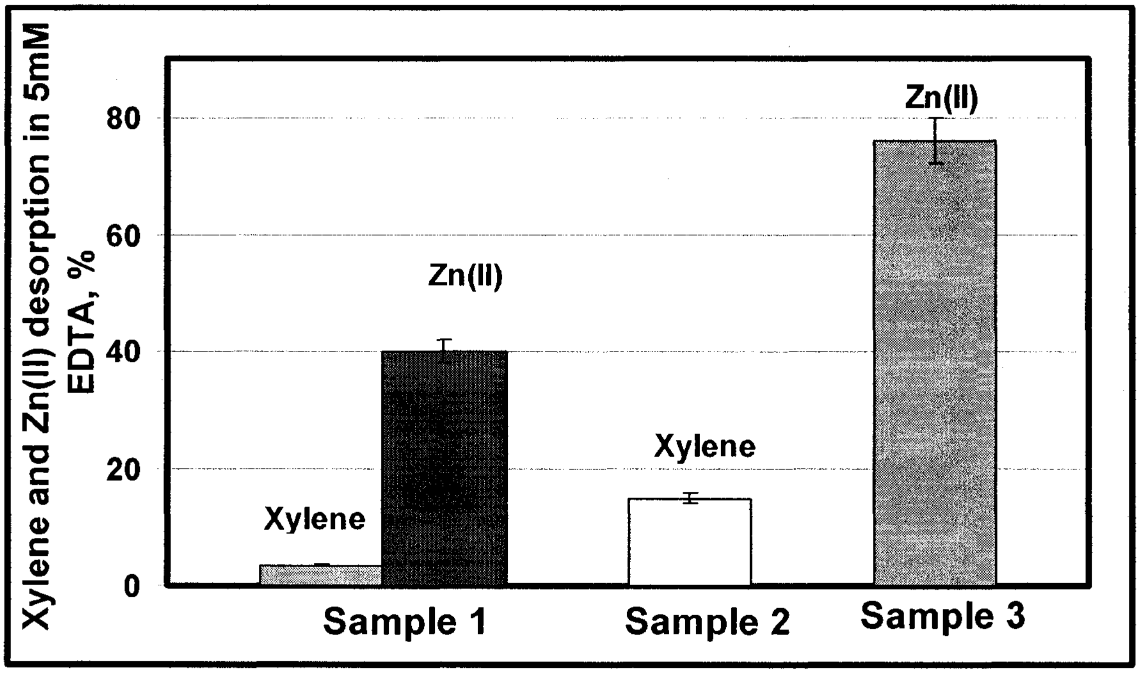


Fig 5.14 Interaction study related to Zn(II) and Xylene desorption in 10mM SDS

5.5.3 Desorption of Xylene and Zn(II) using EDTA

A few batch tests were also conducted to observe the desorption of Xylene and Zn(II) when EDTA was used as washing liquid. Tests were performed with sample1, sample 2 and sample 3. From sample 1, containing both Xylene and Zn(II), EDTA removed 3.4% of Xylene and 40% of Zn(II), (Fig 5.15). From sample 2, containing only Xylene, it removed 15% of Xylene and from sample 3, containing only Zn(II), it removed 76% of Zn(II). There is drastic decrease in the removal of Zn(II) from samples 3 compared to sample 1. The chelating capacity of EDTA was reduced significantly when both Xylene and Zn(II) were present in the soil.



5.15 Interaction study related to Zn(II) and Xylene desorption in 5mM EDTA

5.6 Interaction between Xylene and Ethyl benzene retention in soil samples 2 , 4 and 5

The batch test results based on the study of interactions between Xylene and Ethyl benzene are shown in Fig 5.16, 5.17, and 5.18. For HOC interaction studies, two new soil samples termed as sample 4 and sample 5 were prepared. In sample 4, bentonite was contaminated with both Xylene and Ethyl benzene before adding to sand (98%) In sample 5, bentonite was contaminated with only Ethyl benzene before adding to sand. The preparation of the samples and the testing procedures were identical to that of preparing sample 1.

From soil sample 4, containing both Xylene and Ethyl benzene, Xylene retained in the soil sample was 100.2 mg/kg and Ethyl benzene retained in the soil sample was 143.7 mg/kg, (Fig 5.16). From soil sample 2, containing only Xylene, Xylene retained in the soil was 120mg/kg and from soil sample 5, containing Ethyl benzene, Ethyl benzene retained in the soil was 230mg/kg. The retention of Ethyl benzene in the soil is more compared to that of Xylene. This indicating that Ethyl benzene has higher affinity to soil matrix adsorption sites than Xylene. Fig 5.16 show that Ethyl benzene retention is significantly reduced in the presence of Xylene. Table 5.2 shows the retention capacities of Xylene and Ethyl benzene.

Table 5.2 Retention capacities of Xylene and Ethyl benzene

Sample no.	Compound	Retention in soil mg/kg
2	Xylene	120 mg/kg
4	Xylene and Ethyl benzene	100.2 and 143.7 mg/kg
5	Ethyl benzene	230 mg/kg

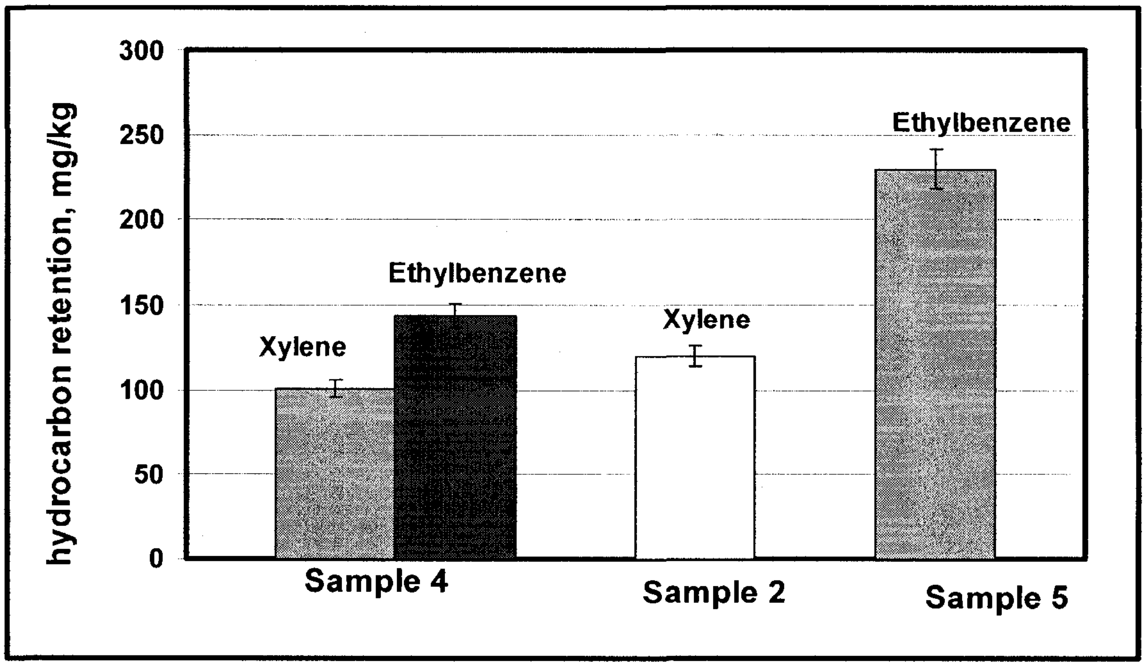


Fig 5.16 Interaction study on Xylene and Ethyl benzene retention

5.6.1 Desorption of Xylene and Ethyl benzene using distilled water

A few batch extraction tests were also conducted to observe the desorption of HOCs by water. From sample 4, distilled water alone removed 9.34% and 10.64% of Xylene and Ethyl benzene respectively. From sample 2, 11% of Xylene was removed by distilled water and from sample 5; it removed 14.6% of Ethyl benzene. Removal of Ethyl benzene from sample 5 was more compared to sample 4.

5.6.2 Desorption of Xylene and Ethyl benzene using SDS

Batch extraction studies were also conducted to observe the desorption of HOCs by SDS, (Fig 5.18). From sample 4, SDS removed 22.9% and 24% of Xylene and Ethyl benzene respectively. From sample 2, 26% of Xylene is removed by distilled water and from sample 5; it removed 36% of Ethyl benzene. Removal of Ethyl benzene is high compared to Xylene this could be due to octanal water partition coefficient is slighter higher for Ethyl benzene. Further one notes that this property renders higher solubility to Ethyl benzene. The removal efficiency of SDS is 2.5 times greater than that of distilled water alone.

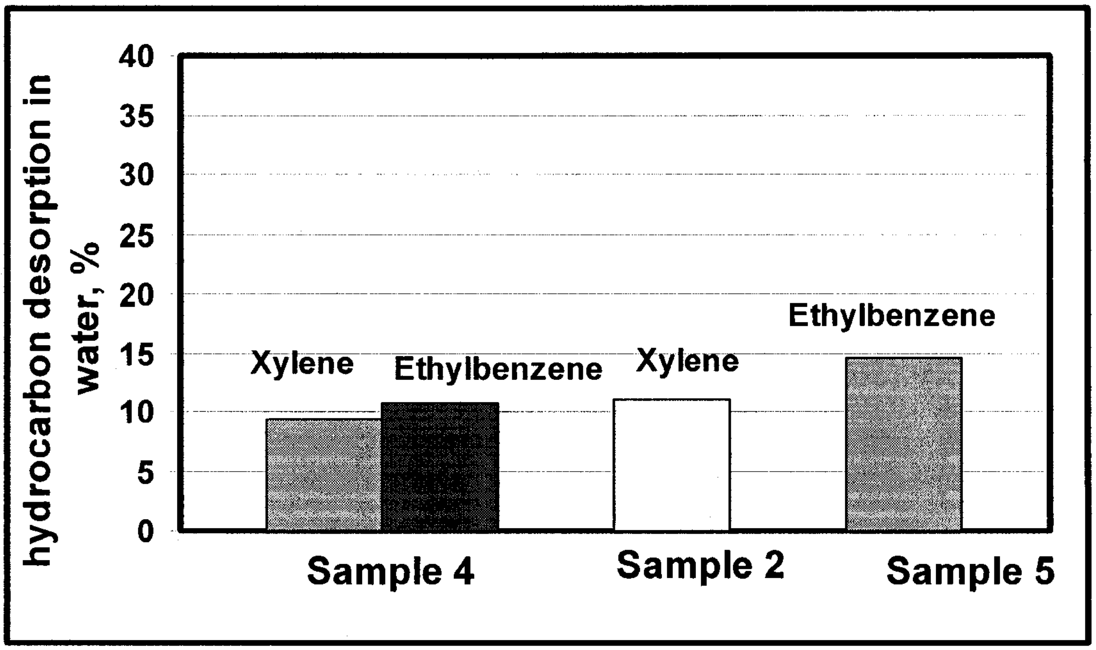


Fig 5.17 Interaction study related to Xylene and Ethyl benzene desorption in water

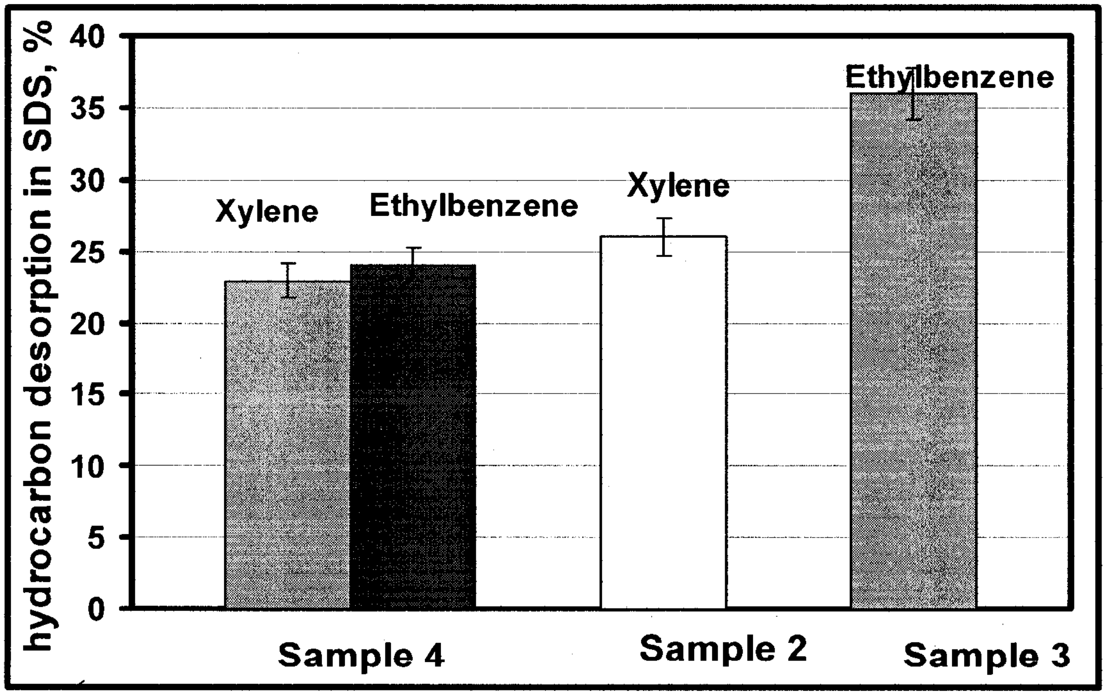


Fig 5.18 Interaction study related toXylene and Ethyl benzene desorption in 10mM SDS

5.7 Column Test Results for hydrocarbons

5.7.1 General comments

The purpose of column tests on the contaminated soil was to determine the removal efficiency in soil columns that simulates in-situ washing process (Smith et.al 1999). According to batch tests reported earlier, SDS 10mM was more effective in removing Xylene compared to Tx-100 and AOT. Hence only SDS 10mM was selected as washing fluid for column experiments. As before, distilled water was the control. The hydrocarbon that was selected is Xylene. For the column tests, the column was initially packed with the soil. The surfactant was continuously introduced at a fixed rate until steady state was achieved.

Column tests were conducted with different flow rates (4ml/min, 12ml/min and 40ml/min) for Xylene removal by 10mM SDS. The flow rate was 12ml/min for Xylene removal by distilled water. The removal efficiencies of Xylene by distilled water and 10mM SDS are shown in Figs 5.19 and 5.20 respectively. Table B.1 – B.4 provides detailed results of the experiment. The removal efficiency was less in the initial pore volumes. The desorption rate of Xylene increased significantly after 15 pore volumes (Fig 5.19). In 40 pore volumes, 33% of Xylene was removed from the column by distilled water alone.

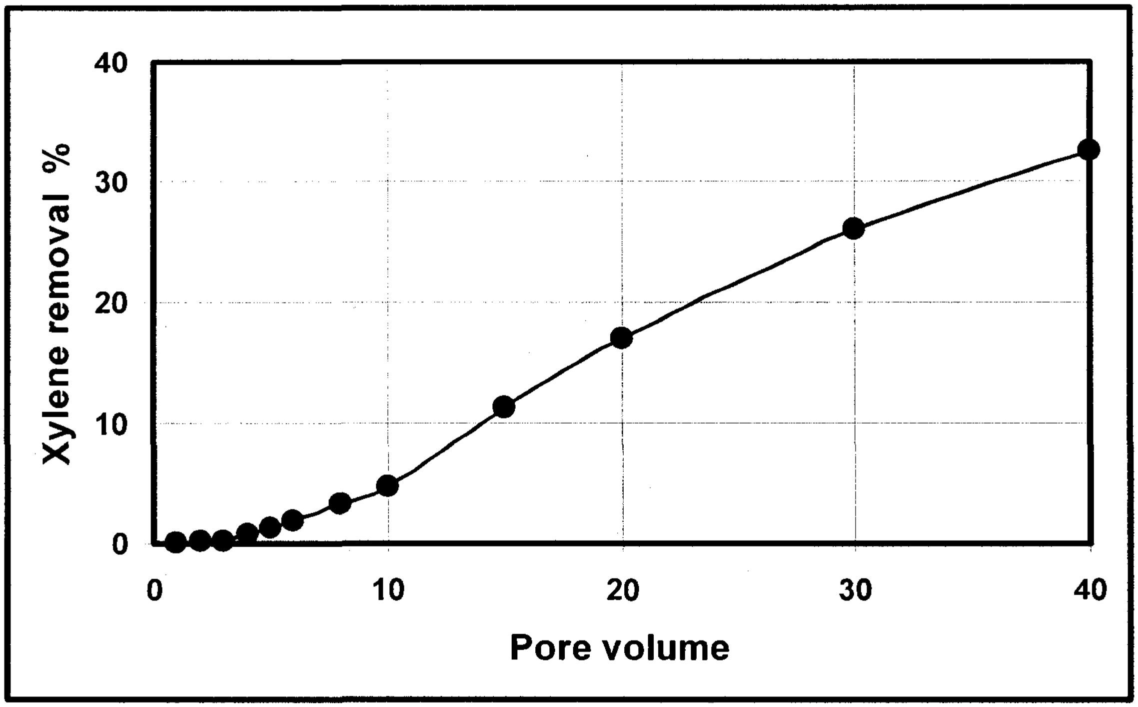


Fig 5.19 Xylene removal from soil column by distilled water

5.7.2 Effect of Flow Rates

Surfactant SDS was used to study its ability to mobilize Xylene trapped in the soil of the column. Different flow rates were used to know their removal efficiencies. The three column experiments conducted at different flow rates are shown in Fig 5.20. Xylene concentration in the first pore volume is very low because its solubility in water is small. The first pore volume of surfactant solution displaces the column pore spaces filled with water only. At the flow rate 4ml/min, 99.9% of the trapped Xylene was removed within 60 pore volumes. 79% of Xylene was removed at 12ml/min flow rate and 68% of Xylene was removed at 60ml/min flow rate in 60 pore volumes. Out of the three flow rates, the slowest flow rate of 4ml/min was effective in removing 99.9%. This denotes the longer contact time between Xylene and the surfactant. It indicates that diffusion may be the main mechanism to desorb Xylene. The removal efficiencies decreases as the flow rate increases because of the decreased residence time of the surfactant in the soil.

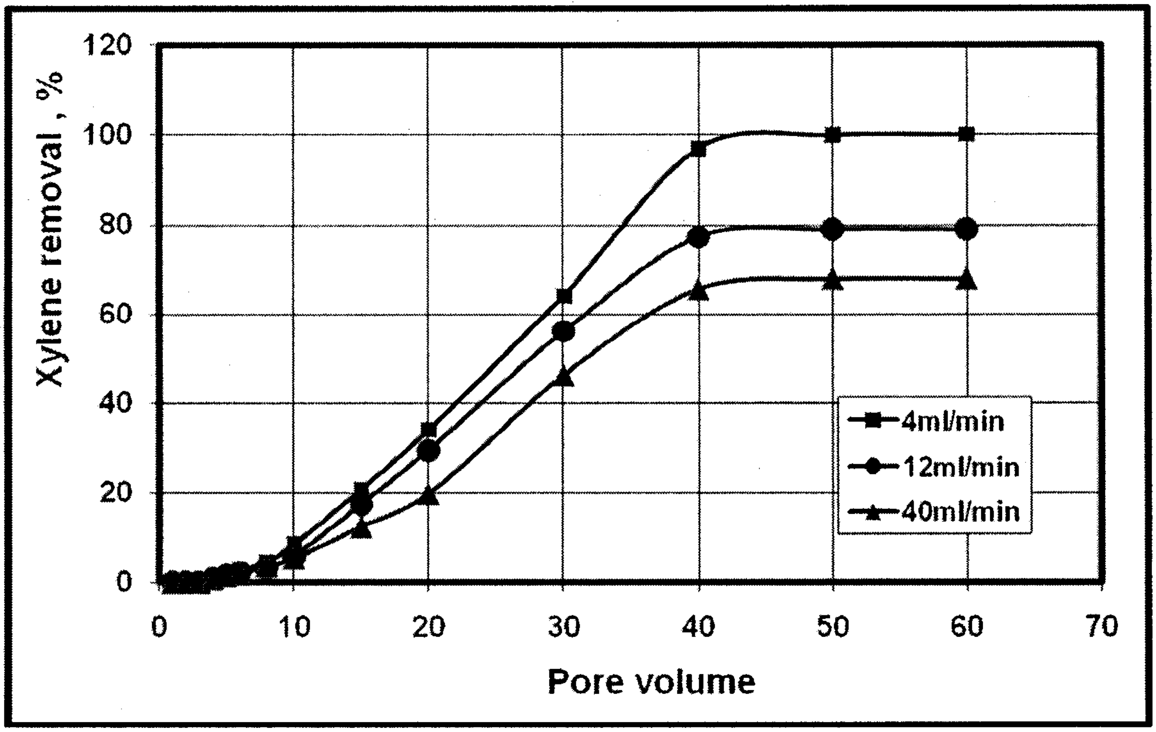


Fig 5.20 Xylene removal by different flow rates with 10mM SDS

5.7.3 Removal of Cu(II), Zn(II) and Xylene from the soil column by 10mM SDS at flow rate 12ml/min

Generally in contaminated sites, both heavy metals and hydrophobic organic compounds are present together. Hence a column test was conducted to see the removal efficiency of the surfactant in the presence of Xylene, Zn(II) and Cu(II), (Fig 5.21). The flow rate to remove Xylene, Zn(II) and Cu(II) was set at 12ml/min. Since an individual test was conducted to see the interference between Zn(II), Cu(II) and Xylene , medium flow rate 12ml/min was selected. Table B. 5 and B.6 show the detailed results of this experiment. The results in Fig 5.21 show that Cu(II) removal rate was 11.47% in 60 pore volumes.

Corresponding Zn(II) removal rate was 18.53% and Xylene removal rate was 59%. Removal rate of Xylene appears to be reduced drastically in the presence of Cu(II) and Zn(II). At the same time one notices that there is a drop in the removal rates of Zn(II) and Cu(II) in the presence of Xylene. The presence of metals in the soil appears to decreases the availability of surfactants to Xylene.

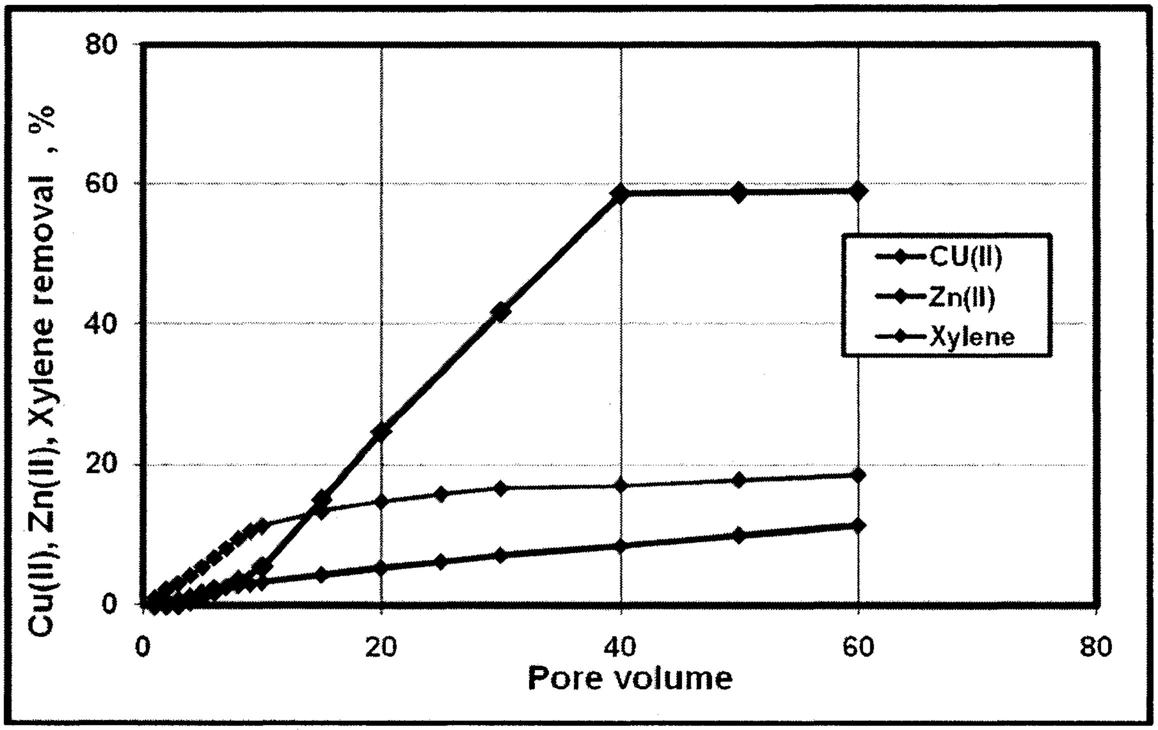


Fig 5.21 Cu(II), Zn(II) and Xylene removal from the soil column by10mM SDS

5.8 Effect of pH

In batch experiments initial and final pH values indicate the range of pH values of the solution during several tests conducted at different concentrations before and after shaking the solution for 24h. pH variations can significantly influence the solubility and removal of metals from soil. Not surprisingly, desorption of metals is increased as pH decreases. In batch tests, when water was used, the initial and final pH were 5.9 and 6.40 respectively. At this pH distilled water removed 0.17% of Cu(II) and 16.9% of

Zn(II). When EDTA was used for removal of Cu(II) and Zn(II), the initial and final pH were 4.15 and 3.69. At this pH the removal efficiency was 57.88% for Cu(II) and 77.36% of Zn(II). This indicates that removal efficiency is high for metals in acidic conditions. In the column tests, pH values were determined after collecting the effluent samples, before performing the AA analysis. In column tests, the pH decreases as the pore volume increases. For hydrocarbons pH range was between 6.17 and 7.94.

CHAPTER 6

Summary , Conclusions and Recommendations

6.1 Summary

The present study shows that soil washing with surfactants is an efficient method for removal of soil contamination. In this study, the remediation based on an artificially contaminated soil and washing with surfactants and a chelating agent were explored. The study was based on laboratory batch and column experiments. The experimental results showed that the, surfactants were effective in removing both heavy metals and hydrocarbons, when present together. Based on the present results the following conclusions can be drawn.

6.2 Conclusions

1. For artificially contaminated soil samples containing Zn(II) and Cu(II) SDS removed 1.40% of Cu(II) and 32% of Zn(II) respectively. These results confirm the large affinity of Cu(II) to bind strongly with soil particles and resist desorption. On the other hand Zn(II) has less affinity to soil particles hence it can be easily removed from the soil particles.

2. In batch tests EDTA was most efficient than surfactants in removing heavy metals. 77.36% of Zn(II) and 57.88% of Cu(II) were removed by EDTA.

3. Column experiments confirmed that the combination of 5mM EDTA and 10mM SDS is an efficient washing solution for removal of Zn(II) and Cu(II). This combination of washing liquids could remove 96.6% of Zn(II) and 74.39% of Cu (II) respectively. The removal efficiency increased as the pore volume increased in the column.

4. . In batch tests, distilled water could remove 9.34% of Xylene and 10.64% of Ethyl benzene respectively. And also in batch tests, 10mM SDS was the most effective extractant for both Xylene and Ethyl benzene.

5. Lastly in batch tests, 22.9% of Xylene and 24% of Ethyl benzene were removed from soil with SDS.

6. In column tests, at the flow rate 4 ml/min, maximum percentage of Xylene removed was 99.9%. Removal efficiency decreased as the flow rate increased because of shorter residence time between the contaminant and surfactant.

6.3 Recommendations for future work

1. Removal efficiency of Ethyl benzene in the presence of heavy metals should be investigated.

2. The use of surfactant to remove heavy metals in the presence of HOCs
from naturally contaminated soils should be investigated.

3. The interferences between the Hydrophobic organic compounds and chelating agents can be investigated.

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Appendix A

RESULTS OF BATCH STUDIES

Table A.1 Extraction of metals by SDS

Soil : Liquid 5g/30ml

No.	SDS Concentration mM	Cu(II) removed mg/l	Ratio to Cu(II) removed by water	Zn(II) removed mg/l	Ratio to Zn(II) removed by water	Initial pH	Final pH
1	0	0.25	1	21.42	1	5.9	6.40
2	1	0.289	1.15	25.78	1.20	5.63	6.32
3	4	0.34	1.36	28.20	1.31	5.96	6.65
4	8	0.45	1.8	29.66	1.39	6.12	6.78
5	10	1.93	7.72	39.41	1.85	6.34	6.78
6	16	1.99	7.96	38.99	1.82	6.66	6.89
7	32	1.98	7.92	38	1.77	6.89	7.01

Cu removal efficiency: (0.25mg/l * 0.03L/0.005kg)/850mg/kg*100 = 0.17%

Zn removal efficiency: (21.42mg/l *0.03L/0.005kg)/760mg/kg*100= 16.9%

Table A.2 Extraction of HOCs by SDS

Soil : Liquid 5g/30ml

No.	SDS Concentration mM	Xylene removed mg/l	Ratio to Xylene removed by water	Ethyl-Benzene removed mg/l	Ratio to Ethyl-benzene removed by water	Initial pH	Final pH
1	0	1.56	1	2.55	1	6.3	7.11
2	1	1.95	1.25	3.28	1.29	6.13	7.26
3	4	2.06	1.32	3.85	1.50	6.27	7.36
4	8	2.51	1.60	4.11	1.62	6.35	7.52
5	10	3.84	2.46	5.78	2.26	6.38	7.71
6	16	3.8	2.43	5.70	2.23	6.38	7.95

Table A.3 Extraction of HOCs by Triton X-100

Soil : Liquid 5g/30ml

No.	Tx-100 Concentration mM	Xylene removed mg/l	Ratio to Xylene removed by water	Ethyl-Benzene removed mg/l	Ratio to Ethyl benzene removed by water	Initial pH	Final pH
1	0	1.56	1	2.55	1	6.3	7.11
2	0.1	2.11	1.35	3.12	1.22	6.17	7.24
3	0.25	2.45	1.57	3.78	1.49	6.27	7.39
4	0.5	3.09	1.99	4.97	1.94	6.29	7.67
5	1	3.02	1.93	4.56	1.79	6.85	7.94

Table A.4 Extraction of HOCs by AOT

Soil : Liquid 5g/30ml

No.	AOT Concentration mM	Xylene removed mg/l	Ratio to Xylene removed by water	Ethyl-Benzene removed mg/l	Ratio to Xylene removed by water	Initial pH	Final pH
1	0	1.56	1	2.55	1	6.3	7.11
2	0.1	1.69	1.08	2.73	1.07	6.26	7.23
3	0.25	1.84	1.18	2.99	1.17	6.38	7.38
4	0.5	1.91	1.22	3.12	1.22	6.67	7.49
5	1	1.94	1.24	3.26	1.27	6.81	7.83
6	1.25	2.24	1.43	3.83	1.50	7.05	7.80
7	2.5	2.00	1.28	3.01	0.84	7.12	7.94

Table A.5 Extraction of metals by EDTA

Soil : Liquid 5g/30ml

No.	Surfactant Concentration mM	Cu(II) removed mg/l	Percentage of Cu(II) removed %	Zn(II) removed Mg/l	Percentage of Zn(II) removed %	Initial pH	Final pH
1	5mM EDTA	82	57.88	98	77.36	4.15	3.69

Appendix B

COLUMN TEST RESULTS 1 PORE VOLUME = 100ML

Table B.1 Removal of Xylene from soil column by distilled water.

No	Pore volume	Xylene removal mg/l	Percentage of Xylene removed, %	pH
1	1(1)	0.26(2)	0.04(3)	6.21
2	2(4)	0.36(5)	0.1	6.25
3	3	0.74	0.23	6.32
4	4	2.89	0.74	6.40
5	5	3.26	1.31	6.60
6	6	3.69	1.96	6.93
7	8	4	3.37	7.10
8	10	4.13	4.8	7.14
9	15	7.34	11.28	7.19
10	20	6.47	17	7.25
11	30	5.15	26.09	7.28
12	40	3.65	32.53	7.32

[(100ml * 10^{-3} L/ml * $1^{1\,*}$ $0.26^{(2)}$ mg/l)/(565g* 10^{-3} kg/g * 100.2 mg/kg)] *100 = $0.04^{(3)}$ %, $0.04^{(3)}$ %+[(100ml*10^{-3} L/ml*$2^{(4)}$ -$1^{(1)}$ *$0.36^{(5)}$/ ($565^{*}10^{-3}$ kg/g* 100.2 mg/kg)]*100=0.1%

Table B.2 Removal of Xylene from Soil column by 10mM SDS

Flow rate = 4ml/min

No.	Pore Volume	Xylene removed(mg/l)	Percentage of Xylene removed, %	pH
1	1	0.33	0.058	6.11
2	2	0.36	0.12	6.15
3	3	0.66	0.23	6.22
4	4	4.51	1.03	6.26
5	5	4.99	1.92	6.35
6	6	5.08	2.81	6.49
7	8	5.11	4.61	6.53
8	10	11	8.49	6.58
9	15	14.03	20.88	7.10
10	20	15	34.12	7.16
11	30	17	64.18	7.22
12	40	18.5	96.85	7.40
13	50	1.7	99.85	7.42
14	60	0.1	99.9	7.40

Table B.3 Removal of Xylene from soil column by 10mM SDS

Flow Rate 12ml/min

No.	Pore Volume	Xylene removed(mg/l)	Percentage of Xylene removed ,%	pH
1	1	0.3	0.05	6.20
2	2	0.34	0.11	6.24
3	3	0.56	0.2	6.46
4	4	3.98	0.9	6.53
5	5	4	1.6	7.10
6	6	4.23	2.35	7.15
7	8	4.85	3.31	7.20
8	10	7.69	6.02	7.22
9	15	12.96	17.46	7.26
10	20	13.79	29.63	7.29
11	30	15	56.12	7.44
12	40	12	77.31	7.60
13	50	1.05	79	7.62
14	60	0.15	79	7.69

Table B.4 Removal of Xylene from soil column by 10mM SDS

Flow Rate 40ml/min

No.	Pore Volume	Xylene removed(mg/l)	Percentage of Xylene removed %	pH
1	1	0.28	0.04	6.24
2	2	0.32	0.09	6.28
3	3	0.48	0.17	6.35
4	4	3.62	0.8	6.47
5	5	3.92	1.49	6.62
6	6	3.99	2.19	6.83
7	8	4.55	3.79	6.99
8	10	4.65	5.43	7.21
9	15	7.99	12.48	7.36
10	20	8.32	19.8	7.36
11	30	15	46.32	7.52
12	40	11	65.75	7.85
13	50	1.45	68	7.95
14	60	0.25	68	7.99

Table B.5 Removal of Cu(II), Zn(II),Xylene from soil column by 10mM SDS Flow Rate 12ml/min

No.	Pore Volume	Cu(II) removed mg/l	Percentage of copper removed, %	Zinc removed mg/l	Percentage of zinc removed,%	pH
1	1	12.78	0.26	50	1.16	6.24
2	2	13.56	0.54	48	2.27	6.34
3	3	15.8	0.86	37.09	3.13	6.48
4	4	21.03	1.29	48	4.25	6.49
5	5	24.16	1.79	53	5.48	6.53
6	6	25.93	2.32	57.98	6.83	6.58
7	7	13.86	2.6	60	8.22	6.58
8	8	11.53	2.84	59	9.59	6.60
9	9	10.72	3.06	46	10.66	6.61
10	10	10.14	3.27	31.08	11.38	6.62
11	15	10.09	4.32	17.43	13.4	6.66
12	20	9.89	5.34	11.77	14.77	6.70
13	25	9.03	6.28	9.12	15.83	6.78
14	30	8.45	7.15	7.21	16.6	7.32
15	40	7.15	8.6	5.34	17.07	7.12
16	50	7	10.05	3.27	17.83	7.22
17	60	6.84	11.47	3.01	18.53	7.26

Table B.6 Removal of Xylene from soil column by 10mM SDS in the presence of Cu(II) and Zn(II)

Flow Rate 12ml/min

No.	Pore Volume	Xylene removed, mg/l	Percentage of Xylene removed,%	pH
1	1	0.22	0.03	6.24
2	2	0.26	0.07	6.34
3	3	0.37	0.13	6.48
4	4	3.27	0.7	6.49
5	5	3.64	1.34	6.53
6	6	4	2.04	6.58
7	8	4.11	3.49	6.62
8	10	5.62	5.47	6.66
9	15	10.85	15.05	6.70
10	20	11	24.7	6.78
11	30	9.67	41.78	7.32
12	40	9.56	58.66	7.12
13	50	0.11	58.85	7.20
14	60	0.1	59	7.26

Table B.7 Removal of Zn(II) from soil column by 10mM SDS+ EDTA

Flow rate = 40ml/min

No.	Pore Volume	Zinc removed(mg/l)	Percentage of zinc removed,%	pH
1	1	198	4.611	6.00
2	2	143	7.99	6.38
3	3	137	11.18	6.56
4	4	121	13.99	6.86
5	5	102	16.36	6.89
6	6	95	18.57	6.92
7	7	82	20.47	6.71
8	8	73	22.17	6.64
9	9	185	26.47	6.6
10	10	180	30.66	6.1
11	15	125	45.21	6.9
12	20	110	58.01	6.71
13	25	82	67.55	6.12
14	30	73	76.05	5.74
15	35	59	82.9	5.48
16	40	42	87.7	4.52
17	45	38	92.12	3.34
18	50	35	96.19	3.07
19	55	2.12	96.4	2.50
20	60	2	96.6	2.64

Table B.8 Removal of Zn(II) from soil column by 10mM SDS + EDTA

Flow rate = 12ml/min

No.	Pore Volume	Zinc removed(mg/l)	Percentage of zinc removed	pH
1	1	175	4.07	4.12
2	2	130	7.1	5.28
3	3	121	9.91	6.83
4	4	116	12.61	6.15
5	5	99	14.91	6.1
6	6	86.5	16.93	6.00
7	7	78.04	18.74	5.46
8	8	62.71	20.2	4.52
9	9	172	24.2	4.39
10	10	166	28.06	3.94
11	15	110	40.86	3.27
12	20	98	52.27	3.30
13	25	74	60.88	3.12
14	30	68	68.74	3.21
15	35	51	74.7	3.15
16	40	37.5	79.08	2.95
17	45	31	82.68	2.69
18	50	28.6	86.01	2.42
19	55	26	89.03	2.16
20	60	8	89.96	2.04

Table B.9 Removal of Zn(II) from soil column by 10mM SDS + EDTA Flow rate 4ml/min

No.	Pore Volume	Zinc removed, mg/l	Percentage of zinc removed,%	pH
1	1	162	3.77	4.54
2	2	126	6.7	5.63
3	3	119	9.47	6.45
4	4	102.5	11.95	6.78
5	5	87.3	13.88	6.1
6	6	74	15.6	6.00
7	7	67.8	17.17	5.45
8	8	53	18.4	4.76
9	9	161	22.14	4.28
10	10	154	25.72	3.95
11	15	96.1	36.91	3.23
12	20	82	46.45	3.28
13	25	63.33	53.82	3.33
14	30	50.07	59.65	3.15
15	35	44.12	64.78	3.09
16	40	36	68.97	2.96
17	45	29.02	72.34	2.85
18	50	27	75.48	2.45
19	55	26	78.5	2.18
20	60	20	80.82	2.06

Table B.10 Removal of Cu(II) from soil column by 10mM SDS + EDTA
Flow Rate 4ml/min

No.	Pore Volume	Cu(II) removed, mg/l	Percentage of Cu(II) removed , %	pH
1	1	21.47	0.44	4.54
2	2	38.67	1.25	5.63
3	3	40.25	2.09	6.45
4	4	44.56	3.01	6.78
5	5	46.37	3.97	6.1
6	6	51.21	5.04	6.00
7	7	53.87	6.16	5.45
8	8	58.88	7.91	4.76
9	9	60	9.16	4.28
10	10	62.01	10.45	3.95
11	15	71.08	18.00	3.23
12	20	75.05	25.66	3.28
13	25	77.25	33.70	3.33
14	30	81.58	42.19	3.15
15	35	79	50.41	3.09
16	40	76	58.22	2.96
17	45	69	65.50	2.85
18	50	36.47	69.29	2.45
19	55	30.12	72.42	2.18
20	60	19	74.39	2.06

Table B.11 Removal of Cu(II) from column by 10mM SDS + EDTA

Flow Rate 12ml/min

No.	Pore Volume	Cu(II) removed(mg/l)	Percentage of Cu(II) removed %	pH
1	1	20.19	0.42	4.12
2	2	35.23	1.15	5.28
3	3	38.13	1.94	6.83
4	4	42.32	2.82	6.15
5	5	45.26	3.76	6.1
6	6	49.59	4.79	6.00
7	7	52.55	5.88	5.46
8	8	56.24	7.05	4.52
9	9	59	8.27	4.39
10	10	61.04	9.54	3.94
11	15	68.12	15.89	3.27
12	20	72.01	22.98	3.30
13	25	74.19	30.47	3.12
14	30	78.72	38.19	3.21
15	35	79.12	46.38	3.15
16	40	73.18	54.61	2.95
17	45	65	61.37	2.69
18	50	49.22	66.49	2.42
19	55	29.01	69.51	2.16
20	60	15	71.07	2.04

Table B.12 Removal of Cu(II) from column by 10mM SDS + EDTA

Flow Rate 40ml/min

No.	Pore Volume	Cu(II) removed, mg/l	Percentage of Cu(II) removed, %	pH
1	1	18.06	0.37	6.00
2	2	22	0.76	6.38
3	3	25	1.28	6.56
4	4	30	1.9	6.86
5	5	33.95	2.6	6.89
6	6	36.05	3.35	6.92
7	7	39.12	4.16	6.71
8	8	42.01	5.03	6.64
9	9	44.68	5.96	6.6
10	10	46.21	6.92	6.1
11	15	47	11.8	6.9
12	20	50.28	17.044	6.71
13	25	58.23	23.1	6.12
14	30	65.32	30	5.74
15	35	70.21	37.3	5.48
16	40	75.02	45.11	4.52
17	45	80	53.4	3.34
18	50	65.24	60.22	3.07
19	55	35	63.86	2.50
20	60	20.11	65.9	2.64