Surfactant Assisted Removal of Copper (II), Cadmium (II), and Lead (II) from a Sandy Soil

A Thesis in the Department

of

Building, Civil and Environmental Engineering

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

Concordia University, Montreal, Quebec, Canada

October, 2006

Library and
Archives Canada

Published Heritage
Branch

395 Wellington Street
Ottawa ON K1A 0N4
Canada

Bibliothèque et
Archives Canada

Direction du
Patrimoine de l'édition

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence
ISBN: 978-0-494-28904-4
Our file Notre référence
ISBN: 978-0-494-28904-4

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

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

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

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

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

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

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

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

Canada

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

ABSTRACT

Surfactant Assisted Removal of Copper (II), Cadmium (II), and Lead (II) from a Sandy Soil

Hesam Shalchian

The role of surfactants in remediation of metal contaminated soils is a subject that has gained considerable scientists attention in many related research fields. In the present study, surfactants with and without a chelating agent are used to remove Cu (II), Cd (II), and Pb (II) from an artificially contaminated sandy soil. SDS (sodium dodecyl sulfate) and AOT (sodium dioctyl sulfosuccinate) are the anionic surfactants. Tx-100 (Triton x-100) is the nonionic surfactant and EDTA (Disodium ethylenediamine tetraacetate) is the chelating agent selected to form the extracting solutions. Batch and column tests were conducted at room temperature ($22^\circ C \pm 2^\circ C$). Batch results indicated that replacing distilled water with SDS can enhance the metal removal rates by a factor of 5.5, 28.8, and 29.1 for Cu (II), Cd (II), and Pb (II), respectively. A combination of SDS and EDTA was found to be an ideal extracting solution for both batch and column tests. In column tests, the mixture was able to remove about 83%, 88%, and 70% of Cu (II), Cd (II), and Pb (II) respectively. This study shows that SDS is an effective extracting reagent. Therefore, it may be considered for in-situ remediation of metal contaminated sites. Results related to competition and interference among metals to get adsorbed or desorbed to sandy soils, are also briefly presented. Lastly, the effect of flow rate and aging of contaminants are discussed.

Acknowledgements

I would like to thank my supervisor Dr. A. S. Ramamurthy for suggesting the research topic. I would like to thank Mr. M.M.Hasan who provided useful suggestion and help during the experiments. The technical assistance of Mr. N. Lang Vo is also appreciated. Finally, I wish to express my appreciation to my parents who dedicated their whole life for my education, and also to my wife, Pouneh, for her support and understanding during the hours I devoted to this research.

Table of Contents

Chapter 3: Fate and transport of heavy metals in soils....24

Chapter 4: Material and methods....35

List of Figures

List of Tables

List of abbreviations

AA	Atomic Adsorption Spectrophotometer
AOT	Aerosol-OT, Sodium Dioctyl Sulphosuccinate
CEC	Cation Exchange Capacity
CMC	Critical micelle Concentration
DTPA	Diethylenetriaminepentaacetate
EDTA	Ethylenediaminetetraacetic Acid
EDTA salt	Disodium Ethylenediaminetetraacetate
EPA	Environmental Protection Agency
HLB	Hydrophilic-Lipophilic Balance
NAPL	Non-Aqueous Phase Liquid
NTA	Nitrilotriacetic Acid
PAHs	Polynuclear Aromatic Hydrocarbon
PCBs	Polychlorinated Biphenyls
PV	Pore Volume
SDS	Sodium Dodecyl Sulphate
Tx-100	Tritron X-100

List of symbols

C	Chemical concentration in the soil solution, M/L^3
D	Diameter, L
F	Section area, L^2
H	Water head, L
i	Hydraulic slope, L/L
J	Flux density, M/L^2T
K	Hydraulic conductivity
K_f	Distribution coefficient, L^3/M
K_d	Linear distribution coefficient, L^3/M
L	Column length, L
Q	Average flow rate, L^3/T
Q	Volume of the collected effluent, L^3
q	Flow rate, L^3/T
S	Amount of solute retained by soil, M/M
$S_{\max}$	Maximum sorption capacity, M/M
V	Water Velocity, L/T
W_{sat}	Water saturated weight, M
W_{dried}	Dried weight, M
ω	Bond strength of molecules on the matrix surface, L^3/M

Chapter 1

Introduction

1.1 Introduction

Heavy metals are defined as a group of nearly 70 metals in the periodic table of elements with the atomic densities greater than 5g/cm^3 [Yaron, 1984; Cameron, 1992]. Some of these metals are essential for the living organisms of plants and animals while the others do not seem to be crucial. At concentrations above a threshold all Heavy metals are a source of concern for their potential reactivity, mobility and toxicity in the soil [Selim, 1997]. Heavy metals in the usual terminology also refer to twelve metals most commonly used and discharged as waste by industry: cadmium, chromium, cobalt, copper, iron, mercury, manganese, molybdenum, nickel, lead, tin, and zinc. In the EPA list of priority pollutants, those which may cause the greatest hazard to humans, animals and plants are considered to be cadmium, copper, lead, mercury, nickel, and zinc [Cameron, 1992]. Prior studies have indicated that industrial and urban aerosols, liquid and solid waste from animals and humans, mining wastes, industrial and agricultural chemicals are the main sources of heavy metals contaminants [Alloway, 1990; Cameron, 1992]. Three of most hazardous heavy metals (e.g. copper, cadmium and lead) have been chosen for this study. Thermal extraction of volatile metals, solidification/stabilization, chemical oxidation and soil washing are various soil remediation techniques that are commonly used [Wang, 2003]. Several studies have been done on the enhanced remediation of contamination from soils using surface active agents (surfactants). Surfactant molecules have a specific structure that contains both hydrophilic and lipophilic moieties. One special characteristic of these molecules is their ability to form aggregates which are known as micelles. Surfactants enhance the removal of heavy metals by various mechanisms such as reducing the interfacial tension and hence, increasing mobilization through solubilization [Sabatini et al, 1995].

Copper is an important element for plants and animals which can be adsorbed by both organic mater and clay minerals of the soil. Soil solutions with concentrations higher than 1 ppm are toxic to most plants. Solutions with concentrations higher than 20ppm are toxic to animals and 1ppm is a safe limit for drinking water. Copper concentration in various types of soil normally does not exceed 20 ppm [Cameron, 1992]

Cadmium is highly toxic to plants and animals and there is no biological need for this metal. Its chronic accumulation in the kidney may interfere with its function. Normally, soils are expected to contain cadmium concentrations of less than 1mg/kg. Cadmium has a higher mobility in soils than many other heavy metals including Pb and Cu [Watts, 1997; Alloway, 1990].

Lead has a long residence time and a low mobility in soil media and mostly adsorbs on the organic matter and can replace some metals from the soil adsorption sites. Natural soils can contain up to 10 ppm of lead. This metal can cause diseases in animals and mental impairment in young children. Hence, it is considered to be a serious health hazard. There is no evidence for the essential role of lead in the metabolism [Alloway, 1990; Cameron, 1992].

The present study evaluates the surfactants potential to enhance the remediation of sandy soils contaminated by Cu (II), Cd (II) and Pb (II). Both batch and column tests were conducted to investigate the transport and sorption/desorption behavior of these three heavy metals. The effect of competition and interaction of these metals were also studied briefly. Two anionic surfactants (sodium dodecyl sulfate (SDS) and sodium dioctyl sulfosuccinate (AOT)), a nonionic surfactant (Tx-100) and a chelating agent ethylenediaminetetraaacetic acid (EDTA) were used as extracting agents.

1.2 Thesis contents

This thesis consists of the following six chapters:

Chapter one gives an introduction to the subject studied and an overview of the thesis content as well as the study objectives.

Chapter two discusses heavy metals and their origins, remediation techniques of metal-contaminated soils, surfactants and their uses and briefly reviews previous studies on surfactant washing techniques.

Chapter three gives an overview on fate and transport of heavy metals in soils and reviews the previous studies related to this subject.

Chapter four discusses the material and experiment methods and conditions which were used in this study.

Chapter five provides a discussion and interpretation of batch and column tests results.

Chapter six provides the summary and conclusion of the study and recommendations for future work.

1.3 Research objectives

The overall objectives of this study are listed below:

1- Determine an optimal soil washing solution to remediate the Cu (II), Cd (II) and Pb (II) from an artificially contaminated sandy soil (98% sand and 2% bentonite) by conducting both batch and column tests.

2- Discuss the mechanism of surfactant enhanced extraction of Cu (II), Cd (II) and Pb (II) from contaminated soils.

3- Briefly investigate the effect of competition and interaction among Cu (II), Cd (II) and Pb (II) in the adsorption/desorption process.

4- Briefly note the effect of contaminant aging and the rates of flow on the metal removal process.

Chapter 2

Literature review

2.1 Soils

Soils can contain all three phases of matter (solid, liquid and gas). They are diverse in composition and behavior. The solid phase consists of various size mineral particles and organic matter [Yaron, 1996]. Soil minerals range from very fine particles of clay to coarse materials such as gravel and stone (Table 2.1).

Spills or direct contact with contaminants are the main sources of soil contamination. Contamination exists in three forms in the soil matrix: solubilized contaminants in the soil moisture, adsorbed contaminants on soil surfaces, and contaminants fixed chemically as solid compounds. The chemical and physical properties of the soil will influence the form of the metal contaminant, its mobility, and the technology selected for remediation [Gerber et al., 1991, Evanko & Dzombak, 1997].

Among physical characteristics of soils, the arrangement of solid minerals is a matter of concern and it directly affects the movement and transport of liquids and gases. This arrangement determines the pore volume of the soil. Organic matter content of the soil can significantly influence some of soil physical properties such as the soil's infiltration rate, water-holding capacity, permeability, aggregate stability and consistence [Pierzinski, 2005].

Major chemical properties of soils are mineral solubility, pH, ion exchange, buffering effects and nutrient availability which can be determined by the quantity of clay minerals and organic matter content of the soil. Metal solubility in soils is influenced by chemical properties such as pH, cation exchange capacity (CEC), and complexation /chelation with organic matter [Evanko & Dzombak, 1997].

Table 2.1 Classification of Soil Particles (U.S. Department of Agriculture system)

Soil Particles	Diameter (mm)	comparison
Stones	>254	>10 in.
Cobbles	75 – 254	3 – 10 in.
Gravel	2 – 75	0.08 – 3 in.
Very coarse sand	2.0 – 1.0	Thickness of a nickel
Coarse sand	1.0 – 0.5	Size of pencil lead
Medium sand	0.5 – 0.25	Salt crystal
Fine sand	0.25 – 0.1	Flat side of a book page
Very fine sand	0.10 – 0.05	Nearly invisible to the eye
Coarse silt	0.05 – 0.02	Root hair
Medium silt	0.02 – 0.01	Nematode
Fine silt	0.01 – 0.002	Fungi
Coarse clay	0.002 – 0.0002	Bacteria
Fine clay	<0.0002	Viruses

[Soils and Environmental Quality, Pierzynski, 2005]

Soil organic matter is defined as the nonliving and heterogeneous mixture of products resulting from microbial and chemical transformation of organic residues. Normally a small part of the soil solid appears as organic matter. However, it has a key role in defining the physical, chemical and surface properties of the soil material [Yaron, 1996]. Soil organic matter can sorb heavy metals such as lead, cadmium and copper and prevent the contamination of both surface and ground water. There are many benefits of soil organic matter but beyond the allowable concentration limits, heavy metals in the soil can be toxic to plants and animals [Pierzinski, 2005].

2.2 Heavy metals

Heavy metals are widely used in industrial, agricultural and military purposes. This results in dispersing theses elements in a wide range and various forms in the environment. Mining, extraction and purification of these metals may also cause environmental problems and concerns [Roundhill, 2001].

Major sources of heavy metal contaminants include the following:

(1) Industrial and urban aerosols, such as those created by fuel combustion, metal ore refining and other industrial processes.

(2) Liquid and solid wastes from animals and humans.

(3) Mining wastes.

(4) Industrial and agricultural chemicals.

(5) Industrial solid wastes resulting from off-specification products, spills, processing wastes, and hazardous by-products.

Plants which are growing on contaminated sites may uptake these heavy metals which were added to the soil. This causes the entry of metals into the tissues of plants and subsequently into the body of humans and animals. Heavy metal contaminated soil can produce apparently normal crops that may be unsafe for human or animal consumption [Cameron, 1992].

Heavy metals in soils can be present in various physicochemical forms. The toxicity level of existing metals is determined by their concentration, soil solution and exchangeable forms. The chemical behavior is controlled by retention and release reactions of the solute and soil matrix. The sorption behavior of most heavy metals is influenced by soil properties such as pH, organic matter, clay and amorphous hydrous oxide content, and cation exchange capacity [Wang, 2003; McBride, 1989].

According to potential reactivity and mobility of heavy metals in the soil environment, they can be involved in a series of chemical and biological reactions such as oxidation – reduction, precipitation – dissolution, volatilization, and surface – solution phase complexation [Selim et al, 1997]. Although guidelines and regulatory controls have been provided for waste water and sewage sludge, still long term effects of these wastes on soil health, soil quality and crop productivity has remained unclear [Ahmad, 2005].

2.2.1 Copper

Copper (Cu) falls in IB group of the periodic table of elements. It has an atomic number of 29 and a molar mass of 63.5g. Cu is reddish colored with a metallic luster and is malleable, ductile and is a good conductor of heat and electricity. Copper sulfide and oxide ores are primary sources for producing copper (Cu). Algicides, chromated copper arsenate (CCA) and copper pipes are also considered as other sources of this metal. Soil solution and chemistry influence the fate and transport of copper to ground- water systems. Soluble forms of copper in aerobic and alkaline systems include $CuCO_3$, the cupric ion, Cu^{2+} and hydroxide complexes such as $CuOH^+$ and $Cu(OH)_2$. In anaerobic systems and in presence of sulfur CuS will form. Sorption of copper to mineral surfaces in the soils reduces the metal mobility. The most toxic species of copper is cupric ion Cu^{2+} [Dzombak and Morel, 1990].

Copper has a relatively low mobility in soils because it has a high tendency to form complexes with organic compounds of low molecular weight. Copper can be release in both monovalent and divalent states. This depends on the aerobic or anaerobic conditions of soil organic matter decomposition. Copper has a shorter retention time than lead because of the preferential uptake by plants. The normal range of copper in leaf tissues is 5 – 30 ppm, while the concentration of 20 – 100ppm can be toxic. Surface soils have high capacities for copper accumulation. The average range is 2 – 100ppm. Agricultural copper-containing materials such as fertilizers, pesticide sprays, agricultural or municipal wastes and industrial emissions are the main sources of soil contamination [Cameron, 1992]. While the average human diet provides 1 – 5 mg Cu/day, excessive amounts of copper accumulation in the liver may cause Wilson's disease [Li, 2004].

2.2.2 Cadmium

Cadmium (Cd) belongs to Group IIB of the periodic table with an atomic number of 48 and a molar mass of 112g. In the pure form, cadmium is a silver-white malleable material [Watts, 1997]. Cadmium is one of the most toxic heavy metals to human and animal health. Food plays the most important role of cadmium entry into the body. Exposures to CdO fumes and tobacco smoking are also other cadmium sources. Due to the very long half-life of cadmium (15-1100 years) in soils, it has been considered as a long-term environmental problem and concern. Many countries have restricted the cadmium use or are planning to do so. Almost all of them have pollution legacy for the various sources of cadmium. Maximum tolerable human uptake of this metal is about 70 μg/day and excessive uptakes result in chronic accumulation and dysfunction in kidneys [Alloway, 1990]. Sulfide ores of lead, zinc and copper can also produce cadmium as a mining by-product. Plating operations and disposal of cadmium-containing wastes are some sources of cadmium contamination. Cadmium-containing wastes include waste from alloys, fungicides, enamels, batteries, pigments, plastics, old motor oil, textile manufacturing, electroplating and rubber. Sewage sludges and some phosphate fertilizers can also be important sources of soil cadmium contamination [Evanko & Dzombak, 1997].

The most common forms of cadmium include Cd^{2+}, cadmium-cyanide complexes, $Cd(OH)_2$ and $CdCO_3$ [Smith et al., 1995]. In reducing conditions and in the presence of sulfur, CdS will form. Solubility of cadmium varies with pH and other chemical factors. Above pH 7.5, cadmium is not readily mobile in soils. It has the highest mobility in the acid soils at pH 4.5 to 5.5. Electroplated coatings on fabricated steel and cast iron parts for corrosion protection are the principal uses of cadmium [Cameron, 1992].

2.2.3 Lead

Lead (Pb) is a member of Group IVB of the periodic table with an atomic number of 82 and a molar mass of 207g. Pb is a dense blue-grey colored metal. This metal has a long residence time in the soils and due to low solubility and freedom from microbial degradation, it is considered to be a long term environmental problem and concern [Aloway, 1990]. Metal smelting, lead battery manufacturing, pigment and chemical manufacturing, and lead-contaminated wastes are primary industrial sources of lead. Different existing forms of lead include lead oxides and hydroxides and lead metal oxyanion complexes. Pb (II) is the more common and reactive form of the lead that forms mononuclear and polynuclear oxides and hydroxides [Smith et al., 1995].

Lead mobility in the soils is limited by adsorption, ion exchange, precipitation and complexation with sorbed organic matter. It is considered to be the least mobile among the heavy metals. It has the ability to replace potassium, barium, strontium and calcium in soil minerals and adsorption sites. More lead has been found in organic soils, thus the organic matter content of the soil can determine the metal migration [Evanko & Dzombak, 1997].

Natural soils can uptake up to 10 ppm of lead. Lead may cause diseases in animals and human such as mental impairment in young children. Contamination can occur by accidental ingestion of contaminated soil, and crops and grass consumed by animals. There is no significant plant uptake for this metal and the level in various plants range from 0.5 to 3 ppm [Cameron, 1992; Alloway, 1990].

2.3 Remediation techniques for metal-contaminated soils

Selecting an appropriate technique of remediation for a specific site is influenced by different physical and chemical forms of the metal contaminant in the soil. The physical characteristics of the site and also types and level of contamination should be obtained accurately to determine an optimum and cost-effective remediation technique [Evanko & Dzombak, 1997].

Remediation technologies of metal-contaminated soil can be classified into five major techniques [LaGrega et al., 1994]: isolation, immobilization, toxicity reduction, physical separation and extraction (Fig. 2.1)

2.3.1 Isolation

Isolation technologies attempt to keep the contamination in a specific area and prevent their transport in the soil. These techniques prevent further contamination of groundwater. It may be an appropriate option when the other remedies are not physically and economically feasible for the site. Capping and subsurface barriers are two most common examples of this method.

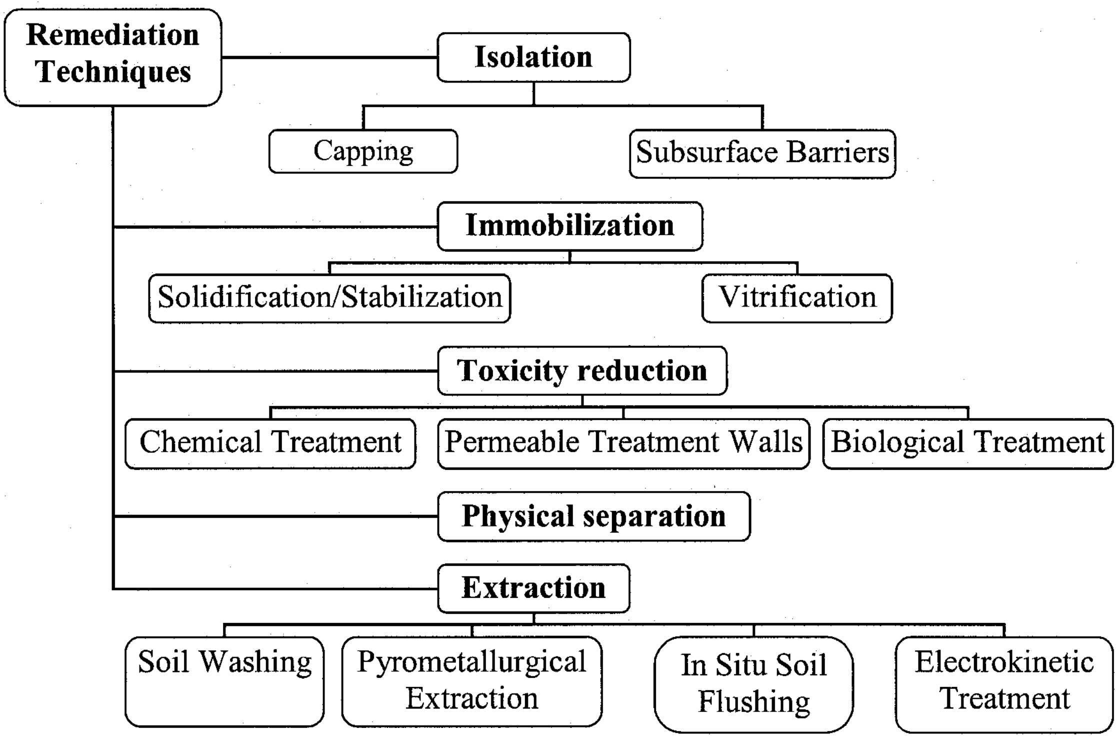


Fig. 2.1 Remediation techniques

2.3.2 Immobilization

Immobilization can be done by reducing physical contacts between the contaminants and surrounding groundwater. There are also chemical methods to make the contaminants more stable and reduce the dissolution in the groundwater. Solidification/ stabilization and vitrification are the most commonly selected methods of metal-contaminated soil remediation

2.3.3 Toxicity reduction

Chemical and biological methods are used to change the form of metal contaminants in order to reduce their toxicity or mobility.

2.3.4 Physical separation

Physical separation is an ex-situ method which attempts to separate the contaminant from the rest of the soil matrix. This method is based on particle size, particle density and magnetic properties of contaminant soil. Separation can be done more easily when the metal contamination is mostly adsorbed on the particular size fraction of soil. Various available techniques include screening, classification, gravity concentration, magnetic separation and froth flotation [Evanko & Dzombak, 1997].

2.3.5 Extraction

Extraction is defined as in-situ or ex-situ processes which attempt to separate the contaminant fractions of soil. Separation can be achieved by contacting of an extracting agent solution with the contaminated soil or by electrokinetic processes [Evanko & Dzombak, 1997]. Electrokinetic methods have proved to be useful procedures to remove heavy metals from soils [Electorowicz et al, 2001]. Soil washing and in-situ soil flushing as two common examples of extraction method are described in the following sections.

2.3.5.1 Soil washing

Soil washing is an ex-situ technique that requires soil excavation prior to remediation. The process usually involves adding an extracting agent solution to the soil and collecting the produced leachate that mostly contains fine particles. Large surface area and surface reactivity of fine particles make them appropriate adsorbents for metals. This process results in a clean coarse material and also reduces the volume of the soil that needs further treatment.

Humic content and cation exchange capacity of the soil strongly influence its washability. A soil with particles at least 60% greater than a 63 μm and less than 20 % (wt) organic matter content can be an appropriate candidate for soil washing. EPA indicates that the best candidate should contain more than 50 % (wt) sand/gravel (particle size greater than 200 μm). Soils with lower cation exchange capacity are more easily washable [Hyman & Dupont, 2001].

Addition of complexing agents to the soil may result in organic residues. Since these organic residues are not desirable, recycling and reusing of extracting agents are very important and can influence the cost effectiveness of the entire process [Roundhill, 2001]. Figure 2.2 illustrates the steps of an aqueous soil washing process with size separation equipment.

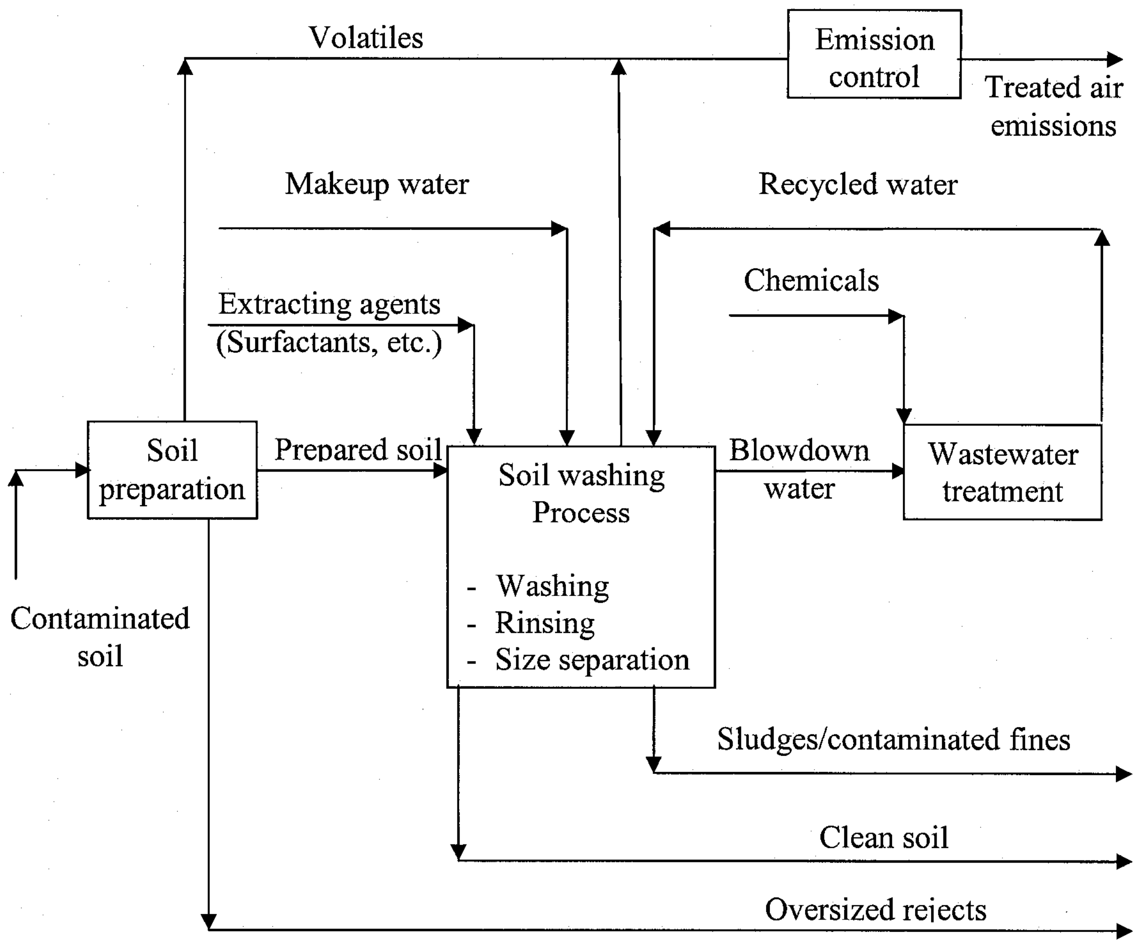


Fig. 2.2 Soil washing process [Hyman & Dupont, 2001]

2.3.5.2 Soil flushing

In-situ soil flushing includes injection and extraction of an aqueous solution for removing the contaminants from the subsurface soil without excavation. In this technique the zone of contamination is flooded with an appropriate washing solution by injecting into or spraying onto the contamination area and the leaching solution is collected and pumped to the surface for further treatments, disposal or recycling. The washing solution increases the mobility and solubility of contaminants and produces a contaminant-bearing fluid which is collected in specific wells. Either water or organic extractants can be used as the washing solution [Smith et al, 1995].

Soil characteristics and uniformity of the soil should be considered because this technique can not be applicable to the soils with high heterogeneity and to sites where hydraulic control of injected water is not possible. This method is applicable for removing hydrocarbons, chlorinated hydrocarbons, metals, salts, pesticides, herbicides, and radioisotopes [Soesilo et al, 1997; Hyman et al, 2001; Anderson, 1993].

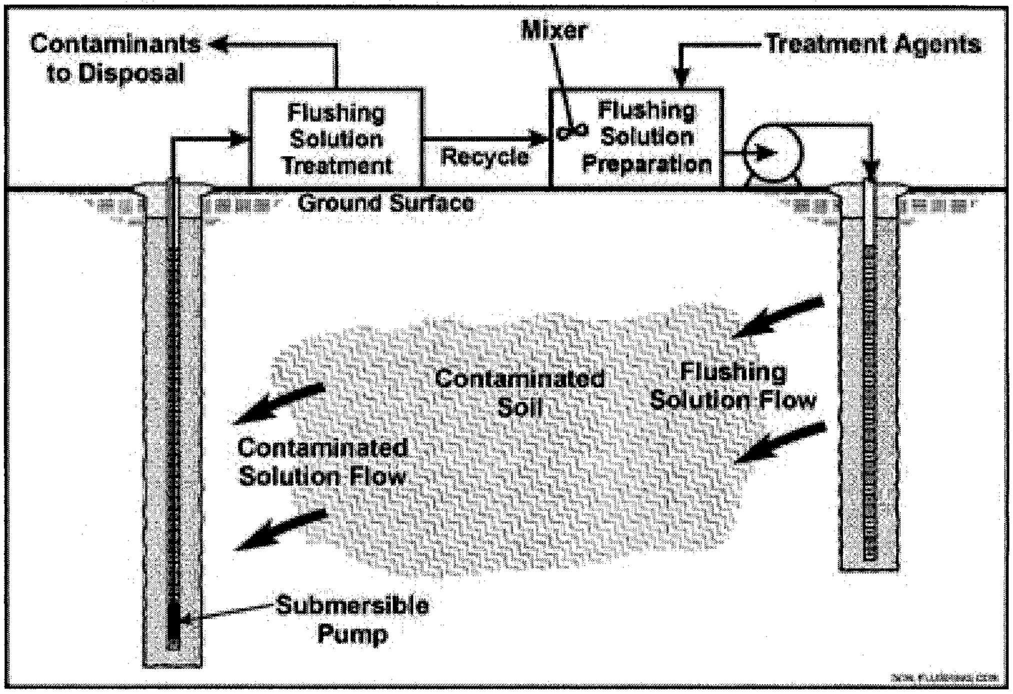


Fig. 2.3 Soil flushing [www.remtech1.com/soil_flushing.htm]

2.4 Surfactants

Surface active agents have molecules with both hydrophilic and lipophilic moieties. Specific molecular structure of surfactants makes them to accumulate in interfaces (e.g. oil-water, air-water, and solid-water). Free energy of the system is minimized when both moieties are in the preferred phase. The term Surface active agent has come from surfactant's ability to alter the interface nature.

According to the nature of their head group, surfactants are classified as anionic, cationic, nonionic and zwitterionic (both cationic and anionic groups). One important characteristic of surfactants is their hydrophilic-lipophilic balance (HLB). Those with high HLBs are more water soluble while those with low HLBs are more oil soluble [Sabatini et al, 1995].

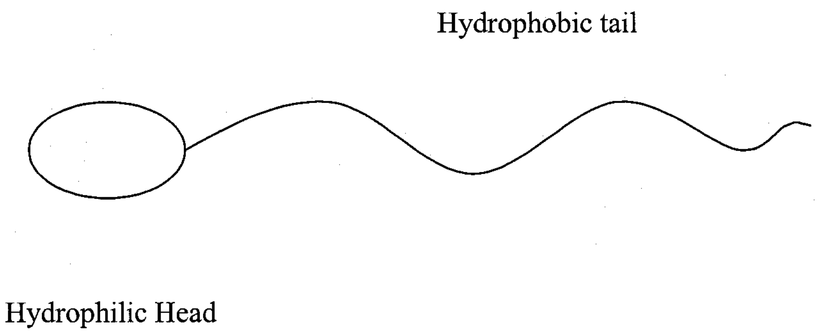


Fig. 2.4 Surfactant molecule

Surfactants have been used in industry as adhesives, flocculating, wetting and foaming agents, emulsifiers and penetrants. They are also used for enhancing oil removal from soils [Mulligan et al, 2001a].

At higher concentrations, surfactants demonstrate a unique characteristic to start forming molecular aggregates known as micelles. This concentration is known as critical micelle concentration (CMC). Micelles have hydrophilic exterior and hydrophobic interior that make them an appropriate adsorption sink for hydrophobic contaminants. This increases the mobility and solubility of contaminants. Surfactants also enhance the removal of contaminants by reducing the interfacial tension (the phases are virtually miscible) [Sabatini et al, 1995].

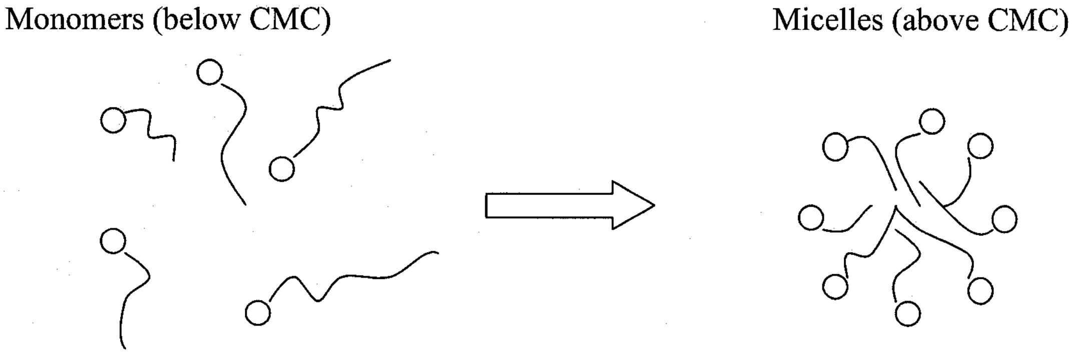


Fig. 2.5 Surfactant micellization

Potential ability of surfactants to enhance the removal of heavy metals from soils has been recently investigated. Replacing extracting and chelating agents such as EDTA with surfactants that are less toxic in the environment is a subject that needs more research and investigation.

2.5 Chelating agents

The term chelate is derived from a Greek root "chela" which means the claw of lobster. Chelating agents can form stable complexes with metal ions. By forming a soluble complex from an insoluble compound, it is possible to remove unwanted heavy metals from soils. One of the most commonly used chelating agents is EDTA (ethylene diamino tetra acetic acid). It contains six donor atoms capable of coordination to a single metal ion and is therefore sexadentate: two basic groups (amino parts) and four acidic groups (acetic ends). EDTA forms very stable complexes with most metals, and some non-metals.

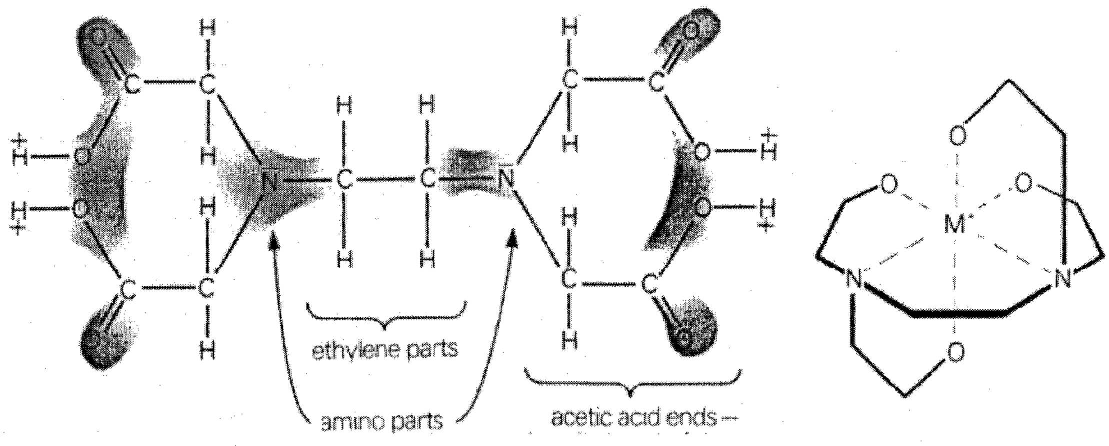


Fig 2.6 EDTA molecular structure

[http://westerhuis-restauratie.nl/pdf/chelating-agents.pdf]

2.6 Previous studies on surfactant and chelating agent enhanced remediation of contaminated soils

Elliot and Brown (1989) compared the washing capability of Nitrilotriaacetic (NTA) and EDTA for extracting Pb from a highly-contaminated soil collected from a battery recycling facility. This study showed the limitations of NTA as a chelating agent and noted EDTA to be a strong and favorite complexing agent.

Cline and Reed (1995) used 6 different washing solutions on 8 different lead-contaminated soils from eastern United States. They used batch washing method and found out that HCL and EDTA obtained the best removal efficiencies.

Washing efficiency of Zn (II) form a soil column was evaluated by Davis and Singh (1995) using chelating agents EDTA and DTPA. They considered the effects of ion strength, flow rate and type of zinc concentration on the removal process. The most efficient washing occurred at lower flow rates and form of zinc contamination strongly influenced the extraction efficiency.

Nivas et al. (1996) used both batch and column experiments for identification of an optimum surfactant/chelating agent solution to remediate chromium contaminated soil. Results demonstrated that surfactants can enhanced the removal 2-2.5 times greater than water and chelating agents alone can enhance the extraction 3.7-5.7 greater than surfactants. A combination of both exhibited very high removal efficiencies.

Reed et al (1996) conducted a flushing test on a sandy loam soil contaminated with Pb (II). They used different washing solution of 0.1N HCl, 0.01M EDTA, and 1 M $CaCl_2$. Pb (II) removal efficiencies by EDTA were 85%, 100%, and 78% respectively. This study introduces EDTA as a good candidate for metal-contaminated soil flushing. However, adverse health effects and recycling and reusing problems of EDTA limit its usage.

Doong et al. (1998) investigated the enhancing remediation of cadmium-contaminated soil using anionic, nonionic and cationic surfactants and chelating agents. They also studied the effect of pH variation on desorption efficiencies of heavy metals. They found that anionic and nonionic surfactants can increase the extraction of cadmium, lead and zinc. However, cationic surfactants decrease the desorption efficiencies. Below CMC concentrations, desorption efficiencies were related linearly to surfactant concentrations, and above CMC they remained relatively constant. They found that cationic surfactants are the most effective at acidic conditions and that increasing the pH can decrease surfactant extracting capability. Addition of EDTA can significantly enhance the remediation of heavy metals. The desorption efficiency was in the following order: Cd>Pb>Zn.

A contaminated soil with textural properties of 60% sand 30% silt and 10% clay was tested with chelating solutions of EDTA, NTA, and citric acid to remediate heavy metals by Peters (1999). Batch test results showed that all examined solutions were effective but due to carcinogen properties of NTA, it is not recommended as the washing solution. Several other chelating agents were also examined and they seemed to be ineffective in mobilizing the heavy metals.

Abumaizar and Smith (1999) investigated the removal of cadmium, chromium, lead, and zinc from a silty sand. They conducted batch and column tests and used Na_2EDTA and $Na_2S_2O_5$ and a combination of both as chelating solutions. The study demonstrated higher removal efficiency for the chelating agent Na_2EDTA. It extracted lead over zinc and cadmium but exhibited little impact on chromium removal.

Mulligan et al. (1999.a, 1999.b) investigated the removal potential of biosurfactants such as surfactin, rhamnolipid and sophorolipid for extracting the heavy metals from high contaminated soils and sediments. The study indicated that these surfactants are appropriate candidates for metal complexation. A Similar study on rhamnolipid metal removal potentials was done by Herman et al. (1995).

In another study Mulligan et al. (2001a) described the use of surfactants as additives to help soil washing, flushing and removing the hydrophobic compounds. In this investigation the use of three biosurfactants were evaluated in extracting copper, cadmium and zinc from metal-contaminated soils. A similar study was done on biosurfactant removal of copper and zinc in contaminated sediments [Mulligan et al., 2001b].

Kedziorek and Bourg (2000) used a chelating agent (EDTA) as an extracting agent for removing lead and cadmium of a contaminated soil. They conducted column tests for percolation of the washing agent. This study demonstrated that extraction is enhanced with increasing of EDTA concentration. However, there is also an optimum concentration when clogging happens and permeability decreases.

Shin et al. (2004) investigated the Cd and PCBs desorption from a contaminated soil using a combination solution of a nonionic surfactant and a ligand. They conducted batch tests and found out that increasing ligand concentration and decreasing the surfactant chain length can increase the Cd desorption. Results showed that a surfactant/ligand solution containing a short chain length (n=7.5 or 9.5) surfactant at low concentration and 0.336 molL^{-1} I^{-} can be an optimum solution for simultaneous removal of heavy metals and PCBs.

Lim et al. (2004) studied the extraction of lead, cadmium and chromium from an acidic contaminated soil using three different types of chelating agents. This study demonstrated that in the neutral conditions, chelating agents are capable of removing lead and cadmium very efficiently and rapidly, whereas chromium extraction needs more time and a higher chelating agent concentration. These agents also showed more removal efficiencies compared to HNO_3.

Wang and Mulligan (2004) used rhamnolipid foam technology for removing cadmium and nickel from a sandy soil. They also conducted similar experiments with foam produced from a chemical surfactant (Tx-100) for comparison. Rhamnolipid foam technology showed high efficiency in extracting of Cd and Ni. A similar study on foam technology and removal capabilities of PCP from soil was conducted earlier by Eftekhari (2000).

Li (2004), investigated the surfactant enhanced washing of Cu (II) and Zn (II) from a contaminated sandy soil. The study demonstrated that surfactants increase the removal efficiency 6 times or more for copper and 1.2 to 1.4 times more for Zinc in comparison with distilled water alone. This also showed that addition of a chelating agent (EDTA) to surfactants can considerably improve the metals extracting performance.

Chapter 3

Fate and transport of heavy metals in soils

3.1 Transport mechanisms

There are three major mechanisms for transport of dissolved chemicals in a porous media such as soil. The first mechanism, advection, is due to bulk movement of the solvent (mostly water). The chemical present in the water is passively carried by this advective movement, resulting in chemical transport. The rate of this transportation can be defined in terms of flux density which is the mass of chemical transport through a surface of unit area per unit of time. Flux density (*J*) in advection is related to chemical concentration (*C*) and water velocity (*V*) due to the following equation:

$$J = CV \qquad J\,[\mathrm{M/L^2T}],\ C\,[\mathrm{M/L^3}],\ V\,[\mathrm{L/T}] \qquad \text{(Eq. 3.1)}$$

In the second transport process dissolved chemical moves from one location with higher concentration to another location with lower concentration and does not need a fluid flow. The random motion of chemical molecules called molecular diffusion. Diffusive transport can be well defined by first Fick's law:

$$J = -D(dC/dx) \qquad \text{(Eq. 3.2)}$$

Here, D is the molecular diffusion coefficient $[\mathrm{L^2/T}]$, C is chemical concentration $[\mathrm{M/L^3}]$, and x is the distance over which a concentration change is being considered. Equation 3.2 can also be expressed in three dimensions as follows:

$$\vec{J} = -D\nabla C \qquad \text{(Eq. 3.3)}$$

The third transport phenomenon is a result of any mixing and spreading of chemical molecules in the porous media that is not related to diffusion. This transport is due to nonuniform velocity distribution through the soil pores which is the result of pore size variation along the flow path. This process can be defined by Fick's first law in equations 3.2 and 3.3. In this case D is called as the mechanical dispersion coefficient [Hemond et al, 1994; Selim et al, 1997].

3.2 Sorption and desorption mechanisms

Adsorption can be defined as the concentrating process of materials at interfaces. In soils adsorption occurs more at the solid-liquid interface. Adsorption can be classified as positive and negative. Positive adsorption is the concentration of the solute on the soil colloidal surfaces. In negative adsorption, the solvent is concentrated on the clay surface which results in more concentration of solute in the bulk solution.

It appears that the soil pH and organic content strongly influence the extent of positive and negative adsorption. Adsorption is directly proportional to the surface area and surface charge. Smaller surface areas and smaller charge densities result in smaller amounts of adsorbed material. Adsorption reactions are reversible and are equilibrium reactions. There is a positive heat of adsorption during the adsorption reactions which means that energy is released during the process. Adsorption generally decreases with increasing of temperature because of higher kinetic energy of the molecules at elevated temperatures and their lower tendency to be concentrated [Tan, 1998].

Adsorption of metal ions in the soil porous media can involve different mechanisms including cation exchange, specific adsorption, organic complexation and co-precipitation [Alloway, 1990].

3.2.1 Cation exchange

Most heavy metals are present in the soil in the form of cations. Therefore, their adsorption depends on the negative charge density on the surfaces of particles in the soil. Ion exchange is related to exchange between ions present in the soil solution and the counter ions which are responsible for balancing the surface charge on colloids. There may be some preferences for the adsorbent in selecting one ion over another one, but these exchanges are all reversible, diffusion controlled and stochiometric.Valency and degree of hydration are two important characteristics which control the replacing power of an ion. Ions with higher valency have more replacing power whereas the ones with greater degree of hydration are less eager to replace.

Cation exchange capacity (CEC) is a measure of the proportion of soil colloids whose surface can function as a cation exchanger. The amount of exchanged cations corresponds to the exchange capacity of the soil [Rump&Krist, 1988]. CEC can range from a few to 60meq/100g in mineral soils, but in soils with high levels of organic content it may exceed 200meq/100g. One can define the anion exchange capacity in a similar way [Alloway, 1990].

3.2.2 Specific adsorption

Specific adsorption occurs when metal ions form covalent bonds in contact with lattice ions. Therefore, generally the amount of adsorbed metal ion is much greater than the amount which is expected from CEC of the soil. Heavy metal ions can also diffuse into minerals such as goethite and then adsorption and fixation happens within the mineral particles. This phenomenon can also amplify the amount of adsorbed ions. Both processes are strongly pH dependent [Alloway, 1990].

3.2.3 Co-precipitation

Co-precipitation is a simultaneous precipitation of a chemical agent and an element by any mechanism and at any rate. Clay minerals, hydrous Fe, Mn oxides, and calcites are the common examples of a mixed solid which is formed due to Co-precipitation [Alloway, 1990].

3.2.4 Organic complexation

Solid phase humic substances such as humic acids can adsorb metals by forming chelate complexes. Forming soluble complexes helps the prevention of heavy metals from adsorption and precipitation and increases their mobility [Alloway, 1990].

3.3 Retention models

Retention reactions in soils have a key role in the fate of chemical contaminants such as heavy metals in groundwater. Predicting the transport of heavy metals in the soil needs models which can identify retention and release reactions such as precipitation-dissolution, ion exchange and adsorption-desorption. Soil properties such as texture, bulk density, pH, organic matter, and the type and amount of clay minerals affect the retention and release reactions. Two of the most commonly used equilibrium reaction models are the Freundlich and the Langmuir equations and isotherms [Selim et al, 1997].

3.3.1 Freundlich isotherm

Freundlich equation is one of the oldest nonlinear sorption equations and has been widely used to describe solute retention by soils. The Freundlich equation is

$$S = K_f C^b \qquad \text{(Eq. 3.4)}$$

Where S is the amount of solute retained by soil, in $\mu g g^{-1}$ or $mg kg^{-1}$; C is the solute concentration in solution in $mg L^{-1}$ or $\mu g mL^{-1}$; K_f is the distribution coefficient in $L kg^{-1}$ or $mL g^{-1}$; and parameter b is dimensionless and typically has a value of b<1. Distribution coefficient describes the partitioning of solute species between solid and liquid phases over the interested concentration range and it functions similar to an equilibrium constant in a chemical reaction [Selim et al, 1997].

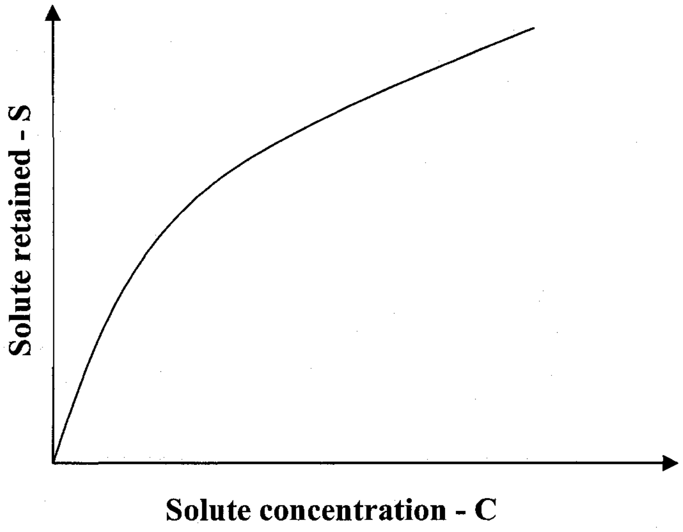


Fig. 3.1 Nonlinear Freundlich retention isotherm

In the case that b = 1 the Freundlich equation is referred as the linear retention equation:

$$S = K_d C \qquad \text{(Eq. 3.5)}$$

Where K_d, is the linear distribution coefficient ($mL g^{-1}$) (Fig.3.2). By taking logarithm Eq. 3.4 changes into

$$\log S = \log K_f + b \log C \qquad \text{(Eq. 3.6)}$$

The log equation gives a straight line or a linear curve (Fig.3.3). $\log K_f$ is the intercept and b represents the slope of the curve or the regression coefficient. In this way a linear presentation of the data in log form is achieved.

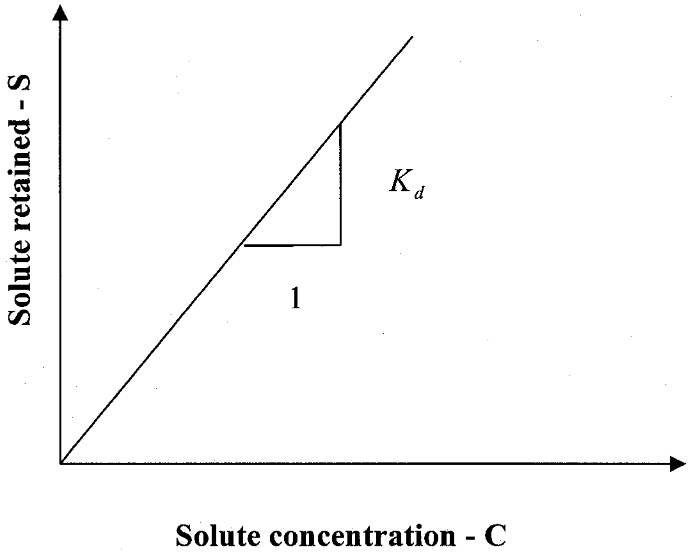


Fig. 3.2 Linear Freundlich retention isotherm

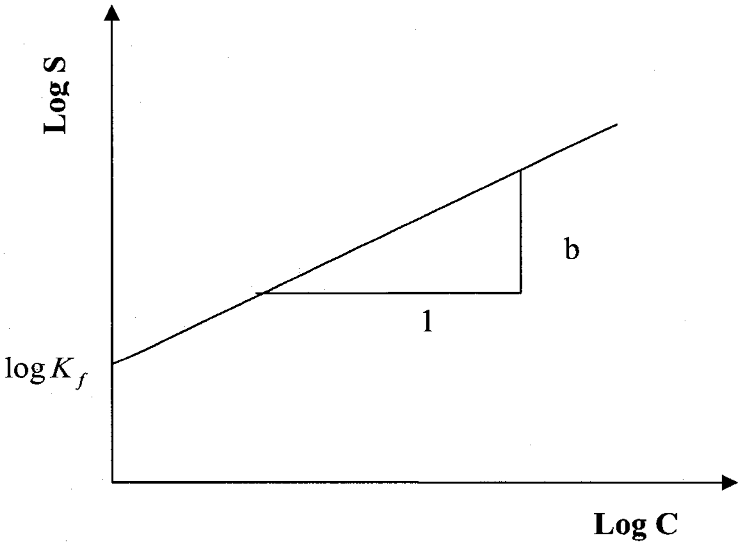


Fig. 3.3 Logarithm presentation of the Freundlich retention equation

3.3.2 Langmuir isotherm

Another method of statistical formulation of retention reactions is given by Langmuir (1918). This equation originally derived for adsorption of gasses by solids when a finite number of adsorption sites in the surface are assumed. The standard form of Langmuir equation is:

$$\frac{S}{S_{\max}} = \frac{\omega C}{1+\omega C} \qquad \text{(Eq. 3.7)}$$

Where ω and $S_{\max}$ are adjustable parameters. Here $\omega\,(mLg^{-1})$ is a measure of bond strength of molecules on the matrix surface and $S_{\max}\,(\mu g g^{-1}$of soil) is the maximum sorption capacity or total amount of available sites per unit soil mass [Tan, 1998, Selim et al, 1997].

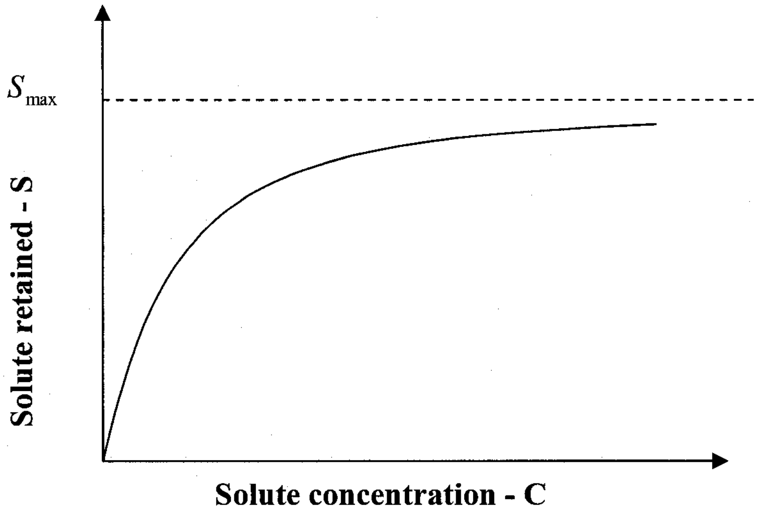


Fig. 3.4 Nonlinear Langmuir retention isotherm

3.4 Previous studies on adsorption-desorption and competitive adsorption of heavy metals in soils

Muralli and Aylmore (1983) studied competitive adsorption during solute transport in soils. They proposed mathematical models and simulations of competitive adsorption and finally they tried to fit the experimental evidences in the proposed simulation models. They stated that adsorption of chemical substances in soils are significantly influenced by competition from other adsorbing chemicals. According to their study both organic and inorganic chemicals are capable of competing for adsorption sites on soils. Factors such as pH, solution concentration, and nature of the competing species influence the competition. They found out that the experimental results are qualitatively similar to those expected from theoretical models.

Harter (1983) studied the effect of pH variation on the adsorption of Lead, Copper, Zinc, and Nickel. Two different soils with varying amount of $Ca(OH)_2$ were used before metal addition. Results demonstrated the key role of pH in adsorption-desorption of heavy metals. Reed et al (1996) also stated that some factors such as pH, soil type and horizon, cation exchange capacity, particle size, natural organic matter, age of contamination and the presence of other organic contaminants can affect heavy metal retention by soils.

Competitive adsorption of Cd, Cu, Pb, and Zn from 0.025 M solutions of $NaClO_4$ onto four soils with different chemical properties was investigated with batch tests by Elliott et al (1986). For two mineral soils the adsorption sequence corresponded to the order of increasing pK for the first hydrolysis product (e.g. $PbOH^+$) which was Pb>Cu>Zn>Cd. For two other soils containing 20 to 40 g Kg^{-1} organic C, the adsorption sequence changed to Pb>Cu>Cd>Zn. This means that organic matter content increased the adsorption of Cd over Zn. They found out that removal of organic matter from soil significantly reduces the CEC and subsequently the adsorption of all heavy metals.

Harter (1992) studied the effect of competing ions on heavy metal sorption by soils. Experiments were conducted with Ca-saturated soil in 0.5 mmol L^{-1} $CaCl_2$ solution, and Ni^{+2}, Co^{+2}, and Cu^{+2} sorption in the case of binary metal-Ca and ternary Ni-Co-Ca or Ni-Cu-Ca systems. Sorption occurred in the order of Cu>Ni, and $Ni \approx Co$. Nickel sorption was equivalent to Ca^{+2} release. This was not true for the other two cases. In the ternary systems, Co^{+2} and 0.016 mmol L^{-1} Cu^{+2} did not decrease the Ni^{+2} sorption. However, at 0.079 mmol L^{-1}, Cu^{+2} causes a decrease in Ni^{+2} sorption. Copper sorption was not affected by Ni^{+2}. On the other hand Co^{+2} decreases with the decrease of Ni^{+2} sorption. Nickel was more eager to compete for Co^{+2} sites than Co^{+2} for Ni^{+2} sites. According to this study neutral pH conditions do not always minimize the metal mobility.

Stability of several isotherms in describing single solute and binary ion exchange of Zn and Cd in two soils was investigated by Hinz et al (1994). Batch experiments were performed for equilibration times of 1 and 14-d and different heavy metal/Ca ratios. According to this study, generally, Langmuir-Freundlich isotherms were suitable for describing single solute isotherms whereas the Rothmund-Kornfeld Ion exchange equation was appropriate for binary data sets (Zn-Ca and Cd-Ca).

Atanassova (1995), studied adsorption-desorption of added copper on two different types of soil, a podzol and a chernozem. High levels of copper adsorption were observed for podzol. A treatment by 0.01 M $CaCl_2$ was performed and copper showed a relatively high mobility, especially in the B-horizon. Clay minerals were the major adsorbent in podzol soil and copper desorption was low in the soil with higher amounts of clay. The Langmuir isotherm seemed to be appropriate for describing copper adsorption.

A study was done by Li et al (1999) on migration of dissolved heavy metals (Cd^{+2}, Pb^{+2}, Cu^{+2}, and Zn^{+2}) in a clay barrier subject to two leachates with different pH values. The conducted numerical model was capable of simulating the processes of water flow, advective-dispersive solute transport, and chemical reactions. Numerical results indicated that with neutral leachate pH, the relative mobility is as following: $Cd^{+2} < Pb^{+2} < Cu^{+2} < Zn^{+2}$. With an acidic leachate, the order changed to $Pb^{+2} < Cu^{+2} < Zn^{+2} < Cd^{+2}$. Thus, pH has a significant effect on Cd^{+2} and Pb^{+2} mobility and a small effect on Cu^{+2} and Zn^{+2}.

Christophi (2000) investigated the competitive adsorption of Cd, Cu, and Pb on goethite. According to this study sorption capacity of metals on goethite surface increased with metal electronegativity Cu>Pb>Cd and the equilibrium constant agreed with hydrated radii Pb< Cu < Cd. A Langmuir isotherm was used to describe the adsorption processes. This study revealed that adsorption competition has a crucial role in the mobility of heavy metals in the environment.

An investigation was done by Tran et al (2002) on desorption of Cd from sand. Batch and flow through tests were conducted for this study and three different pH values (5.5, 6, and 6.5) were used. Results from batch experiments stated that desorbed Cd is much lower than initially adsorbed amount and desorption of Cd can be described appropriately by Freundlich isotherm. In flow through studies in contrast with adsorption, desorption were not significantly affected by pH variations. Changing the pore volume velocity did not show any effect on the desorption coefficient.

Competitive sorption of Pb and Cd on four soils from central Spain was investigated by Serrano et al (2004). Batch tests were conducted and Langmuir equation, ionic strength, and an empirical power function for kinetic sorption were used for characterizing the soil chemical processes and to make comparison between soils, as well as single and binary metal solutions. All soils exhibited greater sorption capacity for Pb than Cd. Sorption of both metals was reduced in the presence of each other. However, it had a greater effect on Cd sorption. Kinetic experiments showed that the Pb sorption was initially faster than Cd sorption from both single and binary solutions. Results demonstrated a significant interaction between Pb and Cd sorption that depends on important soil properties such as clay mineralogy.

Kaoser et al (2004) studied the interaction between Cu and either Pb or Cd in sand-bentonite liners using batch adsorption experiments. Different pH values and different combination of metals were examined. The results indicated that under acidic conditions (pH<6.5), bentonite content, the solution pH, and the presence of Cd or Pb significantly influenced Cu adsorption. Under alkaline conditions, carbonate and hydroxyl precipitation governed the Pb and Cd competition. They found out that Pb and to a lesser extent Cd, significantly increase the mobility of Cu by competing for the exchangeable sites.

Chapter 4

Material and methods

4.1 Introduction

Both batch and column tests were conducted to study the enhanced removal of heavy metals from an artificially contaminated sandy soil. Experimental materials include soil samples, three types of surfactant solution, a chelating agent, target contaminants, Cu (II), Pb (II), and Cd (II) in the form of $CuCl_2$, $PbCl_2$, and $CdCl_2$. Distilled water was used for washing, diluting and making solutions and nitric acid was used for digestion. The material properties as well as the methods used in providing samples and extracting solutions, and the experiment procedures are described in the following sections of this chapter.

4.2 Material properties

4.2.1 Soil samples

The soil used in this study contains 98% sand and 2% bentonite, therefore due to the sand/bentonite ratio and texture triangle it can be classified as a sandy soil. The sand was purchased from Unimin Canada Ltd. and the grain size corresponds to mesh 40. The bentonite was obtained from Sial Inc, Canada and the particle size corresponds to mesh 325. The measured hydraulic conductivity of the mixed soil is 0.0037 ± 0.00015 cm/s (Appendix A). Table 4.1 demonstrates the typical characteristics of sand and bentonite used for providing the soil samples.

4.2.2 Surfactants and chelating agent

A nonionic surfactant (Tx-100), two anionic surfactant (AOT and SDS), and a chelating agent (EDTA) were used for providing extraction solutions. Since cationic surfactants have a higher adsorption tendency to aquifer material (Mulligan et all, 2001a) and also as anionic and nonionic surfactants appeared to be better candidates for removal of metal cations, cationic surfactants were not used in this study. All the surfactants except SDS and the chelating agent were purchased from Fisher Scientific, Canada. SDS and EDTA were obtained from Sigma-Aldrich, Canada. The properties of these extracting agents are described in the table 4.2.

Table 4.1 Characteristics of sand and bentonite

	CEC (meq/100g) (1)	**organic matter content** (2)	**particle size** (3)
Sand	≈ 0	0.07%	mesh 40(D_m=0.42 mm)
Bentonite	110.5(pH5.9)	2.9%	mesh 325 (D_m=0.044 mm)

(1) Li, 2004;Rump and Krist, 1988

(2) determined by combustion at 550° C

(3) US standard sieve size

4.2.3 Contaminants

Target contaminants were purchased in anhydrous forms of $CuCl_2$ (97%), $PbCl_2$ (100%), $CdCl_2$ (99.1%) from Fisher Scientific, Canada. they were dissolved in distilled water in specific weight ratios to provide the target solutions with determined concentration of Cu (II), Pb (II), and Cd (II). These solutions were used to contaminate the soil samples.

4.3 Experimental procedure

4.3.1 Sand preparation

The amount of organic content of the sand was found to be 0.26% wt by a combustion test conducted at 550 °C. Due to high affinity of metal ions to organic matters this amount was not low enough to neglect the adsorption capacity of the sand. Hence, sand was washed two times with hot and cold water and each time it was dried in the oven at 105 °C for 24 hours. This washing procedure reduced the organic content to 0.07% wt, afterwards, CEC of the sand was assumed to be negligible.

4.3.2 Soil contamination

Metal solutions containing 15mM equal molar concentrations of Cu (II), Cd (II), and Pb (II) were added to the bentonite. This corresponds to weight ratios of 190.5, 337.2, and 621.6 mg/Kg of soil for the contaminants Cu (II), Cd (II), and Pb (II). The solution to bentonite ratio was 1L: 0.1Kg. Afterwards the bentonite was shaken on a wrist action shaker (Burrell, Burrell scientific, USA) at 80 rpm for 24 hours at the room temperature of 22 °C ± 2 °C. The mixture was centrifuged then at 3500 rpm for 30 minutes. The supernatant was collected and filtered for AA analysis and the bentonite was dried in the

Table 4.2 Properties of Tx-100 and EDTA

	Tx-100	**EDTA**
Product name	Triton X-100 (99%)	Disodium ethylenediamine tetra acetate
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$^{(1)}$	-

(1) Edwards et al, 1994

Table 4.3 Properties of SDS and AOT

	SDS	**AOT**
Product name	Sodium dodecyl sulfate (>96%)	Sodium dioctyl sulfosuccinate (96%)
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$^{(3)}$

(2) Mukerjee and Mysels, 1971

(3) Nivas et al, 1996

oven at 105 ° C for 24 hours. Following this the dried contaminated bentonite was stored for 1 month at the room temperature. In the next step, the batch test samples were prepared by adding 4.9 g of sand and 0.1 g of bentonite in a plastic sample tube and mix them well to attain a relatively homogeneous soil.

To measure the concentration of metals present in the soil, the collected supernatant form bentonite contamination was analyzed with the Atomic absorption spectrophotometer (Perkin Elmer AAnalyst 100, Perkin Elmer Inc., Canada). A mass balance equation was used to determine the amount of metal retained in the bentonite and consequently in the soil. In order to verify these data, the soil sample was digested with nitric acid. The AA analysis showed less than 5% deviation between the results of these two methods. The average quantities are presented in table 4.4.

Table 4.4 Soil contamination levels	**concentration in mg/Kg soil**
Cu (II)	162
Cd (II)	324
Pb (II)	587

4.3.3 Batch experiments

Batch experiments were conducted at the room temperature of 22 ° C ± 2 ° C. all soil samples were dried initially at 105 ° C for a minimum of 24 hours. Three different surfactants and a cheating agent (SDS, AOT, Tx-100, and EDTA) were used at different concentrations and combinations to study their effect and removal ability of Cu (II), Pb (II), and Cd (II) from the soil. Distilled water was also used for acting as a control. The batch reactor was a 50 mL centrifuge plastic tube. 5 g (4.9 g sand + 0.1 g bentonite) of contaminated soil was weighed by a digital balance (0.001g) and added to the reactor. Next, 40 ml of solutions were added in various concentrations. The samples were equilibrated on a wrist action shaker at 80 rpm for 24 hours. Afterwards the samples were centrifuged for 20 minutes at 3000 rpm and the supernatant was taken for AA analysis. pH measurements were done to find out the pH variations and their effect during the procedure. All the batch tests were done in triplicate and the reported values exhibit the average concentrations.

4.3.4 Column experiments

Column experiments were conducted at the room temperature of $22^\circ C \pm 2^\circ C$. the experiment set up is illustrated in Fig. 4.1. Plexiglas columns (L = 20.5 cm, D = 4.0 cm) 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 from contaminated sites. Each column contains nearly 450 g of contaminated soil sample which were prepared by mixing 98% sand and 2% bentonite in a large glassware using a plastic spatula. Afterwards, 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 was determined

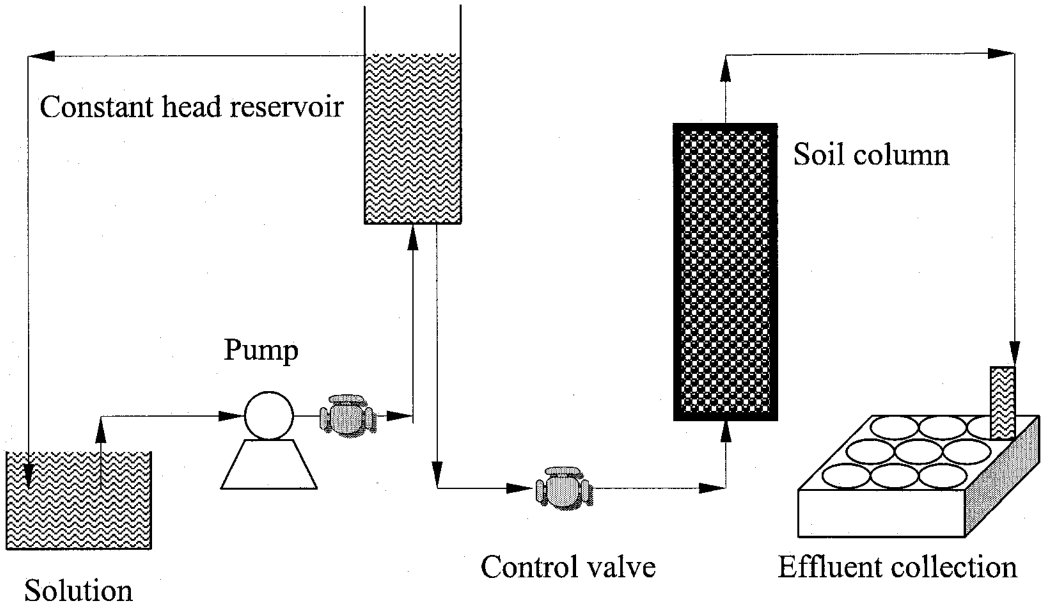


Fig. 4.1 Schematic setup of column experiment

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

$$P_v = (W_{sat} - W_{dried})\, \rho_w^{-1} \qquad \text{Eq (4.1)}$$

Where ρ_w (Kg / m^3) is the density of the water. Pore water velocity can also be calculated from the following equation:

$$V = QL / P_v \qquad \text{Eq (4.2)}$$

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

The most efficient combination of surfactant and chelating agent due to the batch test results were pumped through the soil columns. The effluent is collected manually at specific intervals. All the effluent samples were filtered and prepared for AA analysis.

Finally, the removal efficiency was calculated using the results of AA analysis and initial amount of contamination.

Chapter 5

Results and discussion

5.1 General remarks

Distilled water, two anionic and one nonionic surfactant have been used in this study to investigate their removal effect on Cu (II), Cd (II), and Pb (II). Addition of the EDTA as a chelating agent to improve removal efficiencies has been studied. The results of batch and column experiments, related graphs, and interpretation of the achieved data are described in the following sections of this chapter. All the experiments were conducted at a room temperature of $22^\circ C \pm 2^\circ C$.

5.2 Batch tests

5.2.1 Effects of varying surfactant concentrations

The extraction results of the batch experiments are illustrated in Figs. 5.1 to 5.3, and Tables B.1 to B.3 in appendix B, provide additional data such as pH related to each test. The initial pH values correspond to measured pH of the extracting solution before adding it to the soil sample, and the final values were measured after equilibrating the soil sample and solution for 24 hours. Removed concentrations of Cu (II), Pb (II), and Cd (II) were plotted against the surfactants concentrations.

Results for Tx-100 indicate that desorbed metal concentrations increase with increasing the surfactant concentration, C_s, till the point where C_s = 0.25mM. This concentration is nearly equal to the CMC values reported by Edwards et al (1994) (Table 4.2). Beyond this concentration, metal removal tends to stay relatively constant (Fig. 5.1). It was stated by Doong et al (1996) that due to the high adsorption of Tx-100 on soil particles, more Tx-100 is needed to reach the CMC level in soil-water systems than in water alone.

Results from SDS and AOT tests indicate that the anionic surfactants demonstrate a noticeable increase of metal removal at or near CMC concentrations. Above CMC, the amounts of metal removal do not show any significant variations. A slight decrease in removal rates (Figs. 5.2 and 5.3) may be a result of metal precipitation at higher surfactant concentrations. The precipitated metal does not appear in supernatant which was analyzed for metal concentration.

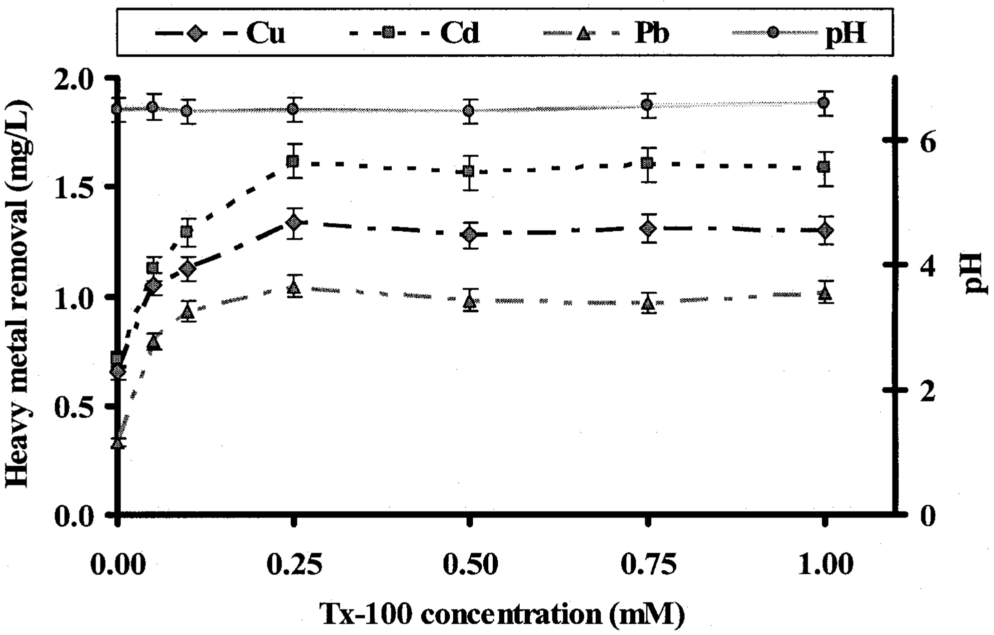


Fig. 5.1 Batch extraction of Cu (II), Cd (II), and Pb (II) from contaminated soil by Tx-100

As stated in chapter 3 surfactants can enhance the removal of heavy metals due to their special molecular structure. This enhancement may be provided by three mechanisms, ion exchange, counter-ion binding, and dissolution-precipitation. Due to surfactant type and the metal ion involved one of these procedures is dominant. In the removal of Cu, Cd, and Pb cations using anionic surfactants (SDS and AOT) counter ion binding and precipitation have played important roles.

Studies have shown that anionic surfactants could bind divalent cations of Cu (II), Cd (II), and Pb (II). With increasing concentrations beyond the CMC, the micelles which trapped the metal cations may commence to precipitate and attach to the soil particles. These precipitates become visible in some cases such as Cu (II). Greenish blue patches were clearly discernible in some sample tubes. Therefore, above CMC concentrations, further increases in metal concentrations in the supernatant should not be expected.

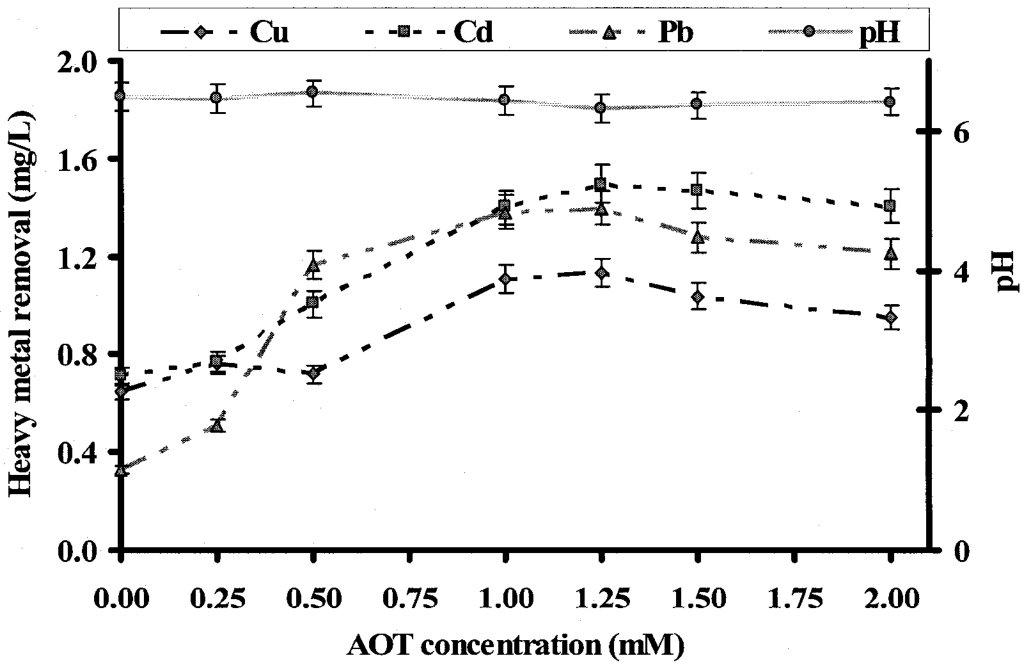


Fig. 5.2 Batch extraction of Cu (II), Cd (II), and Pb (II) from contaminated soil by AOT

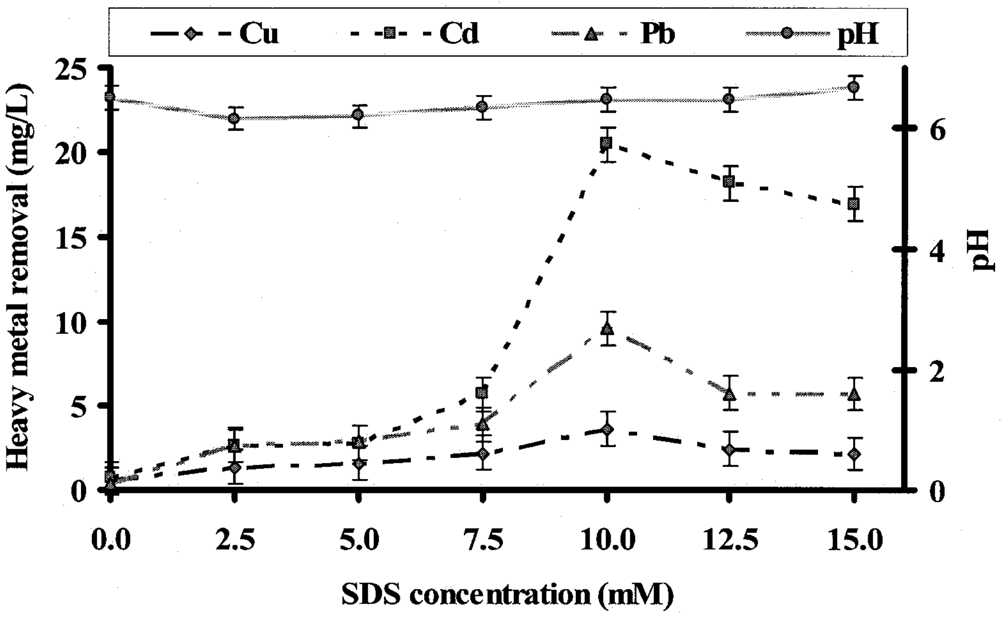


Fig. 5.3 Batch extraction of Cu (II), Cd (II), and Pb (II) from contaminated soil by SDS

5.2.2 Effect of surfactant type

Distilled water as the blank extracting solution removed 0.65mg/L of Cu (II), 0.71mg/L of Cd (II), and 0.33 mg/L of Pb (II) by solubilization (Figs. 5.1 to 5.3). The maximum desorbed concentrations of Cu (II) were 1.33mg/L, 3.60mg/L, and 1.13mg/L by Tx-100, SDS, and AOT solutions respectively. These amounts correspond to 2.05, 5.54, and 1.74 times greater removal of Cu (II) in comparison with distilled water. The highest desorbed concentrations of Cd (II) were 1.62mg/L, 20.46mg/L, and 1.50mg/L by Tx-100, SDS, and AOT amended solutions. These correspond to 2.28, 28.81, and 2.11 times greater removal of Cd (II) in comparison with distilled water. Finally, the maximum desorbed concentrations of Pb (II) were 1.04mg/L, 9.63mg/L, and 1.40mg/L by Tx-100,SDS, and

AOT extracting solutions which correspond to 3.16, 29.18, and 4.23 times greater removals of Pb (II) in comparison with distilled water.

Table 5.1 Summarized results of batch extraction experiments

Surfactant type	**Tx-100**	**SDS**	**AOT**
Optimal concentration (mM)	**0.25**	**10**	**1.25**
Ratio to reported CMC	**1.08**	**1.22**	**1.11**
Max. Cu removed (mg/L)	**1.33**	**3.60**	**1.13**
Ratio to Cu removed by water	**2.05**	**5.54**	**1.74**
Max. Cd removed (mg/L)	**1.62**	**20.46**	**1.50**
Ratio to Cd removed by water	**2.28**	**28.81**	**2.11**
Max. Pb removed (mg/L)	**1.04**	**9.63**	**1.40**
Ratio to Pb removed by water	**3.16**	**29.18**	**4.23**

The CMC of the surfactants reported by other researchers are presented in Table 4.2.These amounts are related to CMC in the water. However, many factors such as pH, temperature, hardness, and additives may influence the observed CMC. There are also some surfactant losses due to their adsorption by the soil. Hence, higher CMCs were noted in the batch experiments where soil was present.

Due to the fact that nonionic surfactants do not carry charges, they can not participate in the ion-exchange and counter-ion bindings processes. Therefore, they are expected to show less removal capability in comparison with anionic surfactants. The results of this study indicated that Tx-100 as a nonionic surfactant can exhibit nearly equal removal efficiency compared to AOT. This may be partially related to the potential of anionic surfactants to precipitate the metal cations from the soil solution. As stated earlier some precipitation was observed in the sample tubes. This could be an appropriate evidence for the stated assumption.

5.2.3 Effect of adding the chelating agent to the surfactant solutions

To study the effect of chelating agent and its combination with surfactants on removal of Cu (II), Cd (II), and Pb (II), batch tests were conducted with chelating agent alone and later in combination with the three surfactants at their optimal concentrations. EDTA was initially selected to provide the chelating agent solution. However, due to its low solubility in distilled water at room temperature, EDTA disodium salt was replaced as a commonly used alternative which had a higher solubility as well as similar complexing characteristics. Fig 5.4 exhibits the extraction efficiencies of Cu (II), Cd (II), and Pb (II) against the various concentrations of the chelating agent.

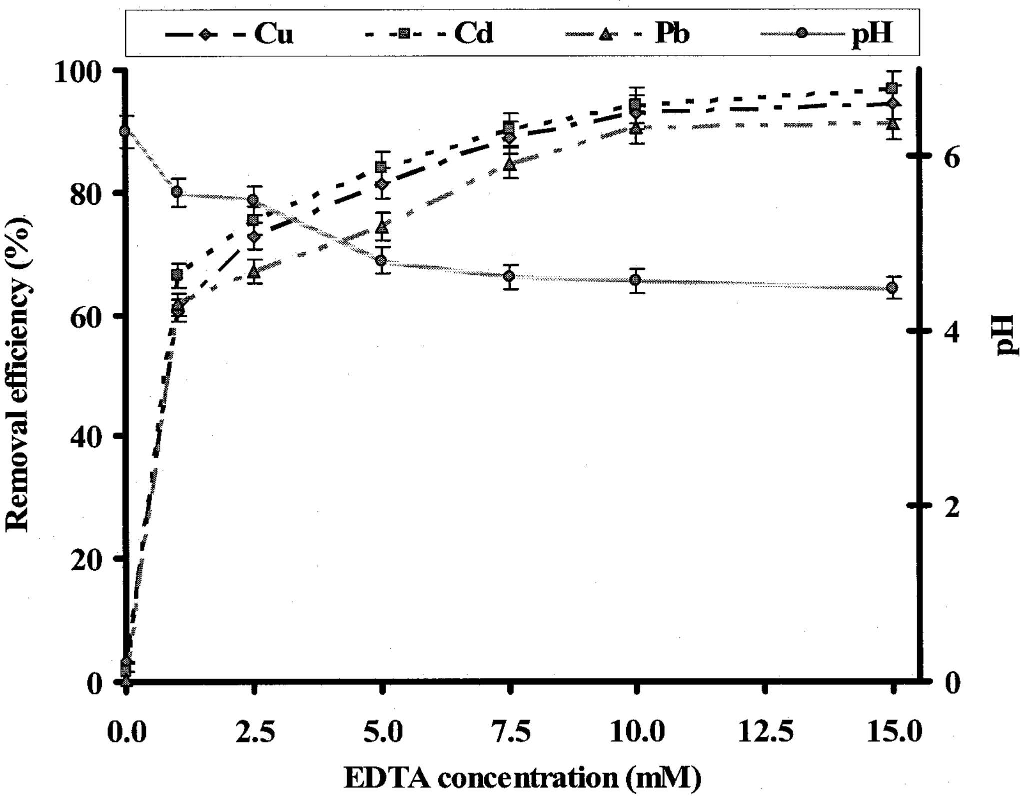


Fig. 5.4 Removal efficiency of Cu (II), Cd (II), and Pb (II) by EDTA

The removal efficiency increased significantly with increasing the concentration of EDTA. Simultaneously, the pH of the solution decreased from 5.60 to 4.50 when EDTA concentration changed from 1mM to 15mM. Increasing the acidic properties of the solution influences the metal solubility and extraction. The EDTA exhibited the following order of increased metal extraction: Cd (II)>Cu (II)>Pb (II).

Figs. 5.5 to 5.7 illustrate the removal efficiencies of Cu (II), Cd (II), and Pb (II) by different combinations of surfactants and EDTA (1mM). The pH values are relevant to each test and related to the final pH during the test. Effect of pH will be discussed in the later sections. Additional data related to these tests are also presented in Table B.5.

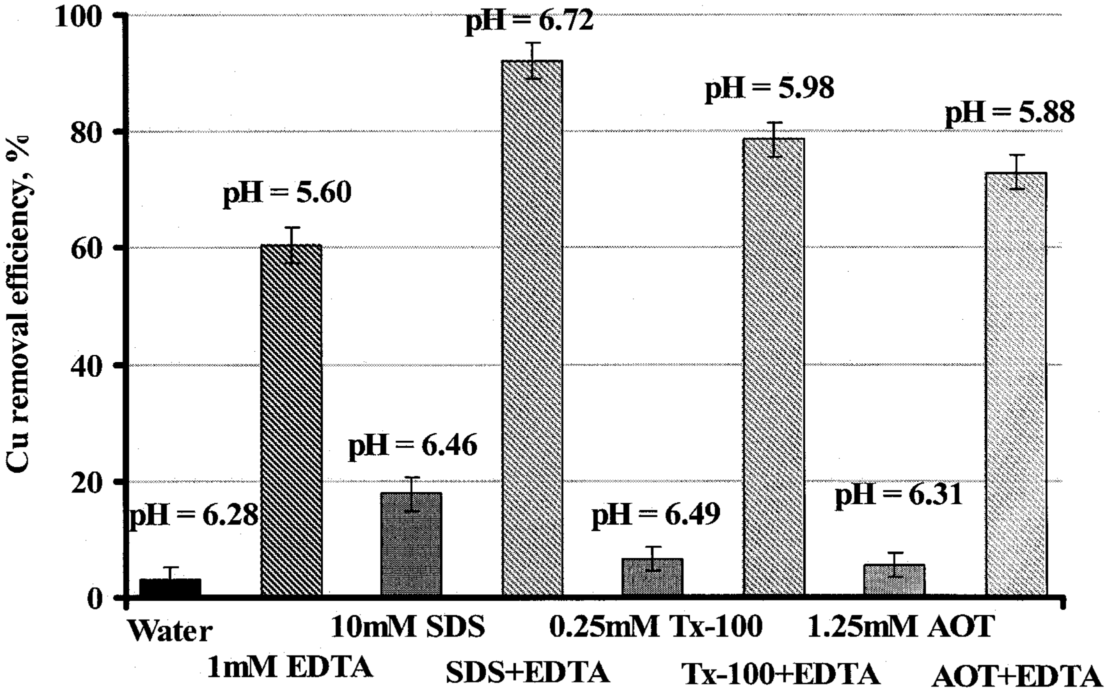


Fig. 5.5 Batch extraction of Cu (II) by surfactants and EDTA (1mM)

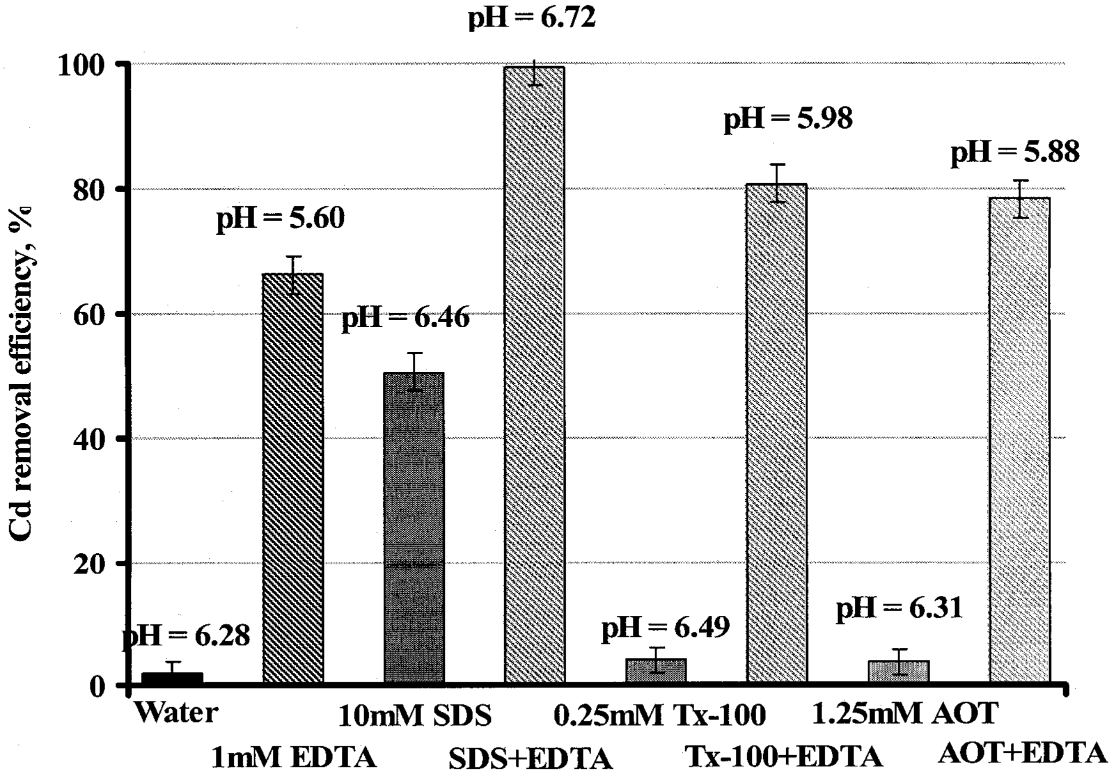


Fig. 5.6 Batch extraction of Cd (II) by surfactants and EDTA (1mM)

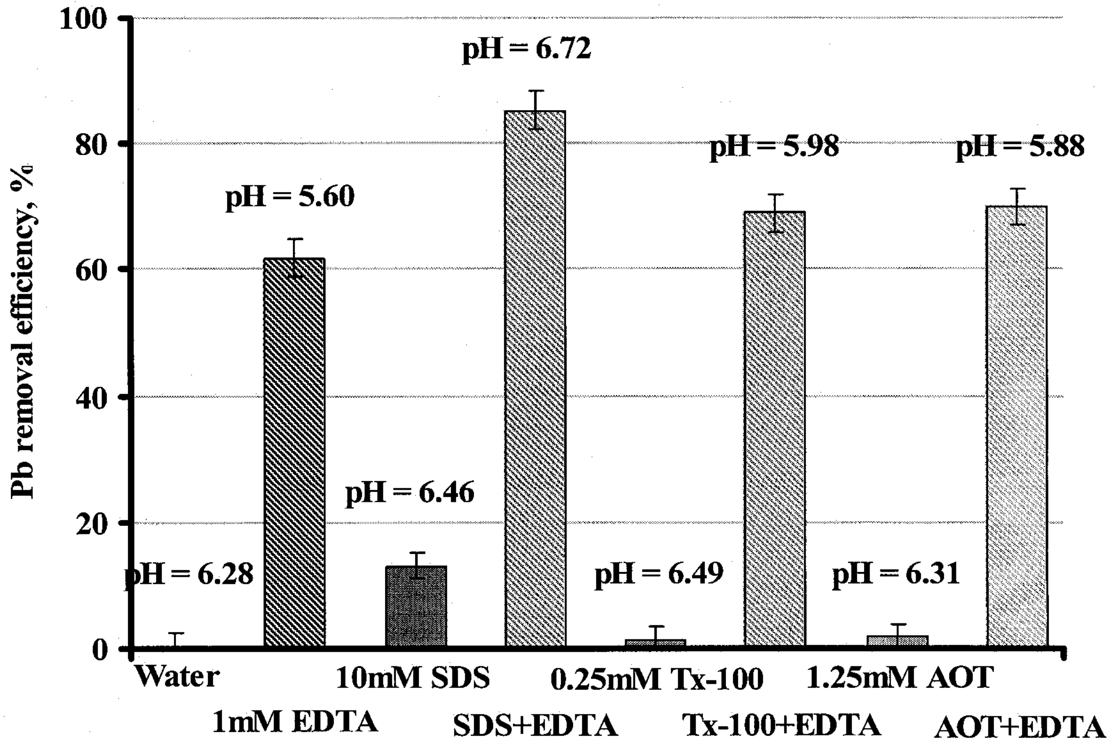


Fig. 5.7 Batch extraction of Pb (II) by surfactants and EDTA (1mM)

Cu (II) removal efficiency by the combination of EDTA and SDS reached 92%. In comparison with the removal by EDTA alone, it has an improved of 30%, which is considerable. Tx-100 and AOT also improved the Cu (II) extraction capability of EDTA by 18% and 12% respectively. The removal of Cd (II) was significantly increased to 99.5% by adding the SDS to EDTA. However, Tx-100 and AOT only improved the metal removal by 14% and 12% respectively. Pb (II) removal was also increased by a combination of EDTA and SDS to 85%. This showed less improvement in comparison with the other two metals. Tx-100 and AOT did not display considerable improvement in the removal of Pb by EDTA. From these tests, it can be concluded that the combination of 10mMSDS and 1mM EDTA can be a very effective extraction solution for all three heavy metals (Cu (II), Cd (II), and Pb (II)).

5.2.4 Effects of metal interaction and competition

Competition between heavy metal ions for the available retention sites in the soil environment has been a subject of many recent investigations (Kaoser et al, 2004; Serrano et al, 2004; Christophi, 2000). Simultaneous presence of heavy metals in the soil and limited adsorption sites on the soil particles is the reason for the onset of competition between ions. This significantly affects both adsorption and desorption efficiencies.

Fig. 5.8 demonstrates the result of AA analysis for soil sample 1 which contains 15mM of each Cu (II), Cd (II), and Pb (II). The retention efficiencies were calculated by finding the ratio of the retained metal and initial metal concentration. Results showed that in nearly neutral conditions when three metals were introduced to the soil sample simultaneously, Cd exhibits higher affinity to the adsorption sites. Generally, the adsorption order of these three metals was as follows: Cd (II)>Pb (II)>Cu (II).

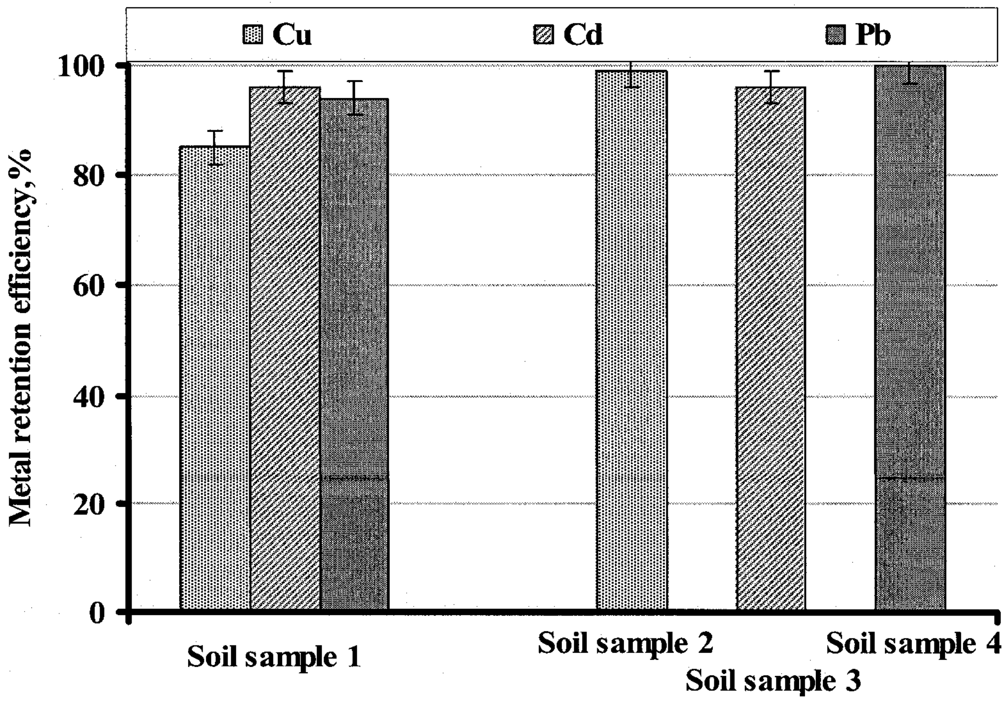


Fig. 5.8 Competitive retention of metals

In order to study the interaction between the three heavy metals present, three new types of soil samples were provided. Soil sample 2, soil sample 3, and soil sample 4 contained the same ratios of sand and bentonite as soil sample 1. However the bentonite portion was contaminated with either 15mM Cu (II) alone (sample 2), or 15mM Cd (II) alone (sample 3) or, 15mM Pb (II) alone (sample 4). The preparation procedures for all the four samples were identical. Results indicated that adsorption of Cu (II) decreased in the presence of other two metals from 99% to 85%. Pb (II) adsorption also exhibited a slight decrease in presence of Cu (II) and Cd (II). However, Cd (II) adsorption remained at the same level. Fig 5.8 suggests that Cd (II) has a slightly higher affinity and retention capability for the available adsorption sites than Cu (II) and Pb (II).

Interaction between metal ions not only affects the metal adsorption but also affects their mobility and desorption. In order to study this effect, desorption tests were conducted on the four soil samples, using the 10mM SDS which was the most efficient washing solution according to batch test results (Fig. 5.9).

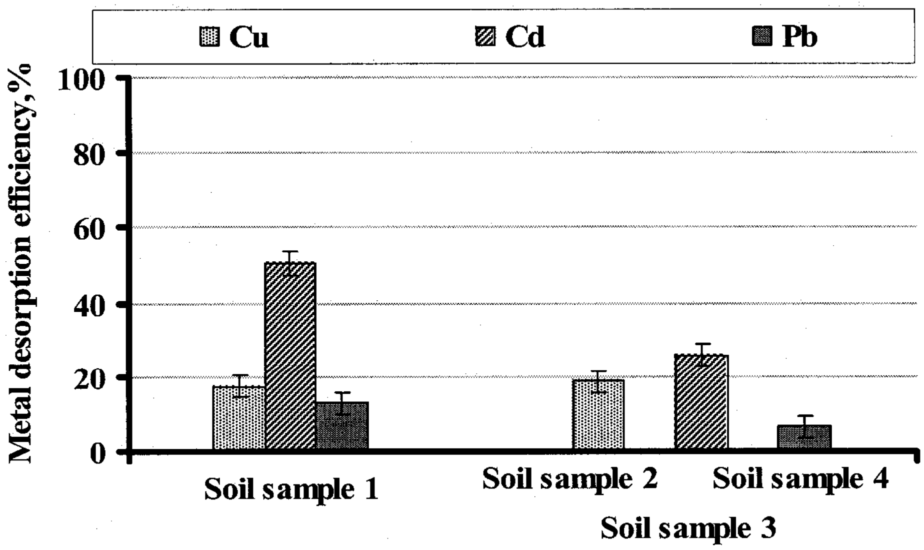


Fig 5.9 Competitive desorption of heavy metals

Test data indicated that Cu (II) desorption experienced a marginal decrease from 19% to 17.78% when Cd (II) and Pb (II) are also present in the soil. However, desorptions of both Cd (II) and Pb (II) increased. The removal efficiency of Cd (II) increased nearly two times from 26% to 51% as well as desorption of Pb (II) which increased from 7% to 13%. This may be due to the low mobility and high tendency of Cu (II) to make complexes with organic compounds. Consequently, available adsorption sites for Cd (II) and Pb (II) were reduced. This may weaken their adsorption capability and enhance their mobility and desorption.

5.2.5 Effect of contaminant aging

Generally, when a contaminant ages, it becomes less mobile because more surface complexes and solids are formed [Reed et al, 1996]. For study the effect of contaminant aging on mobility and desorption, one should study the metal desorption from contaminated soil in terms of years. However, due to time restrictions of the study the desorption tests have been monitored in the period of 12 weeks. The extraction solution used was distilled water. Sampling and AA analysis were performed every two weeks to monitor the desorption capabilities of the three heavy metals (Fig 5.10).

Cu (II) desorption appeared to decrease with time from 0.65 mg/L to 0.53 mg/L, Cd (II) desorption from 0.71 mg/L to 0.59 mg/L and Pb desorption from 0.33 mg/L to 0.27 mg/L. these slight decreases in the desorption amounts of three metals could confirm the less mobility of metal ions due to contaminant aging. Due to limitation of this study the results for contaminant aging may be considered as tentative. Further experiments and more time are needed to provide an accurate conclusion.

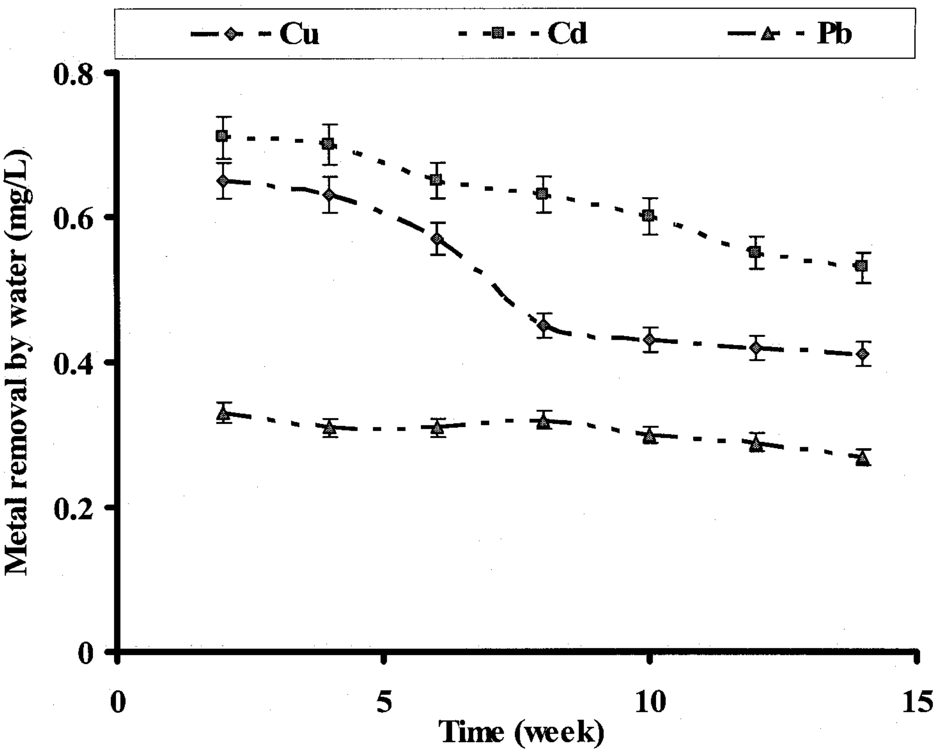


Fig.5.10 Effect of contaminant aging on the heavy metal extraction

5.3 Column tests

For a long time, batch tests have been the most popular method for studying the adsorption and desorption behavior of heavy metals. They are easy to conduct and test conditions are more controllable in batch reactors. However, batch tests are not able to simulate the field conditions. In all the in-situ remediation methods, soil is considered as a fixed medium and the extracting material such as washing solution passes through it. To study and simulate the various field conditions and to find out their effect on heavy metals removal from the soil, column tests were conducted.

Several factors such as pH, organic matter, soil moisture, temperature, contaminant concentration, age of contamination and flow rate affect the removal efficiency in column tests. The column was uniformly packed with the sample soil and different washing solutions were applied in the controlled flow rates. From batch results SDS (10mM) was found to be the most efficient surfactant for metal removal. Other washing solutions selected included distilled water, and EDTA (1mM). A combination of SDS (10mM) and EDTA (1mM) was also used to study the effects of varying flow rate on the removal process. Table 5.2 demonstrates relevant data of the column tests. The mass of the soil used was 450g, the bulk density of the soil was 1.74 g/cm^3, Hydraulic conductivity was 0.0037 ± 0.00015 cm/s (Appendix A), and the pore volume was found to be 103 mL.

Table 5.2 Column test conditions **pore volume = 103 mL**

Washing solution	**Flow rate (mL/min)**	**Pore water velocity (cm/min)**
Distilled water	12	2.4
10mM SDS	12	2.4
1mM Na_2EDTA	12	2.4
1mM Na_2EDTA+10mM SDS	4	0.8
1mM Na_2EDTA+10mM SDS	12	2.4
1mM Na_2EDTA+10mM SDS	20	4

5.3.1 Column test using distilled water and SDS

The results of using distilled water and 10mM SDS for soil washing are illustrated in Figs.5.11 to 5.13. Details related to these tests are available in Tables C-1 and C-2. The results indicated that 50 pore volumes of distilled water could only remove 8.15%, 8.80%, and 1.18% of Cu (II), Cd (II), and Pb (II) respectively. This removal mostly occurred before reaching the 20 pore volumes. On the other hand, SDS showed higher removal efficiencies of 16.27%, 30.78%, and 6.10% for Cu (II), Cd (II), and Pb (II) respectively. These tests indicated that removal of Cu (II) increased nearly 100% when SDS was used as the washing solution. Further, the increase in Cd (II) removal was 250% and the increase in Pb (II) removed was nearly 400%. The removal order of the three metals were as follows Cd (II)>Cu (II)>Pb (II). This is in agreement with the batch test results. This may be attributed to higher mobility of Cd (II) compared to Cu (II) and Pb (II). The metal concentration was relatively high in the first three or four pore volumes of the effluent. This may be due to the short age of contamination which results in weaker binding of metal ions on the surface of soil particles.

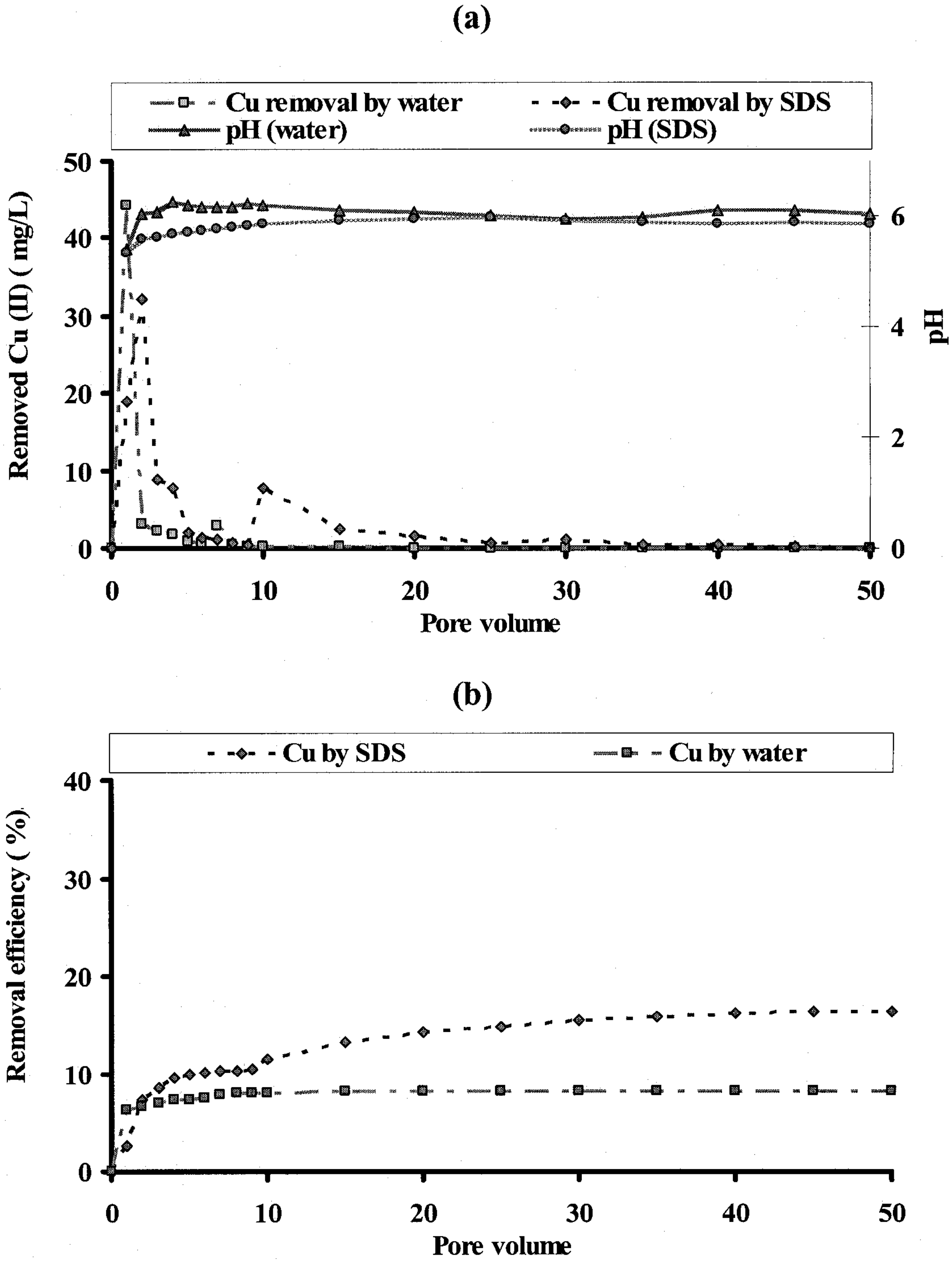


Fig. 5.11 (a) Cu (II) removal from soil column (b) Cu (II) removal efficiency (washing solution: distilled water or 10mM SDS, flow rate: 12mL/min, PV: 103mL)

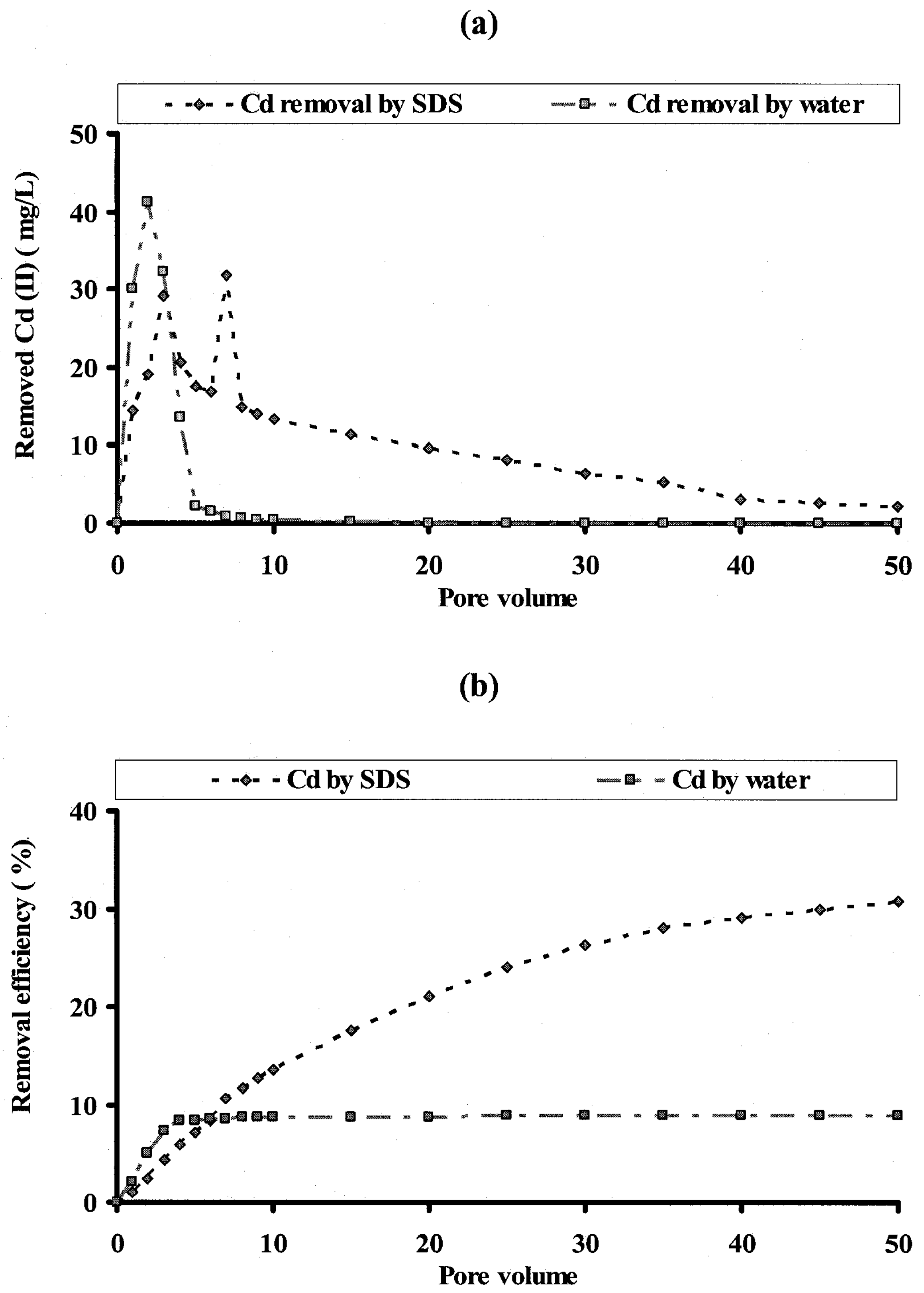


Fig. 5.12 (a) Cd (II) removal from soil column (b) Cd (II) removal efficiency (washing solution: distilled water or 10mM SDS, flow rate: 12ml/min, PV: 103mL)

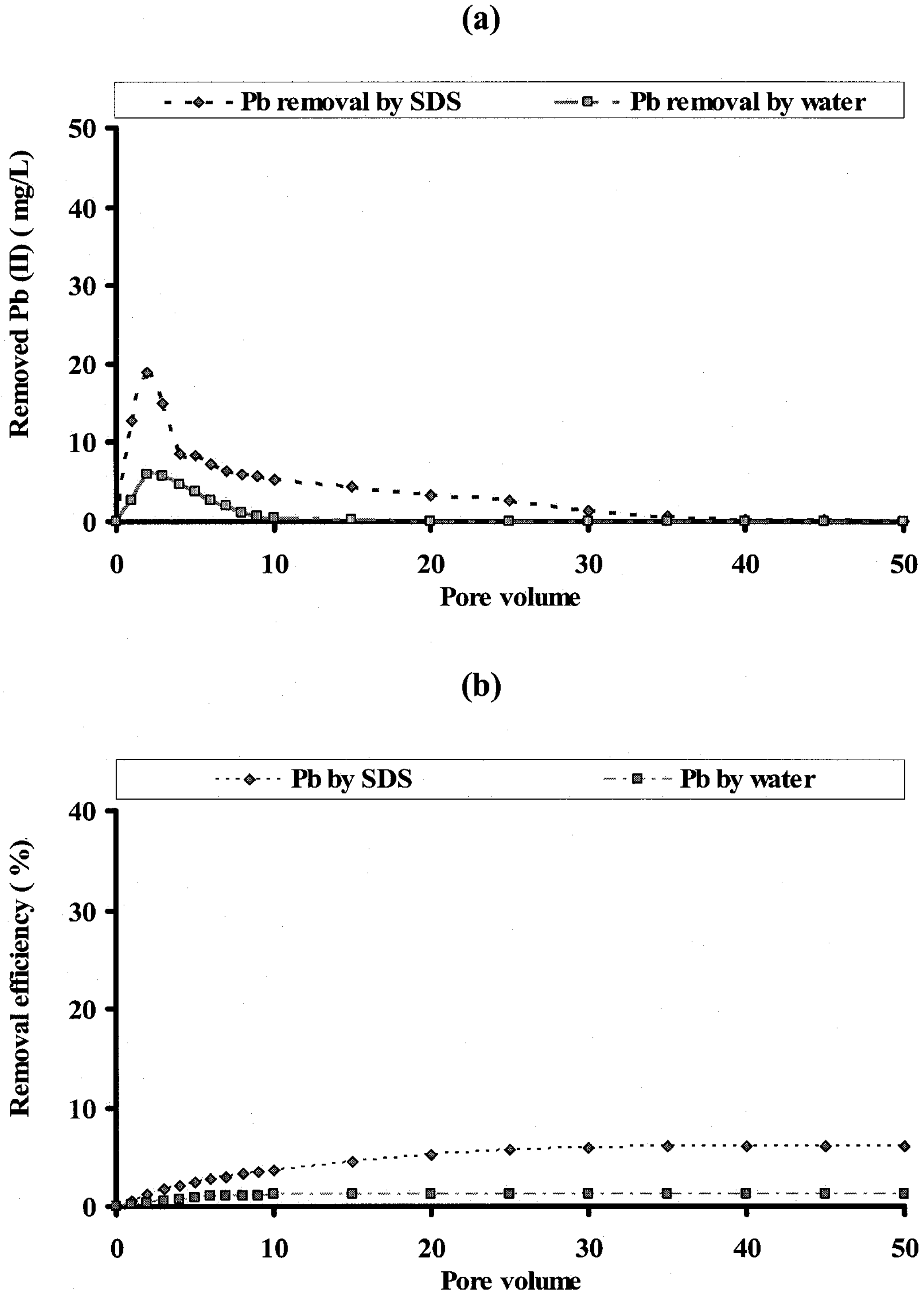
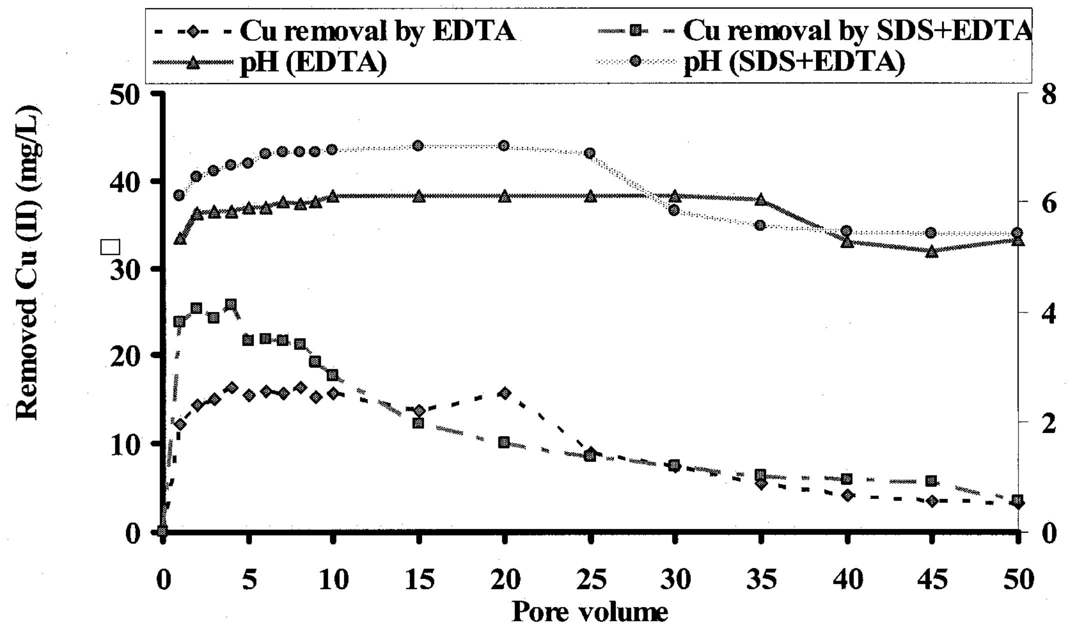


Fig. 5.13 (a) Pb (II) removal from soil column (b) Pb (II) removal efficiency (washing solution: distilled water or 10mM SDS, flow rate: 12ml/min, PV: 103mL)

5.3.2 Column tests and the effect of using the chelating agent and SDS

The results of using 1mM EDTA with and without 10mM SDS are illustrated in Figs. 5.14 to 5.16. Details of the test configuration are available in Tables C-3 to C-4. The results indicated that the addition of SDS to EDTA increases the removal efficiency of all three metals. Fifty pore volumes of EDTA alone could remove 65.4%, 74.4%, and 53.7% of Cu (II), Cd (II), and Pb (II) respectively. More than half the metal removal occurred in the first 20 pore volumes. Adding 10mM SDS to the washing solution increased the efficiencies to 73.6%, 84.4%, and 61.7% for Cu (II), Cd (II), and Pb (II) respectively. This corresponds to improvements of the removal by a factor of 1.12, 1.13, and 1.15 in comparison with EDTA alone. The enhancement in removal efficiency was less than that in the batch tests. This may be due to the fact that the equilibrium conditions were not achieved even after 50 pore volumes in column tests. The removal order was as follows: Cd (II) > Cu (II) >Pb (II). This is in complete agreement with previous results of batch tests.

(a)



(b)

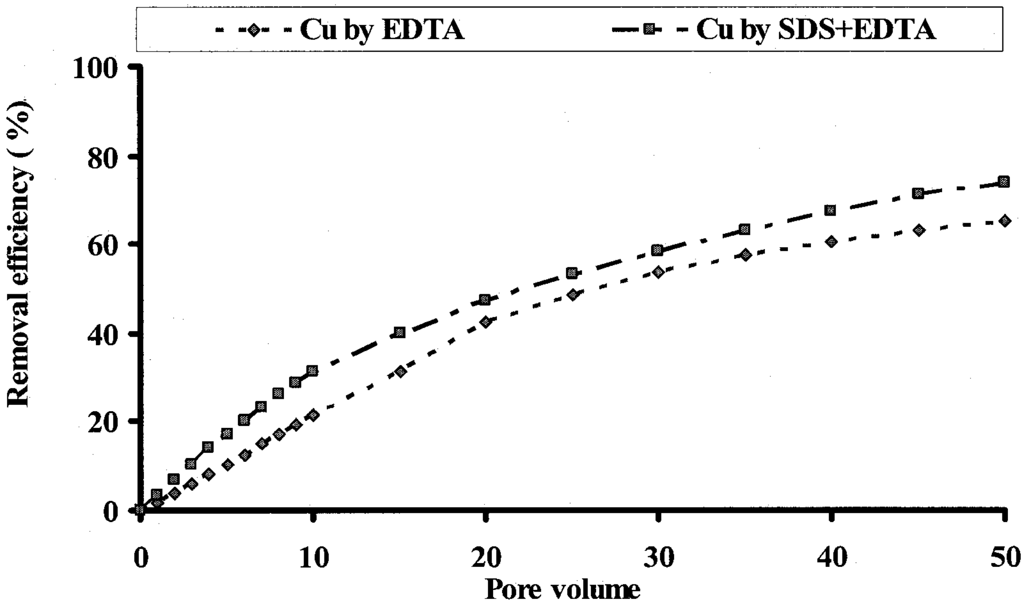
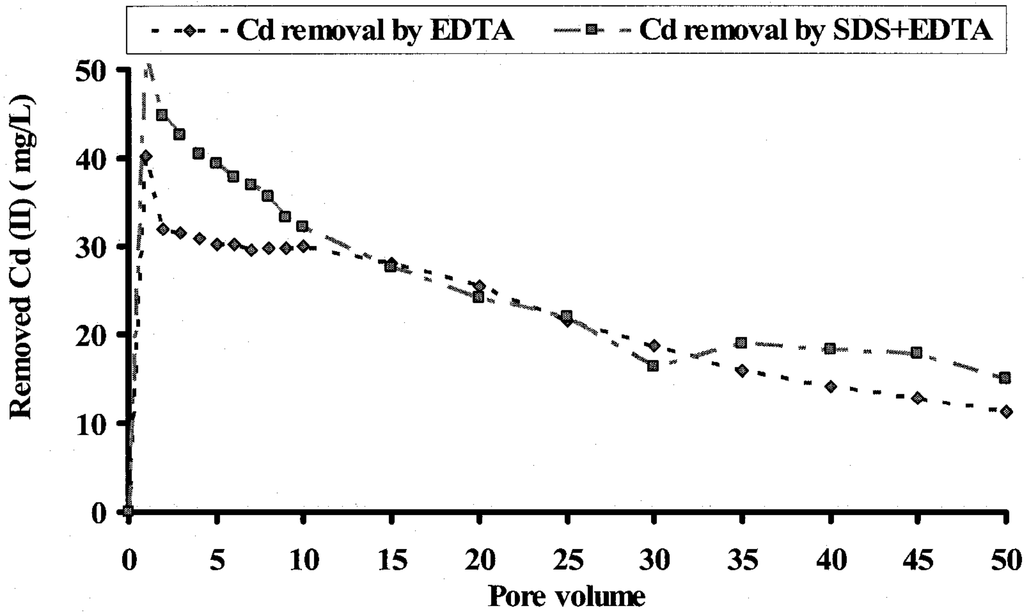


Fig. 5.14 (a) Cu (II) removal from soil column (b) Cu (II) removal efficiency (washing solution: 1mM EDTA with and without 10mM SDS, flow rate: 12ml/min, PV: 103mL)

(a)



(b)

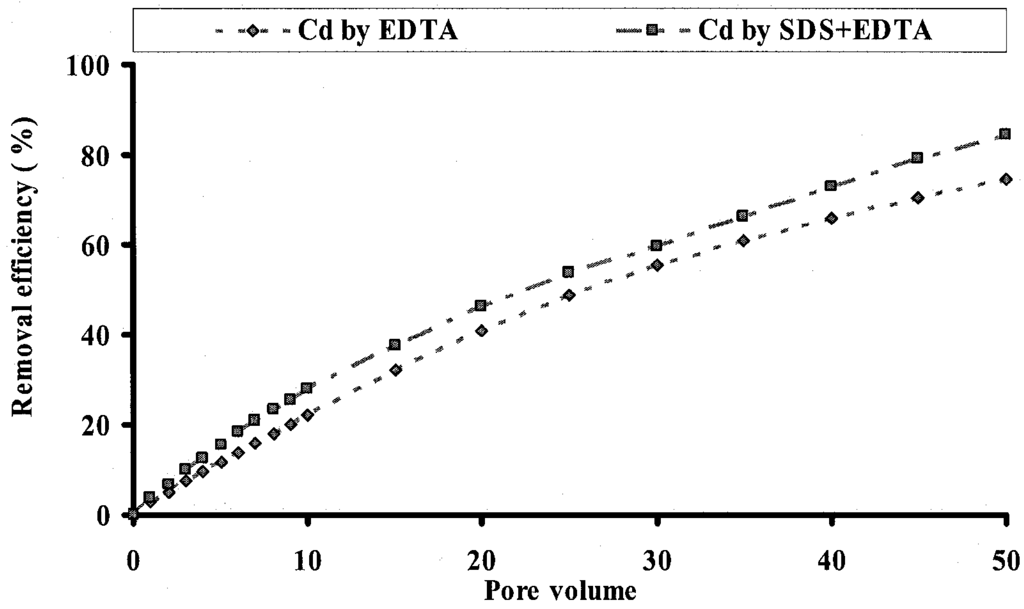


Fig. 5.15 (a) Cd (II) removal from soil column (b) Cd (II) removal efficiency (washing solution: 1mM EDTA with and without 10mM SDS, flow rate: 12ml/min, PV: 103mL)

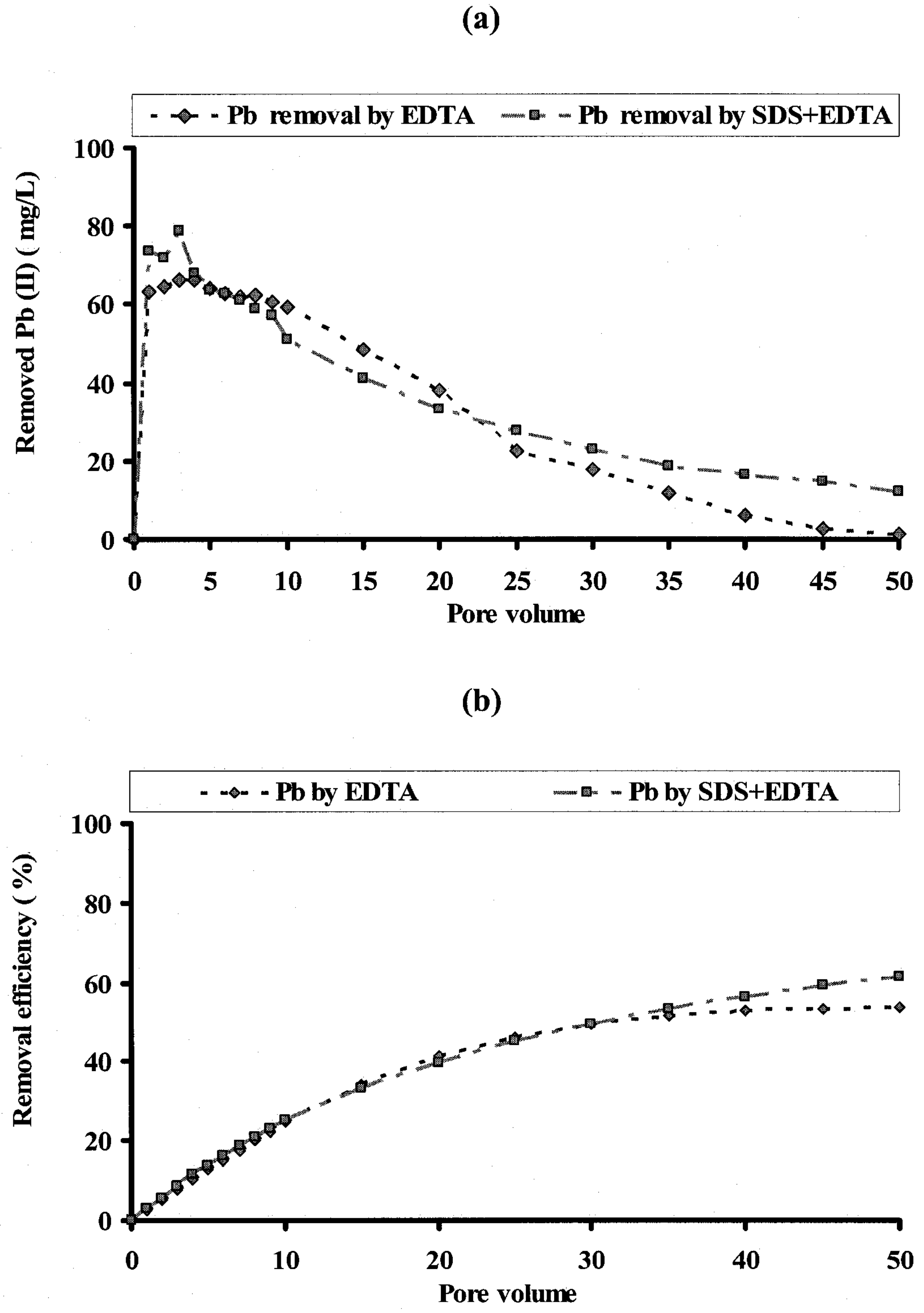


Fig. 5.16 (a) Pb (II) removal from soil column (b) Pb (II) removal efficiency (washing solution: 1mM EDTA with and without 10mM SDS, flow rate: 12ml/min, PV: 103mL)

5.3.3 Column tests and effect of flow variation

Flow rates of 4, 12, and 20 mL/min were used to study the effect of flow rate variation on heavy metal removal from the soil column. The washing solution contained both 1mM EDTA and 10mM SDS. Fifty pore volumes were passed through the column.

Figs. 5.17 to 5.19 illustrate the results related to these tests. Tables C-4 to C-6 provide details of test data. The results show that varying the flow rate influenced the removal rate of heavy metals. For all three metals, the removal efficiencies decreased with increasing the flow rate. Cu (II) removal efficiency reduced from 79.1% to 61.7% when the flow rate was increased from 4 to 20 ml/min. This indicates that reduction in the removal occurred when the flow was increased by a factor of 5. Cd (II) removal efficiency also decreased from 87.3% to 66.6%. This corresponds to nearly 20% reduction in removal rates. No significant changes were observed in Cd (II) removal when the flow rate was increased from 4 to 12 ml/min. For Pb (II), the removal efficiency decreased from 66.9% to 51.6%. This indicates a reduction in the removal by a factor of 1.3. Decreasing the removal efficiencies with increasing flow rates may occur due to shorter contact times between the metal and the extracting agents which result in less dispersion and interaction of the washing agents. Lower residence time results in shorter periods for the washing fluid to penetrate the micro porous medium. Nevertheless, the results demonstrated that flow variation is not a very dominant factor in removal enhancement in comparison to the type of the extracting agent and its concentration. However, using higher flow rates may be considered to shorten the extraction time and consequently economize removal expenses.

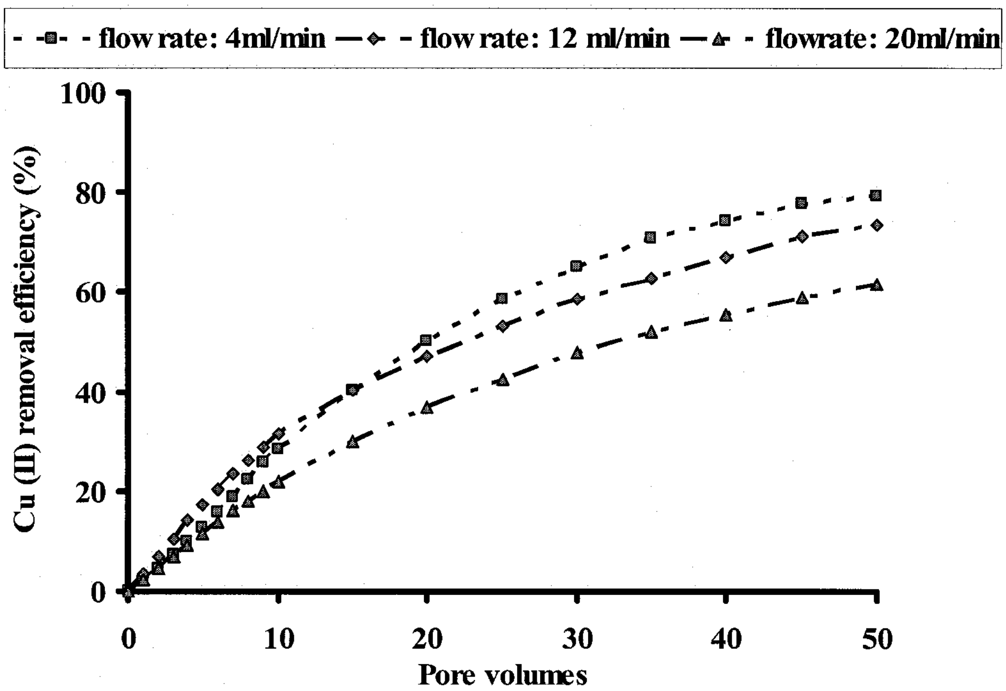


Fig 5.17 Cu (II) removal by 1mM EDTA+10mM SDS in various flow rates,

PV: 103mL

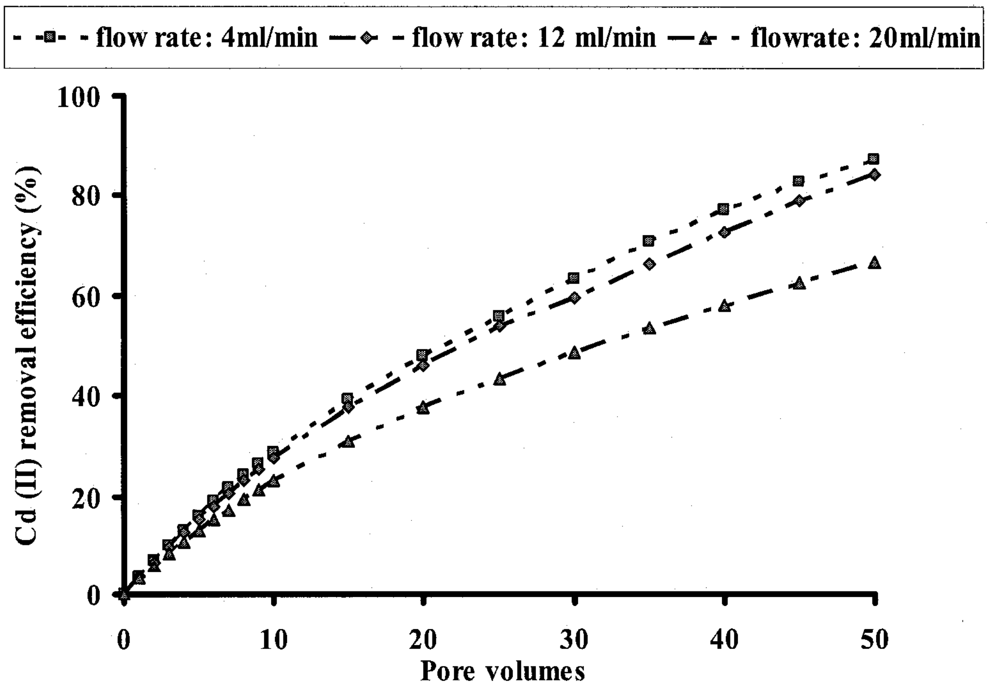


Fig 5.18 Cd (II) removal by 1mM EDTA+10mM SDS in various flow rates,

PV: 103mL

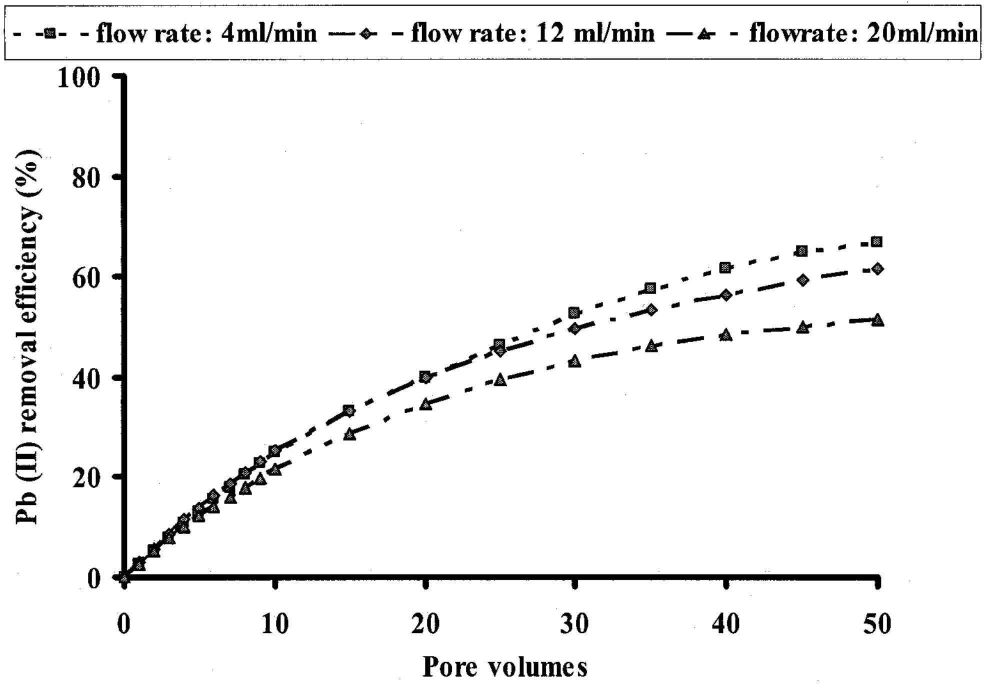


Fig 5.19 Pb (II) removal by 1mM EDTA+10mM SDS in various flow rates, PV: 103mL

5.3.4 Effect of interruption in applying the washing solution

The column with the washing solution of 1mM EDTA and 10mM SDS at the flow rate of 12 ml/min was selected for the interruption study. After 50 pore volumes had passed through the column, the injection of solution was stopped for two weeks. Following this interruption, the injection was resumed at the same flow rate for 5 more pore volumes. The results are illustrated in Figs. 5.20 to 5.22. Related details of data are available in Table C-4.

The metal concentrations in the effluent after the interruption were increased from 3.51 to 26.3 mg/L, 15 to 23.8 mg/L, and 12.3 to 75.5mg/L for Cu (II), Cd (II), and Pb (II) respectively. The two weeks interruption increased the residence time. This allowed the extracting agent to diffuse more in the micro porous medium and release more metal bounds. The pH also increased to 7 after the interruption. This corresponds to nearly neutral conditions. The results indicated that in the cases when time is not an important factor, discontinuous washing of the soil may be considered to increase the removal efficiency.

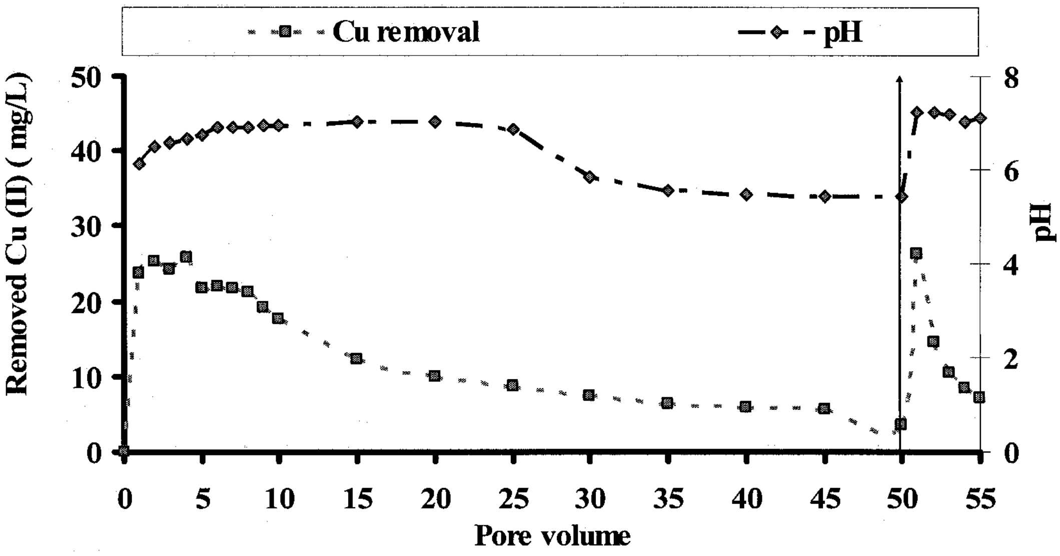


Fig 5.20 Cu (II) removal after two weeks interruption
(washing solution: 1mM EDTA+10mM SDS, flow rate: 12ml/min, PV: 103mL)

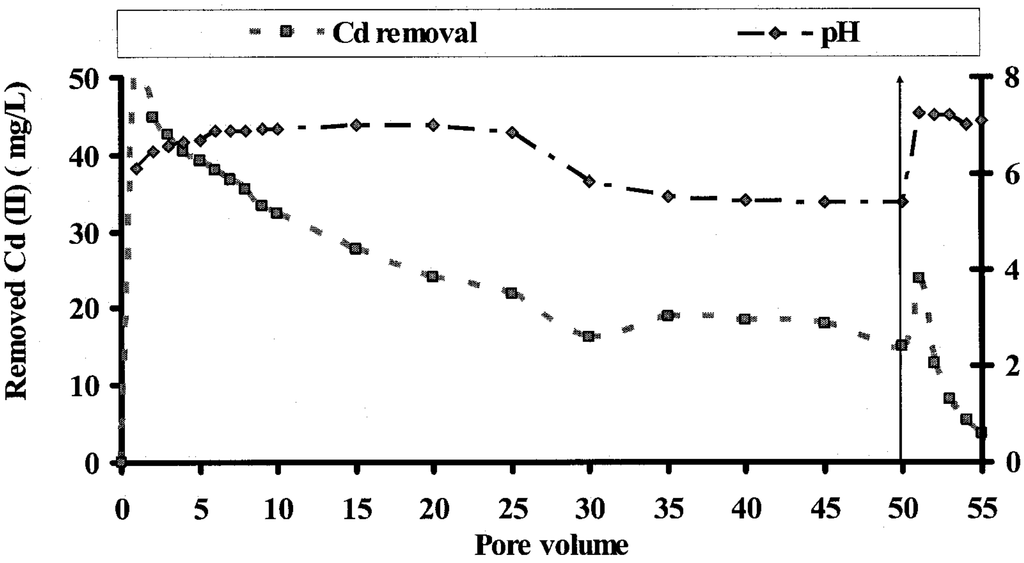


Fig 5.21 Cd (II) removal after two weeks interruption by (washing solution: 1mM EDTA+10mM SDS, flow rate: 12ml/min, PV: 103mL)

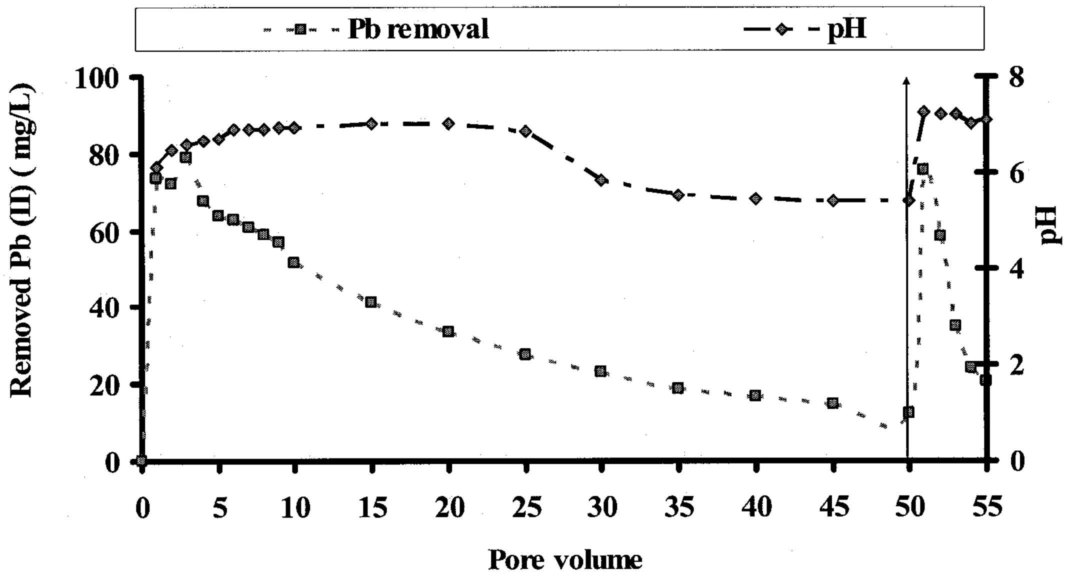


Fig 5.22 Pb (II) removal after two weeks interruption by (washing solution: 1mM EDTA+10mM SDS, flow rate: 12ml/min, PV: 103mL)

5.3.5 Effect of pH

Since hydrogen ions can replace most of the metal cations that are adsorbed to soil particles, pH variations can significantly influence the solubility and removal of metals from soil. Generally, desorption of metals is increased as pH decreases. Thus, metals tend to be more soluble in an acidic environment [Selim and Sparks, 2001].

In the batch tests, the final pH was an indication of the pH value of the solution after 24 hours of shaking and equilibrating with the soil sample and before performing the AA analysis. The results showed that in all experiments except those with the EDTA as the extracting solution pH values laid in the range of 6 to 7. In the experiments using this EDTA alone the pH values decreased from 5.60 to 4.5 with increasing the concentration. This may explain the high removal efficiencies of Cu (II), Cd (II), and Pb (II) when the EDTA concentration reached 15mM.

In the column tests, pH values were determined after collecting the effluent samples, before performing the AA analysis. Results indicated that in all effluents the pH value laid in the range of 5 to 7. In several experiments such as the ones conducted after the interruption or the ones conducted with the low flow rate of 4ml/min the pH values were greater than 7. No sudden variations in pH were observed in the column tests.

Due to the important effect of pH value on removal of heavy metals and in order to conduct a more accurate comparison between washing and extracting solutions one may consider the pH monitoring and control during all experiments.

Chapter 6

Summary and conclusion

6.1 General remarks

The present study attempts to investigate the capability of surfactants to enhance the remediation of a sandy soil contaminated by Cu (II), Cd (II), and Pb (II). Batch and column tests were conducted to study effects of surfactants and a chelating agent as soil washing liquids. The adsorptions-desorption of these metals on soil particles and their transport behaviors are discussed. Effects of competition and interaction associated with adsorption-desorption were briefly noted based on a short study. Specifically, Anionic surfactants (SDS and AOT), a nonionic surfactant (Tx-100) and a chelating agent (EDTA disodium salt) were used in this study.

6.2 Conclusions

- The results of the batch tests demonstrated that all three surfactants used can enhance heavy metal removal from the soil. However, 10mM SDS was found to be the most effective extracting solution. Compared to extraction by distilled water SDS could enhance the removal of Cu (II), Cd (II), and Pb (II), by a factor of 5.5,28.8, and 29.1 times respectively.

- Batch experiments also indicated that EDTA (15mM) as the chelating agent has a great potential for heavy metal removal. However, the use of chelating agents could be a further environmental problem and concern. The study showed that a combination of 1mM EDTA and 10mM SDS could yield the high removal efficiencies of nearly 92%, 99.5%, and 85% for Cu (II), Cd (II), and Pb (II) respectively. This combination used less concentration of the chelating agent and consequently, this poses a less severe threat to the environment.

- Batch experiments also studied the competition and interaction of metals to know the adsorption-desorption mechanism. Both Cu (II) and Pb (II) showed a decrease in their adsorption when Cd (II) was present. This indicated the higher affinity of Cd (II) to the available soil adsorption sites. In terms of desorption, both Cd (II) and Pb (II) experienced an increase in their removal efficiency in the presence of Cu (II) whereas the Cu (II) desorption slightly decreased. This can be due to the capability of Cu (II) to provide stronger bounds with the soil organic material.

- Column experiments confirm that the combination of 1mM EDTA and 10mM SDS is an efficient washing solution. This washing liquid could remove 83%, 88%, and 70% of Cu (II), Cd (II), and Pb (II) respectively

- Slight increase of flow rate decreased the removal efficiencies which may be due to the shorter residence and interaction time of washing agents at higher flow rates

- Interruption test showed that when time is not an important factor in removal process, intermittent application of washing solution can be considered to obtain a better removal efficiency

- The number of pore volumes which were passed through the column was found to be the dominant factor in determining of metal removal efficiencies.

6.3 Recommendations for future work

- Since the naturally contaminated soil may contain a wide range of contaminants, other types and combinations of heavy metals with other contaminants may be studied in order to find out the effect of competition and interaction.

- Cost effectiveness of the metal removal process by surfactants and surfactant losses in the soil can also be investigated.

References

Abumaizar R. J., Smith Edward H., 1999, Heavy metal removal by soil washing, Journal of hazardous material, B70, pp. 71-86

Ahmad I., Hayat S., Pichtel John, 2005, Heavy metal contamination of soil-problems and remedies, Science publishers, Inc.

Alloway B.J., 1990, Heavy metals in soils, John Wiley & Sons, Inc. New York

Anderson W.C., 1993, Innovative site remediation technology: soil washing-soil flushing, Amer. Academy of environmental engineering, Annapolis, Maryland

Atanassova I. D., 1995, Adsorption and desorption of Cu at high equilibrium concentrations by soil and clay samples from Bulgaria, Environmental pollution, 87: 17-21

Cameron R.E., 1992, Guide to site and soil description for hazardous waste site characterization, Vol. 1: Metals, Environmental Protection Agency, EPA/600/4-91/029

Christophi C. A., Axe L., 2000, Competition of Cd, Cu, and Pb adsorption on Goethite, Journal of environmental engineering, Vol. 126, No. 1, pp. 66-74

Cline S. R., Reed B. E., 1995, Lead removal from soils via bench-scale soil washing techniques, Journal of environmental engineering, Vol. 121, No. 10, pp.700-705

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

Davis A. P., Singh I., 1995, Washing of Zinc (II) from contaminated soil column, Journal of environmental engineering, Vol. 121, No.2, pp. 174-185

Doong R., Wen W., and Lei W., 1998, Surfactant enhanced remediation of cadmium contaminated soils, Wat. Sci. Tech. Vol. 37, No. 8, pp. 65-71

Duffield A., 2001, Surfactants enhanced mobilization of non-aqueous phase liquids, M.A.Sc. Thesis, Concordia University, Montreal, Québec, Canada

Dzombak D. A., Morel F. M. M., 1990, Adsorption of inorganic pollutants in aquatic systems. J. Hydraulic Eng., 113:430-475

Edwards D. A., Adeel Z, Luthy R. G., 1994, Distribution of nonionic surfactant and phenanthrene in a sediment/aqueous system, Environ. Sci. Technol. Vol. 28:1550-1560

Eftekhari F., 2000, Foam-surfactant technology in soil remediation, M.A.Sc. Thesis, Concordia University, Montreal, Quebec, Canada

Electorowicz M., Hakimpour M., 2001, Hybrid Electrokinetic Method Applied to mix contamination clayey soil, EREM, 3rd Symposium and status report on electrokinetic remediation, Karlsruhe, Germany, April 2001

Elliot H.A., Brown G.A., 1989, Comparative evaluation of NTA and EDTA for extractive decontamination of Pb-polluted soils, Water, Air, and Soil Pollution, Vol. 45, pp. 361-369

Elliott H.A., Liberati M. R., and Huang C.P., 1986, Competitive adsorption of heavy metals by soils, Journal of environmental quality, Vol.15, No. 3, pp. 214-219

Evanko C. R., Dzombak A. D., 1997, Remediation of metal-contaminated soils and groundwater, ground water remediation technology analysis center

Gerber M. A., Freeman H. D., Baker E. G., Riemath W.F., 1991, Soil washing: a preliminary assessment of its applicability to Hanford , prepared for U. S. department of energy by battle pacific northwest laboratory, Richland, Washington, Report No. PNL-7787; UC902.

Harter R. D., 1992, Competitive sorption of cobalt, copper and nickel ions by a calcium-saturated soil, Soil. Sci. Soc. Am. J. 56:444-449

Harter R. D., 1983, Effect of soil pH on adsorption of Lead, Copper, Zinc, and nickel, Soil Sci. Soc. Am. J. 47:47-51

Herman D. C., Artiola J. F., and Miller R. M., 1995, removal of cadmium, lead and zinc from soil by a rhamnolipid biosurfactant, Environ. Sci. Technol., Vol 29, No. 9, pp. 2280-2285

Hemond H., Fechner-Levy L., 1994, Chemical fate and transport in the environment, San Diego, Calif.; London: Academic, c2000

Hinz C., Selim H. M., 1994, Transport of zinc and cadmium in soils: experimental evidence and modeling approaches, Soil Sci, Am. J., 58:1316-1327

Hyman M., Dupont R.R., 2001, Groundwater and soil remediation, ASCE press

Kaoser S., Barrington S., Elektorowicz M.; Wang L., 2004, Copper adsorption with Pb and Cd in sand-bentonite liners under various pHs, Part I &II, Journal of environmental science and health, Vol. A39, No.9, PP. 2241-2255,PP. 2257-2274

Kedziorek M. A.M., Bourg Alain C.M., 2000, Solubilization of lead and cadmium during the percolation of EDTA through a soil polluted by smelting activities, Journal of contaminant hydrology 40, pp. 381-392

LaGrega M. D., Buckingham P. L., Evans J. C., 1994, Hazardous waste management, McGraw-Hill, Inc.

Li Loretta Y., Wu G. , 1999, Numerical simulation of transport of four heavy metals in kaolinite clay, Journal of environmental engineering, Vol.125, No. 4, pp. 314-324

Li X., 2004, Surfactant enhanced washing of Cu (II) and Zn (II) from a contaminated sandy soil, M.A.Sc. Thesis, Concordia University, Montreal, Quebec, Canada

Lim T. T., Tay J.; Wang J. Y., 2004, Chelating-agent-enhanced heavy metal extraction from a contaminated acidic soil, Journal of environmental engineering, Vol. 130, No.1, pp. 59-66

McBride M. B., 1989, Reactions controlling heavy metal solubility in soils, Adv. Soil. Sci. 10:1-56

Mulligan C. N., Yong R. N.; Gibbs B. F., 1999a, On the use of biosurfactants for the removal of heavy metals from oil-contaminated soil, Process safety progress, Vol. 18, No. 1, pp. 50-54

Mulligan C. N., Yong R. N.; Gibbs B. F, James S., Bennett H.P.J., 1999b, Metal removal from contaminated soil and sediments by the biosurfactant surfactin, Environ. Sci. Technol., Vol 33, No.21, pp 3812-3820

Mulligan C. N., Yong R. N., Gibbs, 2001b, Heavy metal removal from sediments by biosurfactants, Journal of hazardous materials, Vol 85, pp. 111-125

Mulligan C. N., Yong R. N., Gibbs, 2001a, Surfactant-enhanced remediation of contaminated soil: a review, Engineering geology, Vol. 60, pp. 371-380

Murali V. and Aylmore L.A.G., 1983, Competitive adsorption during solute transport in soils: 1.mathematical models, Soil Science, Vol.135, No.3, pp. 143-150

Murali V. and Aylmore L.A.G., 1983, Competitive adsorption during solute transport in soils: 2. simulations of competitive adsorption, Soil Science, Vol.135, No.4, pp. 203-213

Murali V. and Aylmore L.A.G., 1983, Competitive adsorption during solute transport in soils: 3. A review of experimental evidence of competitive adsorption and an evaluation of simple competition models, Soil Science, Vol.136, No.5, pp. 279-290

Myers D. , 2006, Surfactant science and technology, third edition, John Wiley & Sons Inc.

Nivas B.T., Sabatini D.A., Shiau B. J., and Harwell J.H., 1996, Surfactant enhanced remediation of subsurface chromium contamination, Wat. Res. Vol. 30, No. 3, pp. 511-520

Peters R. W., 1999, Chelant extraction of heavy metals from contaminated soils, Journal of hazardous material, 66, pp. 151-210

Pierzynski G. M. , 2005, soils and environmental quality, Boca Raton: Taylor & Francis Group

Reed B. E., Carrier P. C., Moore R., 1996, Flushing of a Pb (II) contaminated soil using HCL, EDTA, and $CaCl_2$, Journal of environmental engineering, Vol.122, No. 1, pp 48-50

Roundhill D. M., 2001, Extraction of metals from soils and waters, Kluwer academic / Plenum publishers

Rump H.H., Krist H., 1988, Laboratory manual for the examination of water, waste water, and soil, Weinheim, Federal Republic of Germany: VCH Verlagsgeselischaft; New York, NY

Sabatini D. A., Knox R. C., 1992, Transport and remediation of subsurface contaminants, American chemical society, Washington, DC

Sabatini D. A., Knox, R. C., Harwell J. H., 1995, Surfactant-enhanced subsurface remediation, emerging technology, American chemical society (ACS), symposium series 594

Selim H. Magdi, A. M. C., 1997, Reactivity and transport of heavy metals in soils, CRC press Inc., Lewis publishers

Selim H. M., Sparks D. L., 2001, Heavy metals release in soils, Lewis publishers

Serrano S., Garrido F., Campbell C. G., Garcia-Gonzalez M. T., 2004, Competitive sorption of cadmium and lead in acid soils of central Spain, Geoderma, 124:91-104

Shin M., Barrington S. F., Marshall W. D., and Kim J. W., 2004, Simultaneous soil Cd and PCB decontamination using a surfactant/ligand solution, Journal of environmental science and health, Vol. A39, Nos. 11-12, pp.2783-2798

Smith L. A., Means J. L. Chen A., Alleman, B., Chapman C. C., Tixier J. S., Brauning S. E., Gavaskar A. R., Royer M. D., 1995, Remedial options for metal-contaminated sites, Lewis Publishers

Soesilo J.A., Wilson S. R., 1997, Site remediation: planning and management, CRC, Lewis Publishers

Tan K. H., 1998, Principles of soil chemistry, Marcel Dekker, Inc.

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

Wang S., 2003, biosurfactant enhanved remediation of heavy metal contaminated soil, M.A.Sc. Thesis, Concordia University, Montreal, Quebec, Canada

Wang S., Mulligan C. N., 2004, rhamnolipid foam enhanced remediation of cadmium and nickel contaminated soil,Water, Air, and Soil pollution, Vol.157, pp. 315-330

Watts R. J., 1998, Hazardous wastes: sources, pathways, receptors, John Wiley & Sons

Yaron B., Dagan G., Goldshmid J., 1984, Pollutants in porous media, Springer-Verlag Berlin Heidelberg New York Tokyo.

APPENDIX A

Measurement of soil hydraulic conductivity

Procedure

1. Measure the column diameter (D) and length (L), and calculate the column section area (F).
2. Pack the soil sample into the column; tap gently on the side of the column to pack the soil in layers of 2cm.
3. Install the experimental setup as in Fig. 4.2, and measure the height difference between the surface water level in the container and top level of the column (H).
4. Collect the outflow in a graduated cylinder.
5. Record the outflow vs. time (at 10 ml intervals) until the time interval for 10ml outflow remains constant for five consecutive samples.
6. calculate the hydraulic conductivity K by he following equations:

(Eq. A.1) $q = \frac{Q}{t}$ (Eq. A.2) $v = \frac{q}{F}$

(Eq. A.3) $i = \frac{H}{L}$ (Eq. A.4) $K = \frac{v}{i}$

7. reload the column, repeat steps 1 to 6, and triplicate the experiment
8. calculate the hydraulic conductivity as the average of three experiments

Experiment and calculation results

D = 4 cm, F = 12.56 cm^2

H = 81 cm, L = 20.5 cm

The calculated results are presented in Table A.1.

Table A.1 Calculations for soil hydraulic conductivity

No.	Q (mL)	T (s)	q = Q/t (mL/s)	V = q/F (cm/s)	i = H/L	Hydraulic conductivity K = V/i (cm/s)
1	400	2251	0.177	0.0140	3.95	0.00354
2	300	1620	0.185	0.0147		0.00372
3	200	1039	0.192	0.0152		0.00384

The average hydraulic conductivity was calculated as following:

$K = (0.00354 + 0.00372 + 0.00384)/3 = 0.0037$

Standard deviation was calculated as following:

$\text{STDEV} = (((0.00354-0.0037)^2 + (0.00372-0.0037)^2 + (0.00384-0.0037)^2)/2)^{0.5} = 0.00015$ cm/s

The range of hydraulic conductivity can be expected as **K = 0.0037 ± 0.00015 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

Table B.1 Metal removal by Tx-100

Soil/solution ratio: 5g/40mL

No.	Surfactant concentration (mM)	Removed Cu		Ratio to Cu removed by D.water	Removed Cd		Ratio to Cd removed by D.water	Removed Pb		Ratio to Pb removed by D.water	Initial pH	Final pH
		mg/l	%		mg/l	%		mg/l	%			
1	0.00	0.65	3.21	1.00	0.71	1.75	1.00	0.33	0.45	1.00	5.73	6.49
2	0.05	1.05	5.20	1.62	1.12	2.77	1.58	0.79	1.08	2.40	4.41	6.53
3	0.10	1.12	5.55	1.73	1.29	3.19	1.82	0.93	1.27	2.82	4.28	6.45
4	0.25	1.33	6.58	2.05	1.62	3.99	2.28	1.04	1.42	3.16	4.27	6.49
5	0.5	1.28	6.30	1.96	1.57	3.87	2.21	0.98	1.34	2.97	4.34	6.44
6	0.75	1.31	6.45	2.01	1.60	3.95	2.25	0.97	1.32	2.93	4.47	6.54
7	1.00	1.30	6.44	2.01	1.58	3.91	2.23	1.02	1.39	3.08	4.50	6.57

Table B.2 Metal removal by SDS **Soil/solution ratio: 5g/40mL**

No.	Surfactant concentration (mM)	Removed Cu		Ratio to Cu removed by D.water	Removed Cd		Ratio to Cd removed by D.water	Removed Pb		Ratio to Pb removed by D.water	Initial pH	Final pH
		mg/l	%		mg/l	%		mg/l	%			
1	0.00	0.65	3.21	1.00	0.71	1.75	1.00	0.33	0.45	1.00	5.73	6.49
2	2.50	1.34	6.62	2.06	2.62	6.47	3.69	2.64	3.60	8.00	5.96	6.14
3	5.00	1.57	7.75	2.42	2.78	6.86	3.91	2.83	3.85	8.57	6.08	6.19
4	7.50	2.19	10.8	3.37	5.69	14.0	8.01	3.89	5.31	11.8	6.29	6.34
5	10.00	3.60	17.8	5.54	20.5	50.5	28.8	9.63	13.1	29.2	6.45	6.46
6	12.50	2.41	11.9	3.71	18.2	44.9	25.6	5.74	7.82	17.4	6.59	6.46
7	15.00	2.15	10.6	3.31	16.9	41.8	23.8	5.71	7.79	17.3	6.71	6.66

Table B.3 Metal removal by AOT

Soil/solution ratio: 5g/40mL

No.	Surfactant concentration (mM)	Removed Cu		Ratio to Cu removed by D.water	Removed Cd		Ratio to Cd removed by D.water	Removed Pb		Ratio to Pb removed by D.water	Initial pH	Final pH
		mg/l	%		mg/l	%		mg/l	%			
1	0.00	0.65	3.21	1.00	0.71	1.75	1.00	0.33	0.45	1.00	5.73	6.49
2	0.25	0.76	3.75	1.17	0.77	1.90	1.08	0.51	0.70	1.55	4.98	6.46
3	0.50	0.72	3.56	1.11	1.01	2.48	1.42	1.17	1.59	3.53	5.15	6.53
4	1.00	1.11	5.46	1.70	1.40	3.46	1.97	1.38	1.88	4.18	5.28	6.43
5	1.25	1.13	5.58	1.74	1.50	3.69	2.11	1.40	1.90	4.23	5.31	6.31
6	1.50	1.04	5.11	1.59	1.47	3.62	2.06	1.28	1.74	3.86	5.31	6.36
7	2.00	0.95	4.69	1.46	1.41	3.47	1.98	1.21	1.65	3.67	5.51	6.41

Table B.4 Metal removal by EDTA **Soil/solution ratio: 5g/40mL**

No.	EDTA concentration (mM)	Removed Cu		Cu Removal efficiency (%)	Removed Cd		Cd Removal efficiency (%)	Removed Pb		Pb Removal efficiency (%)	Initial pH	Final pH
		mg/l	%		mg/l	%		mg/l	%			
1	0.00	0.65	3.21	3.21	0.71	1.75	1.75	0.33	0.45	0.45	6.38	6.28
2	1.00	12.3	60.5	60.5	26.9	66.3	66.3	45.3	61.8	61.8	5.13	5.60
3	2.50	14.8	72.8	72.8	30.5	75.3	75.3	49.2	67.0	67.0	4.72	5.51
4	5.00	16.5	81.3	81.3	34.0	84.0	84.0	54.6	74.4	74.4	4.70	4.82
5	7.50	18.0	88.7	88.7	36.5	90.2	90.2	62.1	84.7	84.7	.4.70	4.62
6	10.00	18.8	92.8	92.8	38.1	94.1	94.1	66.4	90.5	90.5	4.69	4.58
7	15	19.1	94.5	94.5	39.2	96.8	96.8	66.9	91.2	91.2	4.67	4.50

Table B.5 Metal removal by combinations of the surfactants and the chelating agent

Soil/solution ratio: 5g/40mL

No.	Combination	Removed Cu (mg/L)	Cu Removal efficiency (%)	Removed Cd (mg/L)	Cd Removal efficiency (%)	Removed Pb (mg/L)	Pb Removal efficiency (%)	Initial pH	Final pH
1	Distilled water	0.65 (1)	3.21 (2)	0.71 (3)	1.75 (4)	0.33 (5)	0.45 (6)	6.38	6.28
2	1mM EDTA	12.3	60.5	26.9	66.3	45.3	61.8	5.13	5.60
3	10mM SDS	3.60	17.8	20.5	50.5	9.6	13.1	6.45	6.46
4	1mM EDTA + 10mM SDS	18.70	92.2	40.3	99.5	62.4	85.1	5.47	6.72
5	0.25mM Tx-100	1.33	6.6	1.62	3.99	1.04	1.42	4.27	6.49
6	1mM EDTA+ 0.25mM Tx-100	15.9	78.5	32.7	80.8	50.5	68.9	5.13	5.98
7	1.25 Mm AOT	1.13	5.58	1.50	3.69	1.40	1.90	5.31	6.31

Table B.5 (cont.) metal removal by combinations of the surfactants and the chelating agent **Soil/solution ratio: 5g/40mL**

No.	combination	Removed Cu (mg/L)	Cu Removal efficiency (%)	Removed Cd (mg/L)	Cd Removal efficiency (%)	Removed Pb (mg/L)	Pb Removal efficiency (%)	Initial pH	Final pH
8	1mM Na_2EDTA + 1.25mM AOT	14.8	72.9	31.7	78.3	51.3	70	5.17	5.88

Calculation details:

Cu removal efficiency $= [(0.65^{(1)}\, mg/L \times 40mL \times 10^{-3}\, L/mL) \div (5g \times 10^{3}\, mg/g \times 162mg/Kg \times 10^{-6}\, Kg/mg)] \times 100 = 3.21^{(2)}\%$

Cd removal efficiency $= [(0.71^{(3)}\, mg/L \times 40mL \times 10^{-3}\, L/mL) \div (5g \times 10^{3}\, mg/g \times 324mg/Kg \times 10^{-6}\, Kg/mg)] \times 100 = 1.75^{(4)}\%$

Pb removal efficiency $= [(0.33^{(5)}\, mg/L \times 40mL \times 10^{-3}\, L/mL) \div (5g \times 10^{3}\, mg/g \times 587mg/Kg \times 10^{-6}\, Kg/mg)] \times 100 = 0.45^{(6)}\%$

APPENDIX C

Results of column studies

Table C.1 Metal removal from column by distilled water (flow rate: 12mL/min) **Pore volume = 103 mL**

No.	pore volumes	Cu (II) concentration in the effluent (mg/L)	Cu (II) removal efficiency (%)	Cd (II) concentration in the effluent (mg/L)	Cd (II) removal efficiency (%)	Pb (II) concentration in the effluent (mg/L)	Pb (II) removal efficiency (%)	pH
0	0	0	0	0	0	0	0	
1	1(1)	44.17(2)	6.24(3)	30.14	2.13	2.54	0.10	5.41
2	2(4)	3.02(5)	6.67(6)	41.21	5.04	5.86	0.33	6.04
3	3	2.25	6.99	32.25	7.32	5.65	0.55	6.09
4	4	1.84	7.25	13.56	8.28	4.71	0.73	6.25
5	5	0.99	7.39	2.15	8.43	3.73	0.88	6.20
6	6	0.76	7.49	1.51	8.54	2.74	0.98	6.17
7	7	2.80	7.89	0.95	8.60	1.93	1.06	6.16
8	8	0.43	7.95	0.61	8.65	1.06	1.10	6.16
9	9	0.32	7.99	0.39	8.67	0.75	1.13	6.22
10	10	0.22	8.03	0.34	8.70	0.51	1.15	6.20
11	15	0.15	8.13	0.15	8.75	0.13	1.17	6.11
12	20	0.02	8.15	0.09	8.78	0.03	1.18	6.08
13	25	0.00	8.15	0.04	8.80	0.00	1.18	6.01
14	30	0.00	8.15	0.01	8.80	0.00	1.18	5.96
15	35	0.00	8.15	0.00	8.80	0.00	1.18	5.99
16	40	0.00	8.15	0.00	8.80	0.00	1.18	6.10
17	45	0.00	8.15	0.00	8.80	0.00	1.18	6.12
18	50	0.00	8.15	0.00	8.80	0.00	1.18	6.05

Calculation details:

$$[(103mL \times 10^{-3}\,L/mL \times 1^{(1)} \times 44.17^{(2)}\,mg/L) \div (450g \times 10^{-3}\,Kg/g \times 162mg/Kg)] \times 100 = 6.24^{(3)}\%$$

$$6.24^{(3)}\% + [(103mL \times 10^{-3}\,L/mL \times (2^{(4)} - 1^{(1)}) \times 3.02^{(5)}\,mg/L) \div (450g \times 10^{(-3)}\,Kg/g \times 162mg/Kg)] \times 100 = 6.67^{(6)}\%$$

Table C.2 Metal removal from column by 10mM SDS (flow rate: 12mL/min) **Pore volume = 103 mL**

No.	pore volumes	Cu (II) concentration in the effluent (mg/L)	Cu (II) removal efficiency (%)	Cd (II) concentration in the effluent (mg/L)	Cd (II) removal efficiency (%)	Pb (II) concentration in the effluent (mg/L)	Pb (II) removal efficiency (%)	pH
0	0	0	0	0	0	0	0	
1	1	16.10	2.27	45.32	3.20	66.41	2.59	5.69
2	2	16.90	4.66	40.05	6.03	66.49	5.18	6.14
3	3	16.89	7.05	35.04	8.51	64.61	7.70	6.30
4	4	16.21	9.34	33.20	10.85	59.07	10.00	6.53
5	5	16.58	11.68	32.18	13.13	56.09	12.19	6.68
6	6	15.85	13.92	30.49	15.28	52.92	14.26	6.64
7	7	14.99	16.04	29.21	17.34	49.86	16.20	6.66
8	8	14.54	18.09	28.14	19.33	48.17	18.08	6.66
9	9	13.94	20.06	27.19	21.25	46.68	19.90	6.67
10	10	13.11	21.92	26.25	23.11	44.41	21.63	6.67
11	15	11.36	29.94	22.25	30.96	36.87	28.82	6.70
12	20	9.70	36.79	19.18	37.74	30.01	34.67	6.64
13	25	8.30	42.66	16.58	43.60	24.23	39.39	6.22
14	30	7.16	47.71	14.81	48.83	19.53	43.20	5.78
15	35	5.95	51.92	13.52	53.60	15.10	46.14	5.64
16	40	5.16	55.56	12.77	58.11	11.18	48.32	5.52
17	45	4.64	58.84	12.15	62.41	9.40	50.16	5.51
18	50	4.11	61.74	11.73	66.55	7.14	51.55	5.45

Table C.3 Metal removal from column by 1mM EDTA alone (flow rate: 12mL/min) **Pore volume = 103 mL**

No.	pore volumes	Cu (II) concentration in the effluent (mg/L)	Cu (II) removal efficiency (%)	Cd (II) concentration in the effluent (mg/L)	Cd (II) removal efficiency (%)	Pb (II) concentration in the effluent (mg/L)	Pb (II) removal efficiency (%)	pH
0	0	0	0	0	0	0	0	
1	1	12.20	1.72	40.13	2.83	63.28	2.47	5.33
2	2	14.36	3.75	31.92	5.09	64.42	4.98	5.81
3	3	15.11	5.89	31.54	7.32	66.07	7.56	5.82
4	4	16.31	8.19	30.80	9.49	66.07	10.13	5.85
5	5	15.57	10.39	30.21	11.63	64.08	12.63	5.90
6	6	15.90	12.64	30.24	13.76	62.92	15.08	5.92
7	7	15.78	14.87	29.66	15.86	62.05	17.50	6.01
8	8	16.31	17.17	29.71	17.96	62.31	19.93	5.99
9	9	15.21	19.32	29.73	20.06	60.58	22.30	6.01
10	10	15.72	21.54	29.94	22.17	59.14	24.60	6.11
11	15	13.66	31.19	27.99	32.06	48.67	34.09	6.12
12	20	15.82	42.37	25.41	41.04	38.30	41.56	6.11
13	25	8.85	48.62	21.58	48.66	22.56	45.96	6.10
14	30	7.34	53.81	18.72	55.27	17.89	49.44	6.12
15	35	5.52	57.71	15.95	60.90	11.54	51.69	6.06
16	40	4.24	60.70	14.17	65.91	6.15	52.89	5.26
17	45	3.39	63.10	12.90	70.47	2.74	53.43	5.11
18	50	3.21	65.36	11.23	74.43	1.34	53.69	5.30

Table C.4 Metal removal from column by 1mM EDTA + 10mM SDS (flow rate: 12mL/min) Pore volume = 103 mL

No.	pore volumes	Cu (II) concentration in the effluent (mg/L)	Cu (II) removal efficiency (%)	Cd (II) concentration in the effluent (mg/L)	Cd (II) removal efficiency (%)	Pb (II) concentration in the effluent (mg/L)	Pb (II) removal efficiency (%)	pH
0	0	0	0	0	0	0	0	
1	1	23.70	3.35	51.69	3.65	73.72	2.87	6.13
2	2	25.36	6.93	44.87	6.82	71.86	5.68	6.47
3	3	24.33	10.37	42.58	9.83	78.89	8.75	6.57
4	4	25.67	14.00	40.48	12.69	67.87	11.40	6.66
5	5	21.66	17.06	39.33	15.47	63.55	13.88	6.72
6	6	21.82	20.14	37.87	18.14	62.59	16.32	6.89
7	7	21.69	23.20	36.87	20.75	60.92	18.69	6.90
8	8	21.16	26.19	35.55	23.26	58.74	20.98	6.91
9	9	19.24	28.91	33.27	25.61	57.06	23.21	6.93
10	10	17.71	31.41	32.27	27.89	51.27	25.21	6.95
11	15	12.29	40.10	27.62	37.65	41.16	33.23	7.03
12	20	10.06	47.20	24.11	46.16	33.49	39.76	7.02
13	25	8.61	53.29	21.87	53.89	27.58	45.14	6.87
14	30	7.44	58.54	16.21	59.61	23.05	49.63	5.83
15	35	6.30	62.99	18.91	66.29	18.55	53.25	5.54
16	40	5.93	67.18	18.35	72.77	16.51	56.47	5.45
17	45	5.62	71.15	17.86	79.08	14.55	59.31	5.43
18	50	3.51	73.63	15.03	84.39	12.33	61.71	5.41
19	51	26.32	77.35	23.81	86.07	75.47	64.65	7.24
20	52	14.62	79.42	12.67	86.97	58.41	66.93	7.22
21	53	10.49	80.90	8.08	87.54	34.65	68.28	7.20
22	54	8.46	82.09	5.29	87.91	24.09	69.22	7.02
23	55	7.11	83.10	3.61	88.17	20.66	70.03	7.10

Table C.5 Metal removal from column by 1mM EDTA + 10mM SDS (flow rate: 4mL/min) Pore volume = 103 mL

No.	pore volumes	Cu (II) concentration in the effluent (mg/L)	Cu (II) removal efficiency (%)	Cd (II) concentration in the effluent (mg/L)	Cd (II) removal efficiency (%)	Pb (II) concentration in the effluent (mg/L)	Pb (II) removal efficiency (%)	pH
0	0	0	0	0	0	0	0	
1	1	15.51	2.19	51.09	3.61	68.56	2.67	5.68
2	2	16.93	4.58	47.31	6.95	67.26	5.30	6.04
3	3	17.78	7.10	45.40	10.16	65.47	7.85	6.22
4	4	19.50	9.85	43.61	13.24	73.28	10.71	6.42
5	5	20.08	12.69	42.20	16.22	64.59	13.22	6.56
6	6	20.64	15.60	40.33	19.07	62.03	15.64	6.71
7	7	21.70	18.67	39.63	21.87	61.75	18.05	6.89
8	8	26.41	22.40	37.47	24.52	59.24	20.36	7.29
9	9	22.19	25.54	27.40	26.45	59.18	22.67	7.32
10	10	21.03	28.51	34.98	28.92	56.13	24.86	7.39
11	15	16.79	40.37	29.01	39.17	42.88	33.22	7.35
12	20	13.90	50.19	25.16	48.06	34.44	39.93	7.33
13	25	11.84	58.55	22.13	55.87	33.00	46.37	7.32
14	30	9.23	65.07	21.25	63.38	32.12	52.63	7.31
15	35	8.01	70.73	20.59	70.65	25.16	57.53	7.28
16	40	5.25	74.44	18.03	77.02	20.12	61.46	7.30
17	45	4.58	77.68	16.08	82.70	17.54	64.88	7.33
18	50	2.07	79.14	13.05	87.31	10.52	66.93	7.32

Table C.6 Metal removal from column by 1mM EDTA + 10mM SDS (flow rate: 20mL/min) Pore volume = 103 mL

No.	pore volumes	Cu (II) concentration in the effluent (mg/L)	Cu (II) removal efficiency (%)	Cd (II) concentration in the effluent (mg/L)	Cd (II) removal efficiency (%)	Pb (II) concentration in the effluent (mg/L)	Pb (II) removal efficiency (%)	pH
0	0	0	0	0	0	0	0	
1	1	16.10	2.27	45.32	3.20	66.41	2.59	5.69
2	2	16.90	4.66	40.05	6.03	66.49	5.18	6.14
3	3	16.89	7.05	35.04	8.51	64.61	7.70	6.30
4	4	16.21	9.34	33.20	10.85	59.07	10.00	6.53
5	5	16.58	11.68	32.18	13.13	56.09	12.19	6.68
6	6	15.85	13.92	30.49	15.28	52.92	14.26	6.64
7	7	14.99	16.04	29.21	17.34	49.86	16.20	6.66
8	8	14.54	18.09	28.14	19.33	48.17	18.08	6.66
9	9	13.94	20.06	27.19	21.25	46.68	19.90	6.67
10	10	13.11	21.92	26.25	23.11	44.41	21.63	6.67
11	15	11.36	29.94	22.25	30.96	36.87	28.82	6.70
12	20	9.70	36.79	19.18	37.74	30.01	34.67	6.64
13	25	8.30	42.66	16.58	43.60	24.23	39.39	6.22
14	30	7.16	47.71	14.81	48.83	19.53	43.20	5.78
15	35	5.95	51.92	13.52	53.60	15.10	46.14	5.64
16	40	5.16	55.56	12.77	58.11	11.18	48.32	5.52
17	45	4.64	58.84	12.15	62.41	9.40	50.16	5.51
18	50	4.11	61.74	11.73	66.55	7.14	51.55	5.45