

An-Najah National University

Faculty of Graduate Studies

**The Influence Of Surfactants On The Adsorption
Of Heavy Metal Ions Using Inorganic Legands In
Selected Contaminated Soil Samples In Palestine**

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the Degree of Doctoral of Chemistry, Faculty of Graduate Studies, An-
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Dedication

To my parents

To my lovely wife

To my sons:

Attia

Haneen

Mohammad

Mahmoud

Muhi-Aldeen

Omar

Acknowledgement

I am most thankful to my thesis advisors, Prof. Dr. **Radi Salim** and Assoc. Prof. Dr. **Shehdeh Joudeh** for their guidance, support and patience throughout these years. I would also like to thank my committee members, Prof. Dr. **Ibrahim Kayali**, and Prof. Dr. **Ali Z. AbuZuhri**, for their valuable time, insightful questions and suggestions.

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إقرار

أنا الموقع / ة أدناه ، مقدم / ة الرسالة التي تحمل العنوان : -----

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LIST OF SYMBOLS AND ABBREVIATIONS

AAS	Atomic absorption spectrophotometry
ANOVA	Analysis of variance
ASTM	American Society for Testing and Materials
Car	Carbonate bound
CEC	Concentration of readily Exchangeable Cations
[CdI] ⁺	Cadmium monoiodide
[CdI ₃] ⁻	Cadmium trichloride
[CdI ₄] ²⁻	Cadmium tetraiodide
[Cd (NCS)] ⁺	Cadmium monothiocyanate
Cd(NO ₃) ₂ . 4H ₂ O	Cadmium nitrate tetrahydrate
CEC	Cation exchange capacity
CI	Confidence interval
CMC	Critical micelle concentration
CTAB	Hexadecyltrimethylammonium bromide
EDTA	Ethylenediaminetetraacetic acid
Ex	Exchangeable
GC-MS	Gas Chromatography-mass Spectrophotometry
h	Hour
HA	Humic acid
HCB	Hexachlorobenzene
HOCs	Hydrophobic organic compounds
K	First-order rate coefficient (mg kg ⁻¹ min ⁻¹)

LSD	Least square difference
MgCl ₂	Magnesium chloride
Min	Minute
MW	Molecular weight
<i>n</i>	Surfactant alkyl chain length
NH ₂ OH.HCl	Hydroxylamine hydrochloride
NPL	National priority lists
NTA	Nitrilotriacetic acid
Org	Organic matter bound
Ox	Oxide bound
PAHs	Polycyclic aromatic hydrocarbons
PCBs	Polychlorinated biphenyls
PDA	Pyridine-2, 6-dicarboxylic acid
PEO	Polyethylene oxide
R ²	Coefficient of determination
Res	Residual
Sol	Soluble
SOM	Soil organic matter
t	Time
TCP	Tetrachlorophenol
TOM	Total Organic Matter

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ABSTRACT

Heavy metals are persistent pollutants in the environment. Problems associated with the cleanup of sites contaminated by metals have demonstrated the need to develop remediation technologies that are feasible, quick, and effective in a wide range of physical settings. Experiments were conducted to investigate the efficiency of surfactants and ligands on cleanning artificially contaminated red, sandy and white chalk soil samples with heavy metals e.g. (Cd (II), Cu (II), Pb (II) and Zn (II)).

Before contamination, soils were characterized to determine particle size, pH, organic matter content and heavy metal contents.

The results of experimental sorption data fitted very well the Freundlich isotherm model and first order kinetics model.

In this study we have investigated the adsorption of Cd (II), Cu (II), Pb (II) and Zn (II) onto each soil in single and multi-element systems as a function of soil and heavy metal concentrations.

The best pH for adsorption of Cu^{2+} on red soil was found to be 4.0. Adsorption of metals on soil increased in the order $\text{Cu} > \text{Pb} > \text{Zn} \approx \text{Cd}$.

This trend might be related to the increase in the electronegativity of the metal ion.

Surfactants are efficient soil remediation agents for heavy metals. Various concentrations of four different surfactants Triton; X-100, SDS, Tergitol and Tween 80 were used as washing solution for remediation of contaminated soils. Triton X-100 (0.1 M) was the best surfactant to desorb copper from red soil. Tween 80 was the best surfactant to desorb copper from sandy and white chalk soils.

Recently, ligands were enhancing surfactants to desorb heavy metals from contaminated soils. Surfactants in combination with ligands were tested as washing agents for contaminated soils. Different concentrations of three different ligands (I^- , SCN^- and EDTA) along with nonionic surfactant, Triton X-100 were applied as soil washing agents to desorb copper from artificially contaminated soils. Triton X-100 with 0.1 M EDTA showed a higher capacity to desorb copper than did with 0.4 M SCN^- or 0.4 M I^- .

The increase of ligand concentration was a critical factor for increasing leaching capacity. Without the presence of a ligand, the surfactant alone was not able to desorb copper effectively from soil.

CHAPTER 1
INTRODUCTION

1.1. Problem Statement

Heavy metals are one of the most important and frequent soil and sediment contaminants (Riley and Zachara, 1992). Jaffe *et al.* (2003) found significant amounts of various trace metals, including zinc (Zn), lead (Pb), cadmium (Cd), chromium (Cr) and cobalt (Co), along with petroleum hydrocarbons, PAHs, and chlorinated hydrocarbons in marine sediment. They noted that important sources of contamination include industrial and agricultural activities. According to Ho and Hui (2001), high levels of PCBs, PAHs, as well as copper (Cu) and Zn were found in river sediments in an industrial area surrounded by a densely populated area, suggesting that the sources of contamination are related to human activities, such as domestic and industrial discharges, agricultural chemical applications and soil erosion. Industrialized urban areas are often contaminated with both heavy metals and organics such as PAHs and PCBs. Weiss *et al.* (1994) showed that in industrialized areas, particularly those with chemical and steel industries, and densely populated urban areas, soil was contaminated with both heavy metals and organics.

Heavy metals often affect human health, because humans are exposed to heavy metals in soil through the food chain and by direct ingestion of soil particles (Brams *et al.*, 1988). Heavy metals such as Cd and Hg acquired through breathing can cause lung damage and kidney disease (ATSDR, 1999a; ATSDR, 1999b). Lead can affect every organ and system in the human body, and at high levels, causes weakness in

fingers and wrist and damage the nervous system and kidneys (ATSDR, 1999c).

Heavy metals are presently washed from contaminated soils with organic/inorganic acids, chelating agents and surfactants (Reddy *et al.*, 2000; Wasay *et al.*, 2001; Doong *et al.*, 1998). Acids can extract metals from soils since metals become mobile when the soil pH drops under 6.0. Chelating agents, such as ethylenediaminetetraacetic acid (EDTA), are also widely used for metal leaching from soils, because of their capacity to complex with metals. However, strong acids and chelating agents also leach out important quantities of soil nutrients and alter the soil properties. Several mechanisms have been suggested as to how surfactants along with alkali or acid solutions enhance metal leaching: ion exchange, electrostatic interaction, and solubilization (Okuda *et al.*, 1996; Huang *et al.*, 1997; Doong *et al.*, 1998; Hong *et al.*, 2002). Because surfactants are more specific and less aggressive, they are less damaging to soil environment.

Polychlorinated biphenyls (PCBs) are mixtures of a maximum of 209 individual chlorinated compounds. Humans can come in contact with them by eating contaminated foods such as fish, meat and dairy products from contaminated source or by breathing air near hazardous waste sites.

Solubilization results from the partitioning of contaminants into the hydrophobic core of surfactant micelles. Therefore, contaminant solubilization increases with the number of micelles in solution.

In soils, heavy metal ions can be present as soluble compounds like ions and metal complexes or as exchangeable forms. However, heavy metals are generally rendered immobile by associating with different soil fractions and compartments such as carbonate, oxide, hydroxide, organic matter and residual materials (Huang *et al.*, 1995; Tan, 1998). The mobility of heavy metals is often affected by various factors including pH, redox potential, nature of soil components and cation exchange capacity (CEC). In the case of hydrophobic contaminants, soil organic matter (SOM) is mainly responsible for the sorption of contaminants, particularly those which are nonionic in nature.

Molecular adsorption mainly occurs through Van der Waals attraction and hydrogen bonding, and hydrophobic bonding to soil humic and fulvic acids (Tan, 1998; Kookana *et al.*, 2002).

Since they have relatively little impact on the soil environment compared to strong acid and chelating agent, surfactants are promising agents for the remediation of soils contaminated by either heavy metals or organics. However, one type of surfactant alone can only effectively desorb a single type of contaminant, either hydrophilic heavy metals or hydrophobic organics.

Recently, it has been demonstrated that ligand ions can form hydrophobic complexes with heavy metals (Umebayashi *et al.*, 1997; Shin *et al.*, 2000). Specific ligand ions can form complexes with specific heavy metals in the surfactant solution, and, as a result, the metal-ligand complex becomes hydrophobic and can be desorbed by the surfactant

micelle. This leads to the simultaneous desorption of both heavy metals and hydrophobic organics by a single surfactant-ligand solution.

1.2. Potential for Developing Dual Purpose Surfactants

Surfactants are amphiphilic compounds containing both hydrophobic and hydrophilic groups allowing them to both solubilize lipophilic compounds, and remain soluble in water. Specific types of surfactants can remove heavy metals, but are then ineffective in removing organics.

At the surface of the solution, the surfactant molecules orient themselves with the hydrophilic groups extending in the water phase while the hydrophobic groups extend in the other direction. This oriented surface film lowers the surface tension of the water. The surfactant forms a micelle or an aggregate when a critical micelle concentration (CMC) is reached. The CMC is defined as the minimum concentration necessary to initiate micelle formation (Swisher, 1970). Efficient surfactants have a low critical micelle concentration because less surfactant is needed to decrease the surface tension.

Above the CMC, surfactant micelles offer a hydrophobic moiety and a hydrophilic moiety. Thus, hydrophobic contaminants can be easily desorbed from contaminated sites and solubilized within the hydrophobic cores of micelles. Also, the micellar phase has the potential to solubilize heavy metals via electrostatic forces or other chemical interactions. But this occurs only with ionic surfactants and these are ineffective in removing organics.

Numerous studies on the complexation behavior of heavy metals with ligand ions in presence of surfactant solution have been reported (Umebayashi *et al.*, 1997; Shin *et al.*, 2000; Umebayashi *et al.*, 2001). The complexation of heavy metals can be enhanced by ligands in the presence of surfactant solution.

Complexation of Cd (II) ion with ligands, such as thiocyanate (SCN^-) and iodide (I^-) ions, have been studied in micellar solutions of a nonionic surfactant (Umebayashi *et al.*, 1997). For Cd (II)- SCN^- system, $[\text{Cd}(\text{NCS})]^+$ and $[\text{Cd}(\text{NCS})(\text{SCN})]$ were formed in aqueous solution, whereas $[\text{Cd}(\text{NCS})_2(\text{SCN})]^-$ was favored in micelles, though the complexation in micelles was not outstanding. With the Cd (II)-I- system, $[\text{CdI}]^+$, $[\text{CdI}_3]^-$, and $[\text{CdI}_4]^{2-}$ were formed in aqueous solution whereas $[\text{CdI}_3]^-$ and $[\text{CdI}_4]^{2-}$ were formed in micelles. The formation of Cd^{2+} -I⁻ complex in micelles were established by large negative enthalpies of transfer of $[\text{CdI}_3]^-$ and $[\text{CdI}_4]^{2-}$ from aqueous solution to micelles. Thus, a hydrophobic complex with no capacity to form strong hydrogen bonds in water did show strong affinity to micelles.

Although to date, research using the complexation behavior of heavy metals with ligand ions in surfactant solution, has been limited to the decontamination of solutions, but it may also be feasibly applied to contaminated soils. (Fillipi *et al.*, 1997; Akita *et al.*, 1999). Specific ligand ions can extract heavy metals from soils to make complexes and then, the complexes can be solubilized in surfactant micelles. Once specific metals form complexes with specific ligand ions, metal complexes become

relatively hydrophobic, suggesting the possibility of simultaneous removal of metal complexes and organics from soil due to their similar chemical characteristics in terms of hydrophobicity as reported by Abu Zuhri et al., 1987.

1.3 Aim of the work

Where in the past, surfactants alone were used to remediate contaminated soils; this project will innovate by testing surfactants along with a ligand to simultaneously desorb heavy metals.

The general research objective was to test different combinations of ligands and surfactants to desorb heavy metals from three types of contaminated soils.

The more specific research objectives pertain to the remediation of soils contaminated with heavy metals like Cd, Cu, Zn and Pb are:

- 1) To measure the effect of soil concentration on the adsorption of heavy metals on soil.
- 2) To establish which kinetic model best reproduces the complexation and desorption of heavy metals from a contaminated soil, when using a surfactant along with a ligand.
- 3) To measure the effect of pH on adsorption of metal ions on red soil.
- 4) To study the effect of presence of competing ions on the adsorption of heavy metal on red, white chalk and sandy soil.
- 5) To measure the heavy metals desorption efficiency of four different surfactants (Triton X-100, Tween 80, SDS and Tergitol) from three types of contaminated soil in the absence of ligands.

6) To measure the heavy metal desorption efficiency of a surfactant, Triton X-100, with different ligand ions (I^- , SCN^- and EDTA) with three types of contaminated soil.

CHAPTER 2
LITERATURE REVIEW

2.1. Heavy Metals

Heavy metals are chemical elements with a specific gravity that is at least 5 times the specific gravity of water. Heavy metals are often problematic environmental pollutants, with well-known toxic effects on living systems. They are introduced into the environment during mining, refining of ores, combustion of fossil fuels and industrial processes. They cannot be degraded or destroyed (Davydova et al., 2005). To a small extent they enter our bodies via food, drinking water and air. As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning.

2.1.1. Toxicity of Metals

The presence of metals in water and soils can pose a significant threat to human health and ecological systems. Heavy metal toxicity represents an uncommon, yet clinically significant, medical condition. If unrecognized or inappropriately treated, heavy metal toxicity can result in significant mortality. Many metals are essential to biochemical processes in correct concentrations but at higher doses, heavy metals can cause negative health effects such as irreversible brain damage. Some metals such as lead and mercury easily cross the placenta and damage the brain (Levine et al., 2006).

The main toxic effects of the metals studied in this work are summarized in Table (2.1) from the longer list given by Levine et al., 2006.

Table 2.1 The Main Toxic Effects of Metals Studied in This Work

Metal	Effects
Lead	Hypertension and chronic kidney disease
Cadmium	Human carcinogen
Copper	Brain and Liver damage
Zinc	Hemolytic anemia

2.1.2. Mobility and Speciation of Metals in Water and in Soil

Understanding the environmental behavior of a metal by determining its speciation, mobility and occurrence is of paramount importance. The term speciation is related to the distribution of an element among its chemical forms or species. Heavy metals can occur in several forms in water and in soil (Catherine et al., 2002). Based on this information the

most appropriate method for soil and water remediation can be determined (Gerber et al., 1991). Soils are significant sinks of metals, while water represents an important pathway for the dispersion of metals over extremely large areas (Gäbler et al., 1997, Gerber et al., 1991).

The mobility of a metal in soil and in water depends significantly on the chemical form and the speciation of the metal. The mobility of metals in ground-water systems is hindered by reactions that cause metals

to adsorb or precipitate, or chemistry that tends to keep metals associated with the solid phase and prevents them from dissolving. These mechanisms can retard the movement of metals and also provide a long-term source of metal contamination. While various metals undergo similar reactions in a number of aspects, the extent and nature of these reactions vary under particular conditions (Gerber et al., 1991, Levine et al., 2006).

Studies on the mobility of heavy metals in soils have shown that the mobility is strongly influenced by several factors, e.g. pH redox potential, clay mineral content, organic matter content and water content. Various processes, e.g., adsorption-desorption, complex and ion-pair formation or activities of micro organisms are also involved (Gäbler et al., 1997).

Simple and complex cations are the most mobile, exchangeable cations in organic and inorganic complexes are of medium mobility and, chelated cations are slightly mobile (Catherine et al., 2001, Gäbler et al., 1997). Metals in organic particles are only mobile after decomposition or weathering. Precipitated metals are mobile under dissolution conditions (e.g. change in pH) (Catherine et al., 2002).

2.2. Effect of Soil Properties

Chemical and physical properties of the contaminated matrix influence the mobility of metals in soils and groundwater (Catherine et al., 2002, Gerber et al. 199). 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 influence the

form of the metal contaminant, its mobility, and the technology selected for remediation (Gerber et al. 1991).

2.2.1. Chemical Properties

The presence of inorganic anions (carbonate, phosphate, sulphide) in the soil water can influence the soil's ability to fix metals chemically (Levine et al., 2006). These anions can form relatively insoluble complexes with metal ions and cause metals to desorb and precipitate in their presence. Soil pH values generally range between 4.0 and 8.5 with buffering by Al at low pH and by CaCO₃ at high pH. Metal cations are most mobile under acidic conditions while anions tend to sorb to oxide minerals in this pH range. At high pH, cations precipitate or adsorb to mineral surfaces but metal anions are mobilized.

The presence of hydrous metal oxides of Fe, Al, Mn can strongly influence metal concentrations because these minerals can remove cations and anions from solution by ion exchange, specific adsorption and surface precipitation (Gerber et al. 1991). Sorption of metal cations onto hydrous oxides generally increases sharply with pH and is most significant at pH values above the neutral range, while sorption of metal anions is greatest at low pH and decreases as pH is increased. Cation exchange capacity (CEC) refers to the concentration of readily exchangeable cations on a mineral surface and is often used to indicate the affinity of soils for uptake of cations such as metals. Anion exchange capacity (AEC) indicates the affinity of soils to uptake anions, and is usually significantly lower than the CEC of the soil. In addition to hydrous oxides, clays are also

important ion exchange materials for metals. The presence of natural organic matter (NOM) has been shown to influence the sorption of metal ions to mineral surfaces. The natural organic matter has been observed to enhance sorption of Cu^{2+} at low pH, and suppress Cu^{2+} sorption at high pH (Gerber et al. 1991).

2.2.2. Physical Properties

Particle size distribution can influence the level of metal contamination in a soil. Fine particles ($<100\mu\text{m}$) are more reactive and have a higher surface area than coarser material. As a result, the fine fraction of a soil often contains the majority of contamination. The distribution of particle sizes with which a metal contaminant is associated can determine the effectiveness of a number of metal remediation technologies, for example, soil washing (Levine et al., 2006, Gerber et al. 1991).

Moisture influences the chemistry of contaminated soil. The amount of dissolved minerals, pH and redox potential of the soil water depend on the soil moisture content. Soil structure describes the size, shape, arrangement and degree of development of soils into structural units. Soil structure can influence contaminant mobility by limiting the degree of contact between groundwater and contaminants. It has been demonstrated that the speciation of trace metals in natural soils depends on the physical and chemical characteristics of the soil. Soil pH, redox potential and organic, carbonate, clay and oxide content of soil all influence metal speciation and mobility. A study by Kabata (et al., 1992)

showed that zinc and cadmium in soil are mostly associated with exchangeable, water soluble and organic fractions. Copper is mainly organically bound and exchangeable, whereas, lead is slightly mobile and bound to the residual fraction (Catherine et al., 2002, Kabata et al., 1992).

After discharge to an aquatic environment, metals are partitioned between solid and liquid phases. Within each phase, further partitioning occurs among ligands as determined by ligand concentrations and metal-ligand bond strengths. In solid phases, soil, sediment, and surface water particulates, metals may be partitioned into six fractions: (a) dissolved, (b) exchangeable, (c) carbonate, (d) iron-manganese oxide, (e) organic, and (f) crystalline (Elder et al., 1989). Partitioning of a metal ion between these fractions is affected strongly by variations in pH, redox state, organic content, and other environmental factors. The dissolved fraction consists of carbonate complexes, which its abundance increases with pH. Metals in solution, including metal cation and anion complexes and hydrated ions have solubilities which are affected strongly by pH and tend to increase with decreasing the pH of soil.

Exchangeable fractions consist of metals bound to colloidal or particulate material (Elder et al., 1989, Gerber et al. 1991).

Metals associated with carbonate minerals in soil constitute the carbonate fraction, which can be newly precipitated in soil (Salomons et al., 1995). The iron-manganese oxide fraction consists of metals adsorbed to iron-manganese oxide particles or coatings. The organic fraction consists of metals bound to various forms of organic matter. The

crystalline fraction consists of metals contained within the crystal structure of minerals and normally not available to biota. Hydrogen ion activity (pH) is probably the most important factor governing metal speciation, solubility from mineral surfaces, transport, and eventual bioavailability of metals in aqueous solutions. The pH affects both solubility of metal hydroxide minerals and adsorption-desorption processes. Most metal hydroxide minerals have very low solubilities under pH conditions in natural water (Salomons et al., 1995, Elder et al., 1989). Adsorption, which occurs when dissolved metals are attached to surfaces of particulate matter (notably iron, manganese, and aluminium oxide minerals, clay, and organic matter), is also strongly dependent on pH and, of course, the availability of particulate surfaces and total dissolved metal content. Metals tend to be adsorbed at different pH values and sorption capacity of oxide surfaces generally varies from near 0 percent to near 100 percent over a range of about 2 pH units (Bourg et al., 1988, Elder et al., 1989).

The adsorption edge, the pH range over which the rapid change in sorption capacity occurs, varies among metals. The results in precipitation of different metals over a large range of pH units. Consequently, mixing metal-rich acidic water with higher pH metal-poor water may result in dispersion and separation of metals as different metals are adsorbed onto various media over a range of pH values. Cadmium and zinc tend to have adsorption edges at higher pH values than iron and copper, and consequently they are likely to be more mobile and more widely

dispersed. Adsorption edges also vary with concentration of the complexing agent. Thus, increasing the concentration of complexing agent increases the pH of the adsorption edge (Bourg et al., 1988). Major cations such as Mg^{2+} and Ca^{2+} also compete for adsorption sites with metals and can reduce the amount of metal adsorption.

Particulate size and resulting total surface area available for adsorption are both important factors in the adsorption processes and can affect metal bioavailability (Luoma et al., 1989). Small particles with large surface area to mass ratios allow more adsorption than an equivalent mass of large particles with small surface area to mass ratios. Reduced adsorption can increase metal bioavailability by increasing concentrations of dissolved metals in associated water. The size of particles released during mining depends on mining and beneficiation methods. Finely milled ore may release much smaller particles that can both be more widely dispersed by water and wind, and which can also serve as sites of enhanced adsorption. Consequently, mine tailings released into fine-grained sediment such as silty clays found in many places can have much lower environmental impact than those released into sand or coarse-grained sediment with lower surface area and adsorption (Elder et al., 1989). Temperature exerts an important effect on metal speciation, because most chemical reaction rates are highly sensitive to temperature changes (Luoma et al., 1983). An increase of 10 °C can double the biochemical reaction rate. This is often the driving force in earth surface conditions for reactions that are kinetically slow, and enhance the

tendency of a system to reach equilibrium. Temperature may also affect the quantities of metal uptake by an organism because the biological process rates (as noted above) typically double with every 10 °C temperature increment (Luoma et al., 1983). Because increased temperature may affect both influx and efflux rates of metals, the net bioaccumulation may or may not increase (Luoma et al., 1983).

The chemical form and speciation of some of the more important metals are discussed below. The influence of the chemical form on fate and mobility of these metals is also discussed.

Lead

Lead released to groundwater, surface water and land is usually in the form of elemental lead, lead oxides, hydroxides and lead metal oxyanion complexes. Most lead that is released to the environment is retained in the soil. The primary processes influencing the fate of lead in soil include adsorption, ion exchange, precipitation, and complexation with sorbed organic matter. These processes limit the amount of lead that can be transported into the surface water or groundwater. The relatively volatile organolead compound tetramethyl lead may form in anaerobic sediments as a result of alkylation by micro organisms (Gerber et al., 1991, Bourg et al., 1988). The amount of dissolved lead in surface water and groundwater depends on pH, the concentration of dissolved salts and on the types of mineral surfaces present. In surface water and groundwater systems, a significant fraction of lead is undissolved and occurs as precipitates (PbCO_3 , PbO_2 , Pb(OH)_2 , PbSO_4), sorbed ions, surface

coatings on minerals, or as suspended organic matter (Gerber et al., 1991, Bourg et al., 1988).

Zinc

Zinc (Zn) does not occur naturally in elemental form. It is usually extracted from mineral ores as zinc oxide (ZnO). The primary industrial use for Zinc is a corrosion resistant coating for iron or steel. (Smith et al. 1995). Zinc usually occurs in the +2 oxidation state and forms complexes with a number of anions, amino acids and organic acids. Zinc may precipitate as $\text{Zn(OH)}_{2(s)}$, $\text{ZnCO}_{3(s)}$, $\text{ZnS}_{(s)}$, or $\text{Zn(CN)}_{2(s)}$ (Gerber et al., 1991, Luoma et al., 1989, Bourg et al., 1988).

Zinc is one of the most mobile heavy metals in surface water and in groundwater because it is present as soluble compounds at neutral and acidic pH values. At higher pH values, zinc can form carbonate and hydroxide complexes which control zinc solubility. Zinc readily precipitates under reducing conditions and in highly polluted systems when it is present at very high concentrations. Zinc also and may co-precipitate with hydrous oxides of iron or manganese. Sorption to sediments or suspended solids, including hydrous iron and manganese oxides, clay minerals, and organic matter, is the primary factor affecting the fate of zinc in the aquatic environments. Sorption of zinc increases as the pH increases and the salinity decreases (Gerber et al., 1991).

Copper

Copper (Cu) is mined as a primary ore product from copper sulphide and oxide ores. Mining activities are the major source of copper

contamination in groundwater and in surface waters. Other sources of copper include algicides, chromated copper arsenate, pressure treated lumber and copper pipes. Solution and soil chemistry strongly influence the speciation of copper in ground-water systems. In aerobic conditions, sufficiently alkaline systems, CuCO_3 is the dominant soluble copper species (Luoma et al., 1989; Bourg et al., 1988). The cupric ion, Cu^{2+} , and hydroxide complexes, CuOH^+ and $\text{Cu}(\text{OH})_2$, are also commonly present. Copper forms strong solution complexes with humic acids (Dzombak et al., 1990). The affinity of copper for humates increases as pH increases and as the ionic strength decreases. In anaerobic environments, where sulphur is present copper form $\text{CuS}_{(s)}$ compounds. Copper mobility is decreased by sorption to mineral surfaces. Copper ion becomes sorbed strongly to mineral surfaces over a wide range of pH values (Dzombak et al., 1990). The cupric ion (Cu^{2+}) is the most toxic species of copper. Copper toxicity has also been demonstrated for CuOH^+ and $\text{Cu}_2(\text{OH})_2^{2+}$ (LaGrega et al., 1994).

Cadmium

Cadmium (Cd) occurs naturally in the form of CdS or CdCO_3 . Cadmium is recovered as a by-product from the mining of sulfide ores of lead, zinc and copper. Sources of cadmium contamination include plating operations and the disposal of cadmium-containing wastes (LaGrega et al., 1994).

The chemical form of cadmium encountered in the environment depends on solution and on the soil chemistry as well as on the treatment

of the waste prior to disposal. The most common forms of cadmium include Cd^{2+} , cadmium-cyanide complexes, and $\text{Cd}(\text{OH})_2$ (LaGrega et al., 1994, Luoma et al., 1989, Bourg et al., 1988). Hydroxide ($\text{Cd}(\text{OH})_2$) and carbonate (CdCO_3) solids dominate at high pH whereas Cd^{2+} and aqueous sulfate species are the dominant forms of cadmium at lower pH (<8). Under reducing conditions when sulfur is present, the stable solid $\text{CdS}_{(s)}$ is formed. Cadmium will also precipitate in the presence of phosphate, arsenate, chromate and other anions, although solubility will vary with pH and other chemical factors (Bourg et al., 1988).

Cadmium is relatively mobile in surface water and ground-water systems and exists primarily as hydrated ions or as complexes with humic acids and other organic ligands. Under acidic conditions, cadmium may also form complexes with chloride and sulfate ions. Cadmium is removed from natural waters by precipitation and sorption to mineral surfaces, especially oxide minerals, at higher pH values (>pH 6). Removal by these mechanisms increases as pH increases. Sorption is also influenced by the cation exchange capacity (CEC) of clays, carbonate minerals, and organic matter present in soils and sediments. Under reducing conditions, precipitation as CdS controls the mobility of cadmium (Luoma et al., 1989, Bourg et al., 1988).

2.3. Soil Remediation Technologies

Soil remediation methods and the agents used depend on the soil texture and the concentrations and types of pollutants. The main contaminant groups include non-volatile hydrocarbons, volatile

hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), organic pesticides, polychlorinated biphenyls (PCBs), heavy metals and free and complex cyanides.

Soil remediation methods also include physical and chemical treatment, biological treatment, fixation and encapsulation, and thermal treatment (Boulding, 1995). Each technology is specific to a range of contaminants. Remediation agents such as surfactants are more specific to soil washing and flushing methods.

2.3.1. Soil Washing and Soil Flushing

Soil washing is a water-based process employing extraction and separation. The process includes excavation of the contaminated soil, mechanical screening to remove oversize materials, separation processes to produce coarse- and fine-grained fractions, treatment of the fractions, and management of the residuals.

Soil flushing is another technique that uses water or extracting agents to mobilize the contaminants from a contaminated soil. While soil washing is an *ex-situ* remediation method, soil flushing is an *in-situ* treatment. Soil flushing can be divided into three activities. These are site characterization, fluid injection, and contaminant mobilization and recovery techniques.

Soil washing and flushing is useful in removing a broad range of organic, inorganic, and radioactive contaminants from soil. But, water has a low complexing capacity and is ineffective on soils contaminated with highly concentrated metals or hydrophobic organics. Soils contaminated

with heavy metals and PCBs often require washing with water containing a number of remediation agents. Because the chemical behavior of heavy metals and PCBs is quite different, heavy metals are remediated using acids and chelating agents, while PCBs are remediated using surfactants (Wastech, 1993; Pierzynski *et al.*, 2000).

2.3.2. Examples on the Remediation Agents for Heavy Metals

Remediation methods applied for heavy metals have used extracting agents such as organic or inorganic acids, chelating agents and surfactants (Wasay *et al.*, 1998; Abumaizar and Smith, 1999; Reddy and Chinthamreddy, 2000 ; Neilson *et al.*, 2003). Since heavy metals become mobile when the pH drops below 6.0, strong acids have been found to be efficient extracting agents for heavy metals in soils. In a study involving seven contaminated soils, Van Benschoten *et al.* (1997) reported that a non-detrital Pb fraction was removed under acidic condition, leaving a residual or detrital highly immobile, and fraction in the soils. The percent Pb removals varied from 22 to 93 %, suggesting that Pb was bound more strongly in some soils than others. Weak organic acids such as citrate and tartarate are also effective in removing metals from soils. Wasay *et al.* (2001) showed that at pH 5, ammonium citrate removed 43, 37, 92, and 75% of Cr, Mn, Pb, and Hg, respectively. Ammonium tartarate likewise removed 45%, 41%, 91%, and 75% of Cr, Mn, Pb and Hg, respectively, at pH 4.5 (Wasay *et al.*, 2001).

Chelating agents, such as ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA), are widely used for leaching metal from

soils since they form strong soluble complexes with metals. EDTA and NTA both formed complexes extracting Pb from contaminated soils (Elliott and Brown, 1989; Brown and Elliott, 1992). As compared to NTA, EDTA was more efficient, demonstrating a molar chelant/Pb ratio above 1:1, and adsorbing 10 to 30% more Pb than by NTA. Pyridine-2, 6-dicarboxylic acid (PDA) is a chelator for Cd. A batch experiment showed that PDA was effective in extracting 90% of Cd from spiked soil and also reversibly released Cd under high pH conditions (Hong and Chen, 1996). According to Sun *et al.* (2001) EDTA showed similar extraction efficiencies for Zn, Cd, Cu and Pb from four contaminated soils. Sequential fractionation experiment showed the mobility of metals to follow the order $Cu > Cd > Zn > Pb$.

Although strong acids and chelators are quite effective as remediation agents in removing toxic metals from soil, these agents are not environmental friendly since they are toxic and disturb the physical, chemical and biological properties of soil. In a study of remediation effect on soil properties, EDTA was shown to extract large amounts of soil minerals such as Ca, Mg, and Fe (Wasay *et al.*, 1998). Soils treated with 0.1 M HCl lost from 8 to 11% and 13 to 14 % of their total weight after 30 min and after 24 h, respectively (Tuin and Tels, 1990).

Surfactants have also shown a great ability to remove metals from soil with fewer toxic effects than acids or chelators. Cationic, anionic, and nonionic surfactants have been used to remediate heavy metal from contaminated soils from their heavy metal content (Doong *et al.*, 1998).

They found that the addition of anionic and nonionic surfactants could enhance the extraction rates of Cd, Pb, and Zn while the addition of a cationic surfactant decreased the extraction efficiency of heavy metals. Cationic surfactants were more effective in extracting heavy metals than nonionic or anionic surfactants under acidic condition.

2.4. Surfactants

Surfactants are interesting remediation agents as they have the unique characteristics of being capable of altering the surface properties of liquids. Surface properties can be changed by the addition of small amount of such compounds. This phenomenon is called surface activity. In most cases, surface activity appears in a lowering of surface tension

Compounds that lower the surface tension are called surface active compounds. Surfactants are the most powerful compounds that depress the surface tension of water.

Since surfactants have hydrophilic and hydrophobic groups in one molecule, they exhibit affinity to both water and oils. Surfactants are used in our daily life and by many kinds of industries due to their particular properties such as surface tension reduction, solubility enhancement wettability and foaming capacity (Tsujii, 1998).

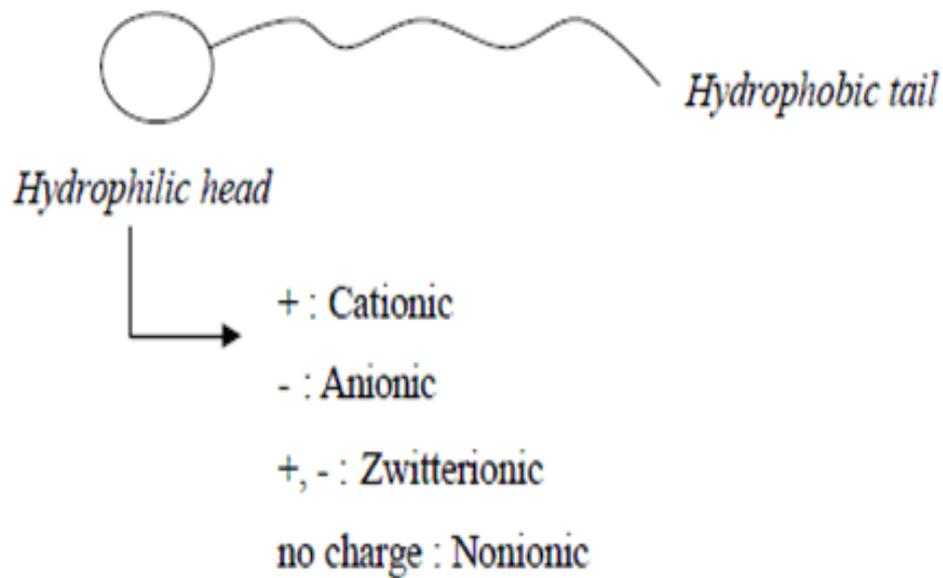


Figure 2.1 Representation of a Surfactant Monomer. (Tusgii, 1998)

2.4.1. Types of Surfactants

Surfactants are classified as either ionic or nonionic, depending upon the character of their hydrophilic group (Figure 2.1). The hydrophobic group establishes the degree of hydrophobic property of the surfactant, based on the length of the hydrocarbon chain. The most popular hydrophobic group used in surfactants is a hydrocarbon that has a total of

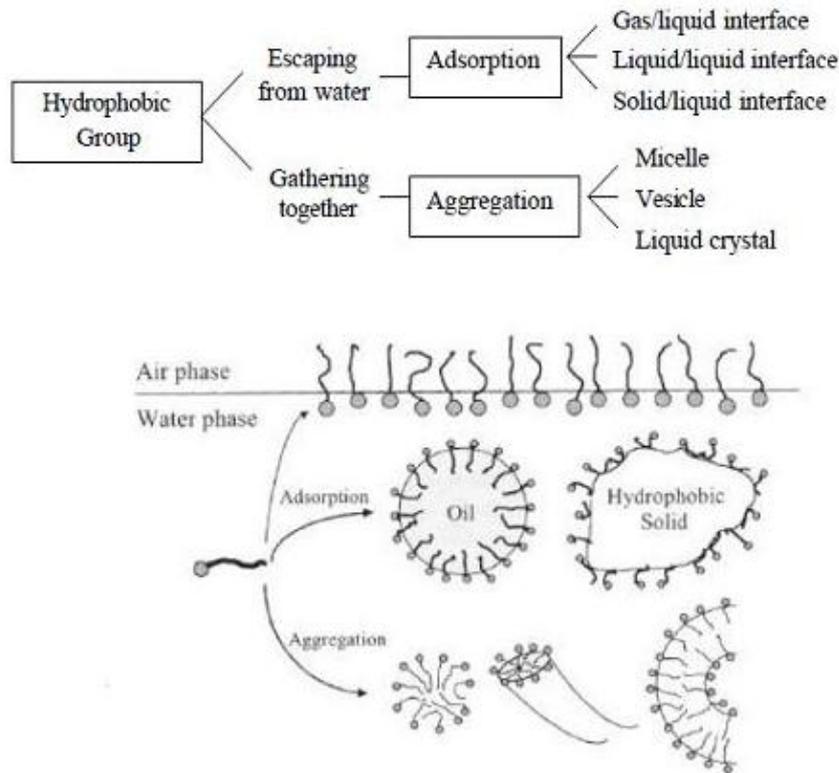


Figure 2.2 Schematic Representation for Surfactant Properties in Aqueous Solutions.
(Tsuji, 1998)

10 to 20 carbon atoms. Surfactants can be made synthetically using fatty acids, paraffins, alkylbenzenes, alcohols, and polyoxypropylenes as a source of hydrophobic groups (Swisher, 1970). The typical types of synthetic surfactants include Alkylbenzene sulfonates (anionic), alkyltrimethyl-ammonium salts (cationic), alkylcarboxy betaine (zwitterionic), and polyoxyethylene alkyl ether (nonionic) (Tsuji, 1998).

2.4.2. Properties of Surfactants

There are two fundamental properties of surfactants in aqueous solutions which are adsorption and aggregation. Surfactants are soluble in water because their hydrophilic group can reduce surface tension despite the hydrophobic group within the same molecule.

On the other hand, the hydrophobic group has a strong tendency to escape from water molecules and adsorb at the surface of the solution or at interfaces between the aqueous solution and the hydrophobic solid submerged in the solution (Figure 2.2). As a result, surfactant molecules show very unique oriented adsorption and the surfaces or boundaries of the solution are more concentrated than the main body of the solution.

This oriented surface film results in lowering of the surface tension of the water, bubble and foam formation. A surfactant's ability to lower surface tension is an important factor determining the efficacy of the surfactant. Generally, an efficient surfactant is able to lower the surface tension of water from 72 to 35 mN/m.

When significant levels of surfactants are added to aqueous solution, the hydrophobic groups start to aggregate to avoid contact with water molecules (Figure 2.2).

Aggregation of surfactants results in the formation of micelles. Critical micelle concentration (CMC) is the minimum concentration of surfactant required for the formation of micelles.

Beyond CMC, the concentration of single surfactant molecules remains relatively constant. In the micelles, surfactant molecules are oriented with their hydrophobic groups clustered together while the hydrophilic groups extend outwards (Figure 2.2). The micelle technique can be applied for remediation purposes since micelles have hydrophobic portions which can solubilize hydrophobic contaminants.

2.4.3. Biosurfactants

Biosurfactants are compounds produced biologically from bacteria or yeast from various substrates such as sugars, alkanes and oils. The composition and microbial yields of biosurfactants depend on several factors such as the nature of the substrate, the concentration of nutrients in the medium, and the culture condition (Banat, 1995).

Biosurfactants have been replacing commercial surfactants for the purpose of remediation, because of their low toxicity and high biodegradability (Fiebig *et al.*, 1997). Rhamnolipids produced by *Pseudomonas aeruginosa* have been one of the most widely used biosurfactants for remediation purposes (Van Dyke *et al.*, 1993). In a series of column experiments, rhamnolipid treatment was very effective in removing Cd from various soils (Torrens *et al.*, 1998). The results showed that 15 to 36% of the Cd was removed by the initial electrolyte treatment and an additional 8 to 54% of the Cd was removed by rhamnolipid treatment. Another study with rhamnolipid showed that they enhanced the removal of phenanthrene mainly by micellar solubilization and also by influencing sorption kinetics (Noordman, 1998).

2.5. Removal Mechanism by Surfactants

Surfactants have been extensively employed to remove PCBs in soil washing and flushing processes. Only special types of surfactants can remove metals, but then they are not very aggressive in removing PCBs simultaneously. PCBs are mainly bound to the hydrophobic portion of the soil organic matter by nonspecific hydrophobic mechanisms, while metal

ions are bound to the surface of soils by specific chemical interactions. Several studies of the desorption of HOCs such as PCBs, PAHs, hexachlorobenzene (HCB), and tetrachlorophenol (TCP), using surfactants have investigated their mechanisms of action (Jafvert *et al.*, 1995; Park and Boyd, 1999; Chu and Chan, 2003). The main desorption mechanism were described as the partitioning of organic contaminants into hydrophobic micelles by hydrophobic interaction.

The mechanisms by which metals are removed are slightly different, than those undergone by PCBs, and also depend on the types of metals and surfactants. In a study where surfactants were used to remediate Cd from contaminated soil, enhancement of metal removal occurred mainly below CMC and increased slowly above the CMC (Doong *et al.*, 1998).

This suggested that an ion exchange mechanism was occurring during Cd extraction. Mulligan *et al.* (1999) also investigated the mechanism for metal removal from soil by biosurfactants. The removal occurred through extraction from the soil surface by the surfactant, followed by complexation with the metal.

2.6. Metal Complexation in the Surfactant-Ligand Solution

Metal complexation is the reaction of a metal ion and a ligand through electron-pair sharing. The metal ion serves as an electron-pair acceptor and the ligand serves as electron-pair donor.

Metal complexation behaviors have been studied in surfactant micelles and it has been elucidated that metal complexation behaviors in

micellar solution are different from those occurring in aqueous solution (Shin *et al.*, 1997; Umebayashi *et al.*, 1997; Shin *et al.*, 2000; Umebayashi *et al.*, 2001). In researching the interaction between thiocyanate ions (SCN⁻) and a series of metal ions in micelles, it was shown that [Co (NCS)₄]²⁻ and [Zn (NCS)₄]²⁻ were commonly formed in the surfactant solution, while these species were rarely formed in aqueous solution (Umebayashi *et al.*, 1997). In a study of complexation of the cadmium ion with iodide ions in micellar solutions, [CdI₃]⁻ and [CdI₄]²⁻ complexes were formed in both aqueous and micellar phases and the formation of both complexes was enhanced in micellar phase. (Shin *et al.*, 2000). The complexation in micelles was found to be accompanied by relatively large negative enthalpies for the transfer of [CdI₃]⁻ and [CdI₄]²⁻ complexes from aqueous solution to the micelles. Thus, a hydrophobic complex with no capacity to form strong hydrogen bonds in water did develop strong affinity to micelles.

2.7. Present Applications of Surfactant-Ligand Complexes

In recent years, surfactant micelle-mediated extraction, particularly those using various ligands, has been applied to aqueous solutions to remove metal ions such as Cd, Cu, Zn, Co and Ni (Fillipi *et al.*, 1997; Fillipi *et al.*, 1998; Akita *et al.*, 1999; Udin and Kathiresan, 2000). Used along with the surfactant micelles, the hydrophobic ligand can enhance complexation with a target metal ion and then become solubilized as a complex within the micellar pseudo-phase.

Fillipi *et al.* (1998) extracted Cu using the hydrophobic ligand 1-phenyl-3-isoehtyl-1,3-propanedione with the cationic surfactant CTAB (*n*hexadecyltrimethylammonium bromide). Along with ultra-filtration, Akita *et al.* (1999) and Abu Zuhri *et al.*, 1998 used a nonionic surfactant with a micelle-solubilized hydrophobic ligand to effectively separate cobalt (Co) and nickel (Ni) from aqueous solution.

2.8. Toxicity of Ligands and Surfactants

Surfactants and ligands are less toxic to soils compared to other chemical agents such as strong acids and chelating agents. Strong acids possess H⁺ ions that can be easily adsorbed by the soil reaction site resulting in a drop in soil pH. Chelating agents such as EDTA can extract not only heavy metals but important soil mineral including Ca, Mg, and Fe because of their high complexation ability with most types of metals (Wasay, *et al.*, 1998).

However, nonionic and anionic surfactants are less adsorbed by the soil compared to acids since they have either no charge or a negative charge which are not strongly adsorbed to the soil reaction site. A study also showed that under aerobic condition, nonionic surfactants were successfully degraded (Mezzanotte, *et al.*, 2003). For ligands such as I⁻ and SCN⁻, they are not expected to be strongly adsorbed to the soil reaction site because of their negative charge. Unlike cyanide, thiocyanate has a relatively low toxicity and kinetic studies showed that SCN⁻ can be degradable at a relatively high rate of 292 mg /L.day (Boucabeille and Bories, 1994).

2.9. Kinetics of Metal Desorption From Soil

The most accurate description of the soil desorption process for a given metal, when using a specific surfactant-ligand combination is the parabolic diffusion equation which can be applied to diffusion-controlled reactions of ions being desorbed from soils (R. Salim et al. 1992; Sparks 1999; Krishnamurti et al. 1999a, 1999b; Tse and Lo 2002). The mathematical expression for the parabolic diffusion reaction is:

$$y = R t^{1/2} + a$$

Where y is the amount of ion desorbed in time t , R is the overall diffusion coefficient, and a is a constant.

A plot of y versus $t^{1/2}$ gives a straight line with a slope R and an intercept of a .

This shows that the rate of adsorption of copper is proportional to the concentration of copper remaining unabsorbed at a certain time, irrespective of the initial concentration of copper in solution.

2.10. Adsorption Isotherms

The adsorption equilibrium is usually described by an isotherm equation whose parameters express the surface properties and affinity of adsorbent.

Adsorption isotherm can be generated based on theoretical models where Langmuir and Freundlich models are the most commonly used ones.

The Freundlich equation is an empirical equation based on adsorption on a heterogeneous surface. The equation is commonly represented as:

$$\log C_s = \log K + \frac{1}{n} \log C_1$$

Where C_s is the concentration of metal ion adsorbed on red soil (mg/g) and C_1 is the concentration of metal ion remained in solution (mg/L).

K and n are the Freundlich constants characteristics of the system, indicating the adsorption capacity and adsorption intensity respectively.

The Langmuir model assumes that uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. The Langmuir equation may be written as:

$$1/C_s = 1/b + 1/ab (1/C_1)$$

Where C_s and C_1 are defined in the Freundlich Isotherm, a is the constant indicative of the bonding energy between the adsorbent and the adsorbed species and b the constant indicative of the mass of the adsorbed species required for a monolayer converge of a unit mass of adsorbent.

CHAPTER 3

EXPERIMENTAL AND MATERIAL

3.1. Soil Sampling and Characterization

Soil samples of most common soils of Palestine were selected for the study. The soils were identified and classified based on sieve analysis and hydrometer test (ASTM H-152). The organic matter of the soil was determined by chromic acid method (WREP-125 2nd Edition. 1998), the electrical conductivity was measured by using conductivity meter (IS 2720-part 21, 1977). Total soluble solid were estimated from electrical conductivity, the soil pH was measured by using a direct reading type pH meter (JENWAY 3540 PH & Conductivity Meter) with glass electrode and calomel reference electrode. The specific gravity was determined by pyknometer method (IS 2720-part 3/sec 1, 1987). The moisture percentage of each soil was determined, and taken into account when an exact weight is required for analysis. The properties of the collected soils are given in table (3.1). The soils were sieved through IS (International Standard) sieve No. 40 (0.42 mm aperture as per IS 2720-part 4, 1987). The fraction passing through the sieve was collected and preserved in air tight plastic containers for further studies.

3.2. Soil Characteristics

The texture and organic matter contents for each soil were determined in the laboratory. The methods used are described below:

3.2.1. Total Organic Matter Content (T.O.M)

A 0.5 sample of dried soil was placed in 125 mL Erlenmeyer flask, 5.0 mL of 1.0 N $K_2Cr_2O_7$, 10.0 mL of concentrated H_2SO_4 were added gradually during 1 minute. After 30 minutes, 100 mL distilled water and 0.30 mL of 0.025 M ortho-phenanthroline-ferrous complex were added. A greenish cast color to dark blue green was obtained. The contents titrated against 0.05 N ferrous sulfate solution, until a blue to orange red color obtained. A blank of $K_2Cr_2O_7$ solution was treated as samples. (WREP-125 2nd Edition, 1998).

The following equation used to calculate the T.O.M. %: Organic carbon (%) = $((5 - m_{eq} FeSO_4) \times 0.399) - \text{blank}$ / sample dry weight (g)

T.O.M. (%) = 1.27 X Organic carbon (%). The results are shown in Table (3.1).

3.2.2. Texture (Hydrometer Method)

A 50 g sample of dried soil was placed in a 1-litre beaker, 125 mL of 4% solution of sodium hexametaphosphate (calgon) (prepared by adding 40 g of calgon to 1000 mL of distilled water and mixed thoroughly) was added and allowed to soak for about 8 to 12 hours. In the second day the mixture was mixed well and poured into mixer cup to make it about two- thirds full, the mixture then was poured in to a second graduated 1000 mL cylinder, then filled with distilled water up to the 1000 mL mark. The hydrometer readings were taken

at cumulative times: $t = 0.25$ min, 0.5 mm, 1 min, 2 min, 4 min, 8 min, 15 min, 30 min, 1 hr, 2 hr, 4 hr, 8 hr and 24 hr.

A table was prepared in which the first column was the time (min), the second one was the hydrometer reading (R), the third was (Rc) which is the corrected hydrometer reading for calculation of percent finer = $R + F_T - F_Z$, where F_T and F_Z are a temperature and zero correction factors.

Column four was the percent finer = $aR_{cp} (100) / W_s$, where W_s = dry weight (g) of soil used for the hydrometer analysis, a = correction for specific gravity = $G_s (1.65) / (G_s - 1) 2.65$.

Column five is the (Rcl) = corrected hydrometer reading for determination of effective length = $R + F_m$; where F_m is a meniscus correction.

Column 6 is the determined L (effective length) corresponding to the Values of R_{cl} .

Column 7 is the determined (A) value from previous tables.

Column 8 is the determined ((D) (mm)) = $A \sqrt{L}$ (cm) / t (min)

A graph was plotted between % finer Vs. D (mm) on log scales. From the graph, the % silt is the area between 0.075-0.002, and the % clay is the area < 0.002 , (*American Society for Testing and Materials* (ASTM)).

Table 3.1 Properties of Different Soils Used for the Present Study

Soil properties	Red Soil	Calk Soil	Sandy Soil
specific gravity (g/cm ³)	2.5	2.2	2.7
pH value *	8.5	7.1	8.5
Electrical conductivity,(Ec), μ s	230.0	184.1	84.5
Clay (%)	39.0	46.0	2.0
Silt (%)	61.0	54.0	3.0
Organic matter (%)	9.6	8.4	0.3
Moister content (%)	8.0	2.0	0.2

* The soil pH was determined by shaking 5 g of air-dry soil with 10 mL of deionized water for 60 min, letting the solution rest overnight, and then measuring the solution with a pH meter.

3.3. Cleaning Soil

A special column was prepared for this purpose (50 cm long with a radius of 2.5 cm with a stopcock to control the rate flow of washing solution). In each column 200 g of soil was washed by 500 ml of distilled water followed by 500 ml of 0.1 M perchloric (which is suitable for Beckman flame Atomic Absorption (R. Salim 1980)) acid then 500 ml of distilled water. The soil was dried at 95 °C for 24 hours using universal ovens (memmert UNB 100-500, U B 400-500).

1.0 g of soil was digested with concentrated nitric acid (Method 3050A, Acid Digestion of Sediment, Sludges', and Soil by Neil Wilson 9/5/95) and tested for elemental analysis. No metals (Cu^{2+} , Cd^{2+} , Zn^{2+} and Pb^{2+}) were present in the cleaned soil.

3.3.1 Methods of Cleaning Soil: Comparison

A clean sample of red soil (1.0kg) was contaminated with four metals as follow:

- 1) 20 ml of 4.0 grams of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ in 1.0 liter of distilled water.
- 2) 20 ml of 4.0 grams of $\text{Cd}(\text{NO}_3)_2$ in 1.0 liter of distilled water.
- 3) 20 ml of 4.0 grams of $\text{Pb}(\text{NO}_3)_2$ in 1.0 liter of distilled water.
- 4) 20 ml of 4.0grams of $\text{Zn}(\text{NO}_3)_2$ in 1.0 liter of distilled water.

The solution of the above metals were mixed and homogenized together.

The mixture of the soil with the contaminated metals was dried in the oven at 95°C for 24 hours.

Five samples of 150 g of the contaminated sample were placed in five columns where the flow of solution was drain freely from the column then the following solutions were added separately for clean-up purpose.

- 1) Column one, a 500 ml of 0.1 M of CaCl_2 .
- 2) Column two, a 500 ml of 0.1 M of HClO_4 .
- 3) Column three, a 500 ml of 0.1 M of HNO_3 .

4) Column four, a 500 ml of 0.1 M of EDTA.

5) Column five, a 500 ml of distilled water.

A waiting time of 18 hours were taken for the solution of each one in the column mentioned above to be drained out. The drained solution was analyzed for the heavy metals analysis and we have no results till now.

3.4. The Effect of Soil Concentration on the Adsorption of Copper Ions on Red Soil

Several weights of clean red soil (0, 2, 4, 6, 8, 10, 12 g) were taken and mixed with 250 ml of copper ions solution (50 ppm). The supernatant (top layer) was taken and analyzed for copper concentration at several time from zero to 72 hours as follow : 0, 1.33, 3, 24, 72 hours. For metal analysis Atomic Absorption Spectrophotometer (Model: Perkin Elmer 3100, Beckman Flame) was used. The results are shown in Table (4.1) and Figure (4.1).

3.4.1. The Effect of Copper Concentration on the Adsorption of Copper Ions on Red Soil

4.0 grams of clean red soil was placed in 100 ml of different concentrations of copper (30, 40, 50 ppm).

The samples were shaken four few minutes and left for 72 hours to have complete adsorption of copper.

The analytes were sampled from the above prepared sample at 0,1,3,24,72 hours. The results are shown in Tables (4.2- 4.5) and Figures (4.2-4.7).

3. 5. The Effect of Competitive Ions on Adsorption of Heavy Metals on Red Soil

Two types of experiments were done for this study; the first experiment was done as follow: different weights of red soil (0, 2, 4, 6, 8, 10, 12g) were mixed with 100 ml (50ppm) single metal like copper, and then the same weights were mixed with 100 ml of 50 ppm of the four metals together. The second experiment was done as follow: different concentrations of (10 – 300 ppm) of each metal was mixed with 1.0 gram of red soil then treated by the previous method. In each study the samples were shaken using (Wrist Action, SHAKER, BURRELL, and MODEL 75) for 24 hours. The samples were left to stabilize for two hours. A 10 ml of the supernatant of each sample was centrifuged for 15 minutes at 2500 rpm. The sample was analyzed for the specified metals and the results represented in Tables (4.6-4.15) and Figures (4.8-4.17).

3.5.1. The Effect of Competitive Ions on the Adsorption of Heavy Metals on White Chalk and on Sandy Soil

The same procedure was followed for the study of competition of the adsorption of white chalk and sandy soils. The results are shown in tables (4.16-4.25) and figures (4.18-4.27).

3.6. The Effect of pH on the Adsorption of Copper Ions on Red Soil at Room Temperature (25°C)

In this experiment the adsorptive behavior of Cu^{2+} on red soil at different pH values, Table (4.26), Figure (4.28) have been studied. For this study a 10 gram of red soil have been placed in 330- ml glass Stoppard bottles. After that, 100 mL of copper solution with a concentration of 125 ppm has been added to the bottles at different pH values. The initial pH of the sorbate (metal solution) was adjusted for each set of the experiment by adding 0.1 M HCl or 0.1 M NaOH).

The soil sample has been shaken in a shaker for 24 hours at constant temperature and then left for additional 24 hours. A 10 mL of supernatant solution was centrifuged at 2500 rpm for 15 minutes.

The amount of metal sorbed by the soil was calculated from the initial metal concentration of the solution and metal content of the supernatant after the specified period 24 hours of shaking.

(This procedure was repeated twice for each experiment.)

3.7 Desorption of Copper from Artificially Contaminated Red, Sandy and White Chalk Soil Using Different Types and Concentrations of Surfactants in the Absence of Ligands

To study the effect of desorption of copper from soil. A 1.0 kg of each soil (red, sandy, chalk) were taken and added to 4.0 liters of 5.0 M concentration of copper solution. The soil was soaked in the solution for

two days. After that, the solution was put in cloth bag to filtrate the solution out. The contaminated soil left in the cloth bag was dried in the oven at 95°C for 24 hours.

A sample of 4.0 grams of the dried contaminated soil of each kind was placed in a glass bottle.

A five different concentrations (0.005, 0.05, 0.5, 1.0, and 2.0%) of four surfactants, anionic surfactant SDS (Sodium dodecyl sulfate, $C_{12}H_{25}OSO_3^-Na^+$), the nonionic surfactant Triton X-100 (octylphenyleneoxide, $C_8H_{17}C_6H_4(OC_2H_4)_{10}OH$), the nonionic surfactant Tween-80 (Polyoxyethylene (20) Sorbian monooleate and nonionic surfactant Tergitol (Branched Secondary Alcohol Ethoxylate) were tested in the study.

These prepared different surfactants were added to each 5.0 gram of the soil in the bottle. A total of sixty solutions were prepared, twenty solutions of each soil. The prepared solutions were shaken for 24 hours using the shaker (Wrist Action, SHAKER, BURRELL, and MODEL 75) and 10 ml of each one were centrifuged at 2500 rpm. The supernatant was analyzed using Atomic Absorption. The results are shown in Table (4.27) and Figure (4.29) for red soil; Table (4.29) and Figure (4.31) for white chalk and Table (3.28) and Figure (3.30) for sandy soil.

3.8. Desorption of Copper from Artificially Contaminated Red, Sandy and white chalk Soil Using Different Types and Concentrations of Surfactants Triton X-100 with Ligands

From the study of surfactants in section 3.7 it was shown that Triton X-100 was the best among other surfactants for red soil. So 0.01 % of Triton X-100 was prepared in a 2.0 liter flask.

Different weights of KI (0.83g, 1.66g, 3.33g, 4.98g and 6.64g which is equivalent to 0.05 M, 0.1M, 0.2M, 0.3M and 0.4M KI respectively; were added in a 100 ml volumetric flask. The flask was filled with the 0.01 % of Triton X-100. The whole solution of KI and Triton X-100 (100 ml) was transferred to the bottle which has 4.0 grams contaminated soil.

The same solutions were prepared in the same way using SCN^- and EDTA. This preparation of solutions was repeated for the three types of soil. The results are shown in Tables (4.30-4.32) and Figures (4.32, 4.33) for red soil, Table (4.33-4.35) and Figure (4.34,4.35) for sandy soil and Table (4.36-4.38) and Figure (4.36, 4.37) for white chalk soil.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. The Effect of Soil Concentration on the Adsorption of Copper Ions on Red Soil

To study the effect of soil concentration on the adsorption of heavy metals on red soil, various concentrations of red soil ranging between 0.0 to 10 g/100mL were allowed to adsorb Cu^{+2} ions from 50 ppm copper nitrate solution for 72 hours. These results are summarized in (Table 4.1) and (Figure 4.1). These results indicate that increasing soil concentration will increase the uptake of copper from the solution. This agrees with previous results on the adsorption of lead on river mud by R. Salim, 1980.

Table 4.1 The Effect of Soil Concentration on the Adsorption of Copper Ions on Red Soil from 100mL of 50 ppm Cu^{2+} Solution

Time (hrs.)	Soil concentration (0.0-10.0 g/100mL)				
	0.0	1.0	2.0	6.0	10.0
	C_1 ppm	C_1 ppm	C_1 ppm	C_1 ppm	C_1 ppm
0.0	50.0	46.3	45.2	45.1	44.2
1.5	45.2	44.1	36.2	21.2	18.4
3.0	44.9	38.4	26.6	5.5	3.2
24.0	29.6	22.3	14.2	3.7	2.7
72.0	28.5	16.6	12.4	1.2	1.1

C_1 : Concentration of copper remaining unadsorbed in solution.

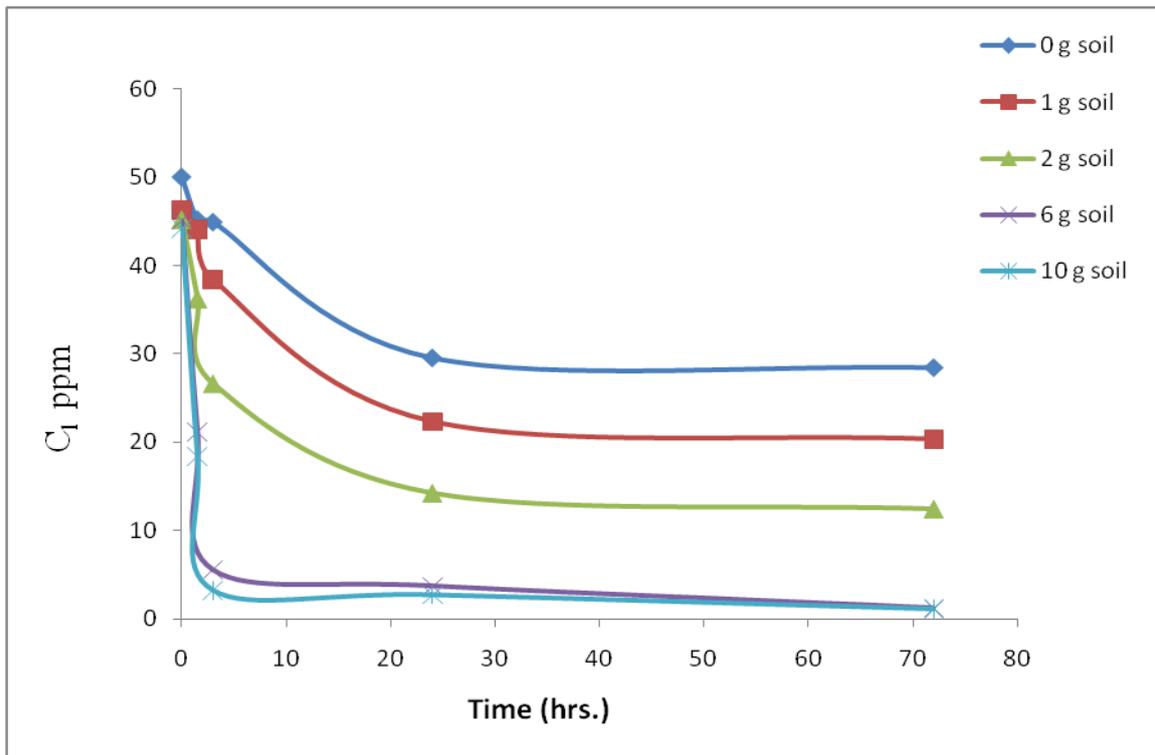


Figure 4.1 The Effect of Soil Concentration on the Adsorption of Copper Ions on Red Soil from 50 ppm Copper Solution

4.1.1. The Effect of Copper Concentration on the Adsorption of Copper Ions on Red Soil

To study the kinetic sorption of copper on red soil a set of experiments were done to measure the adsorption of three concentrations of copper (50ppm, 40ppm and 30ppm) with time in order to calculate the rate of adsorption in each concentration of copper in solution and hence to find the reaction order of the adsorption process and finally to apply the Freundlich and Langmuir adsorption isotherms on the results (R. Salim., 1980, 2008) and (Soon-An Ong et al., 2007).

The results of these experiments are shown in Tables (4.2 - 4.5) and Figures (4.2 - 4.7).

Order of reaction:

For each initial concentration of copper shown on the table 4.2, a graph was plotted between the concentrations of copper adsorbed on red soil C_s (mg/g) against \sqrt{t} (hour). The graphs were straight lines and from the slopes of these lines (i.e. $dC_s/d\sqrt{t}$), the rate of adsorption (dC_s/dt) was calculated from the formula: $(dC_s/dt)_t = \frac{1}{2\sqrt{t}}(dC_s/d\sqrt{t})$.

Table 4.2 Adsorption of Copper Ions on Red Soil

t, h	$t^{1/2}$, h	Cu ²⁺ (50ppm)		Cu ²⁺ (40ppm)		Cu ²⁺ (30ppm)	
		C_s (mg/g)	C_1 (ppm)	C_s (mg/g)	C_1 (ppm)	C_s (mg/g)	C_1 (ppm)
1.0	1.0	46.7	3.3	34.0	6.0	28.5	1.5
3.0	1.7	46.9	3.1	34.5	5.5	28.6	1.4
12.0	3.5	47.2	2.8	35.5	4.5	28.7	1.3
24.0	4.9	47.5	2.5	36.3	3.7	28.8	1.2
72.0	8.5	48.4	1.6	38.8	1.2	28.9	1.1

C_s : Concentration of copper adsorbed on soil.

C_1 : Concentration of copper remaining unabsorbed in solution.

t: Time of adsorption (hours).

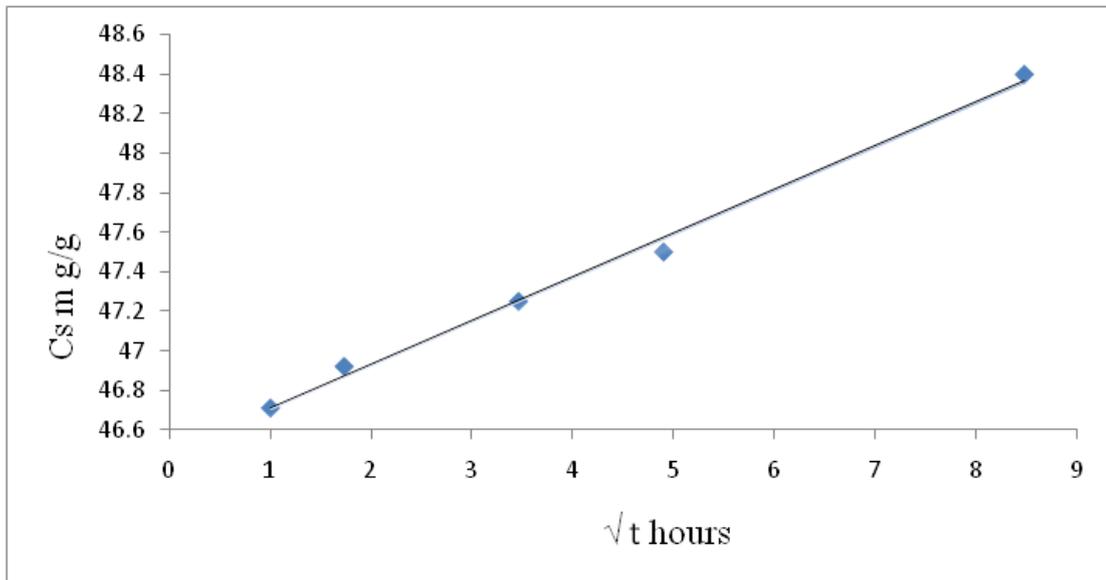


Figure 4.2 Adsorption of Copper Ions (50 ppm) on Red Soil Slope = 0.220 = dC_s/d at 50 ppm

$$\text{Rate} = (dC_s/dt)_t = (1/(2\sqrt{t})) \times (dC_s/\sqrt{t})_t = 0.0633 \text{ ppm/g/hourr}$$

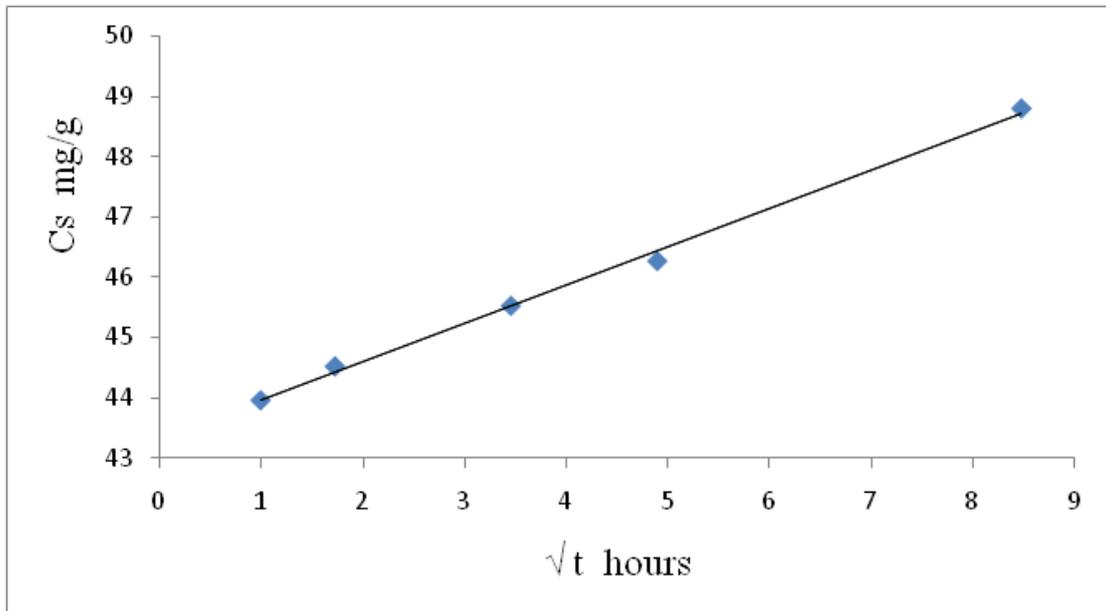


Figure 4.3 Adsorption of Copper Ions (40 ppm) on red soil

$$\text{Slope} = 0.633 = dC_s/d\sqrt{t} \text{ at 40 ppm}$$

$$\text{Rate} = (dC_s/dt)_t = (1/(2\sqrt{t})) \times (dC_s/d\sqrt{t})_t = 0.183 \text{ ppm/g/hour}$$

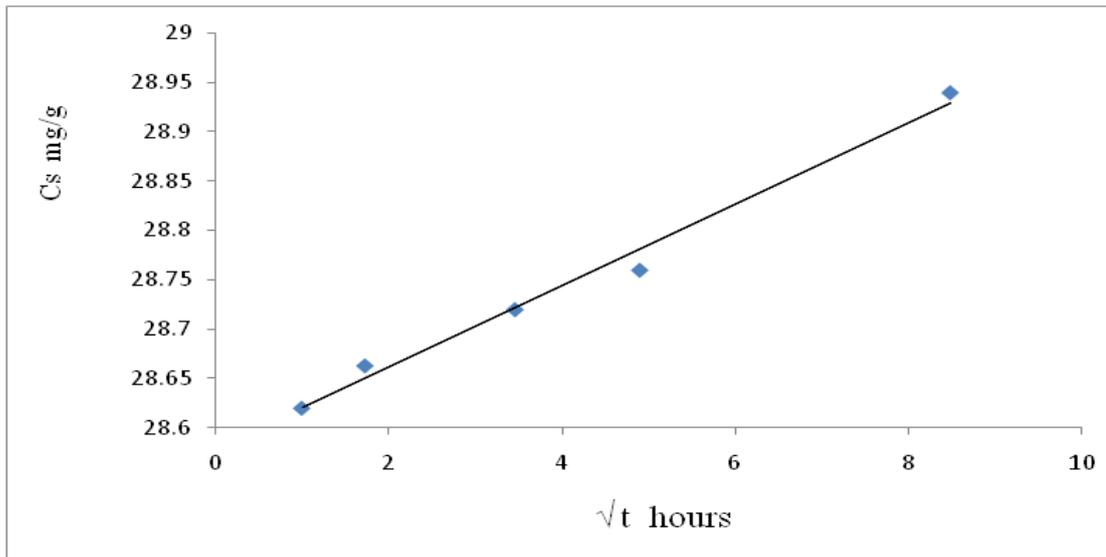


Figure 4.4 Adsorption of Copper Ions (30 ppm) on Red Soil

Slope = 0.041 = $dC_s/d\sqrt{t}$ at 30 ppm

Rate = $(d C_s/dt) t = (1/ (2\sqrt{t})) \times (d/ C_s d\sqrt{t})_t = 0.0118$ ppm/g/hour

Plotting the rate of adsorption of copper (dC_s/dt) against concentration of copper in solution (C_1) gives a straight line (Fig. 4.5).

Table 4.3 The Dependence of the Rate of Copper Adsorption on Red Soil on the Concentration of Copper Remaining in Solution

Rate of adsorption	C_1 ppm after 3 hours	C_1 ppm after 24 hours
0.0118	1.4	1.2
0.0633	3.1	2.5
0.1826	5.5	3.7

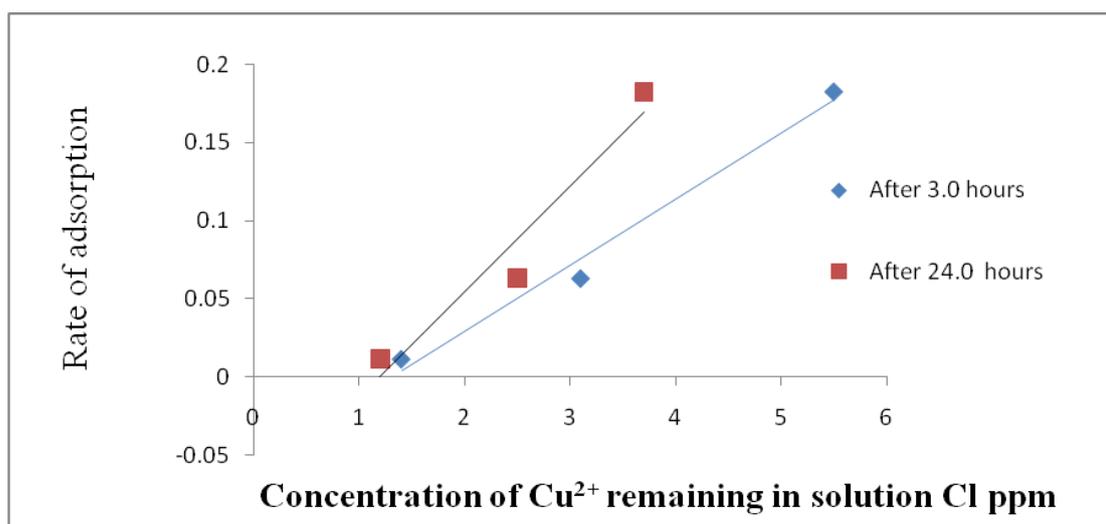


Figure 4.5 The Dependence of the Rate of Copper Adsorption on Red Soil on the Concentration of Copper Remaining in Solution after 3 and 24 hours

From the previous tables and figures it was shown that the rate of adsorption of copper is proportional to the concentration of copper remaining unabsorbed at a certain time, irrespective of the initial concentration of copper in solution. Therefore it can be concluded that the adsorption process of copper on red soil is a first order reaction with respect to copper. A similar conclusion was reported by Augustine et al. 2007.

Application of the Adsorption Isotherms:

The Freundlich and Langmuir adsorption isotherms are the most widely applied isotherms for the adsorption of metal ions on a wide variety of adsorbents.

The Freundlich isotherm is an empirical one appropriate for the adsorption process where non-uniformity of the surface of adsorbent is

expected. To apply the Freundlich Equation on our work various concentrations of copper ranging between 10-300 ppm were adsorbed at constant weights of red soil for 24 hours. The results are shown in Table (4.4) and Figure (4.6).

Table 4.4 The Application of Freundlich Equation for the Adsorption of Copper on Red Soil After 24 Hours

C_s (mg/g)	C_1 (mg/L)	Log C_s (mg/g)	Log C_1 (mg/L)
12.3	10.0	1.1	1.0
32.8	20.0	1.5	1.3
59.0	30.0	1.8	1.5
87.3	40.0	1.9	1.6
121.0	50.0	2.1	1.7

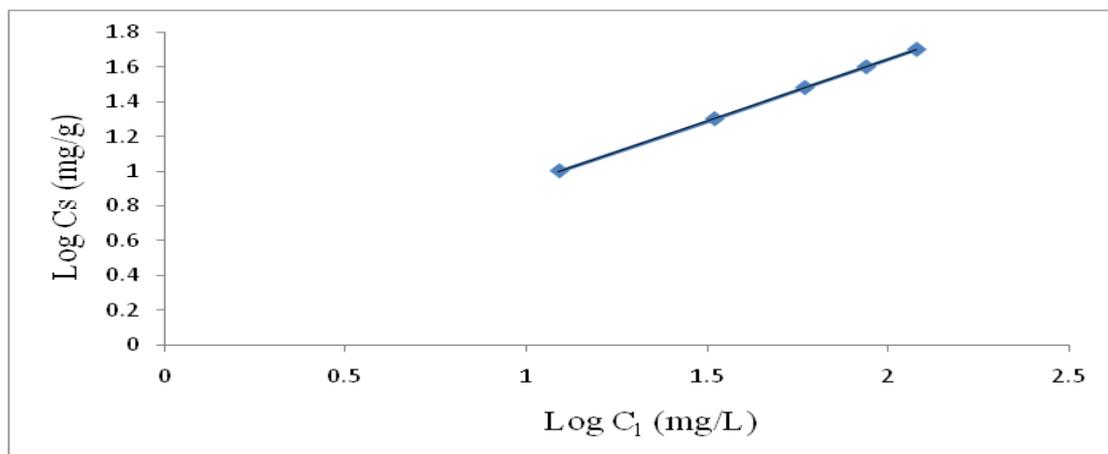


Figure 4.6 The Application of the Freundlich Equation for the Adsorption Copper on Red Soil After 24 hours

A straight line obtained in Figure (4.6) shows that the results of Table (4.6) agree with the Freundlich Equation.

$$\log C_s = \log K + \frac{1}{n} \log C_1$$

Where C_s is the concentration of Cu^{+2} adsorbed on red soil and C_1 is the concentration of Cu^{+2} remained in solution. K and n are constants. From figure (4.6), the values of n and K are 1.4 and 1.25 respectively.

The Langmuir adsorption isotherm is commonly applied to monolayer chemisorption of gases. However, several authors have applied this isotherm for the adsorption of metal ions on sorbents. This isotherm is mainly applied when no strong adsorption is expected and when the adsorption surface is uniform. A commonly used formula of the Langmuir adsorption isotherm is

$$1/C_s = 1/b + 1/ab (1/C_1)$$

Where C_s , C_1 are defined in the Freundlich Isotherm and a is the constant indicative of the bonding energy between the adsorbent and the adsorbed species and b the constant indicative of the mass of the adsorbed species required for a monolayer converge of a unit mass of adsorbent.

Table 4.5 The Application of Langmuir Isotherm for the Adsorption Copper on Red Soil after 24 Hours

C_s mg/g	C_1 (mg/L)	$1/C_s$	$1/C_1$
12.3	10.0	0.0813	0.100
32.8	20.0	0.0305	0.050
59.0	30.0	0.0169	0.033
87.3	40.0	0.0115	0.025
121.0	50.0	0.0080	0.020

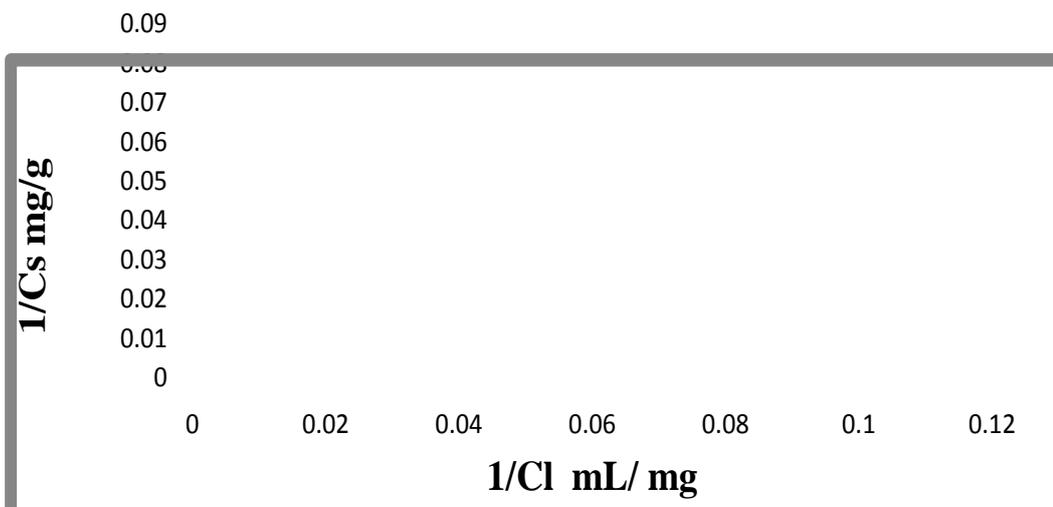


Figure 4.7 The Application of Langmuir Isotherm for the Adsorption Copper on Red Soil after 24 Hours

Both the Freundlich and Langmuir adsorption isotherms showed linear relationship on the present results shown in figures 4.6 and 4.7 for the Freundlich and Langmuir adsorption isotherms, respectively). The parameters of the Freundlich adsorption isotherm were calculated from

the results of figure 4.6. The value of parameter n is equal to 1.4 ($n \sim 1$), indicating a low coverage of copper on red soil. The value of this parameter shows also the decrease of the intensity of adsorption of copper with decreasing efficiency of removal of copper by washing solutions.

The value of the parameter K also indicates decreasing efficiency of removal of copper by normal washing solutions.

The parameters of the Langmuir adsorption isotherm, a and b , were found to be erroneous and with negative values (where a is equal to - 73.45 and b is equal to 1.08). This suggests the unsuitability of this isotherm for application on the present results. The negative values of the Langmuir parameters can be attributed to the non-uniformity of soil particles surfaces and to the high strength of adsorption of copper on red soil. These results agree with the conclusions of R. Salim (1980 & 2008), Barrow (1987), Augustine et al. (2007) and Ming-qin Jiang et al., (2010).

Rate-limiting step

Adsorption of metal ions on soil particles follow a three step processes (Salim et al., 1992):

- 1) Film diffusion: in which metal ion reach by diffusion, driven by concentration gradient, the surface of soil particles.

2) Intra-pore diffusion: in which most of the adsorbed metal ions have to enter the pores of the soil particles in order to reach the internal adsorption sites.

3) Adsorption: in which the metal ion become adsorbed on the adsorption sites.

The straight line relations found between C_s and \sqrt{t} , as shown in figures 4.2, 4.3 and 4.4 suggest that the diffusion is the rate limiting step. The same conclusions was also suggested for the uptake of cadmium on beach leaves (Salim et al., 1992)

4.2 The Effect of Competitive Ions on the Adsorption of Heavy Metals on Red Soil

The effect of presence of competing ions on the adsorption of metal ions on red soil was studied using the ions Pb, Cu, Zn and Cd.

The adsorption of each metal ion on red soil was examined alone and in presence of the other ions. Two types of study were done, first study was done at constant metal ion concentration (50ppm) and variable red soil concentration (0-12g/100mL), and the second study was done at constant red soil concentration and variable copper ion concentration (10-300 ppm). The results of these two types of experiments are shown in Tables (4.6-4.15) and Figures (4.8-4.17).

When increasing the initial metal ion concentration from 10 to 300 ppm and from 2.0 to 12 gram/100mL of soil resulted in an increase in the

metal ion adsorbed for both single metal and multi-metal ions competitive adsorption.

When the initial concentration of Pb was 10.0, and 20.0 ppm like in Figure (4.9) and 2.0g/100 mL like in Figure (4.8) more than 90% of lead ions was adsorbed. At higher concentrations (150 ppm) 70% of Pb adsorbed onto the red soil in single metal compared with 35% of Pb ion adsorbed from multi-metal competitive adsorption. This may be attributed to the presence of a large number of adsorption sites were available to the metal ions at low concentrations and the competition on these sites is obvious at high concentrations ,the same results was reported by Bhaltcharyya, K. G.,S. S. Gupta 2008.

Table 4.6 Adsorption of Lead Ions on Red Soil from 100 mL of 50 ppm Pb²⁺ Ions in Solution and 100 mL of 50 ppm of Four Metal Ions (Pb²⁺ + Cu²⁺ + Zn²⁺ + Cd²⁺) in Solution

Soil conc. g/100mL	Pb ²⁺ ions (ppm) remained in solution from a solution containing Pb ²⁺ ions alone	Pb ²⁺ ions (ppm) remained in a solution from a solution containing four metal ions
0.0	50.0	50.0
2.0	19.5	18.6
4.0	18.7	18.2
6.0	18.7	19.4
8.0	17.8	18.9
10.0	18.0	18.4
12.0	19.0	18.4

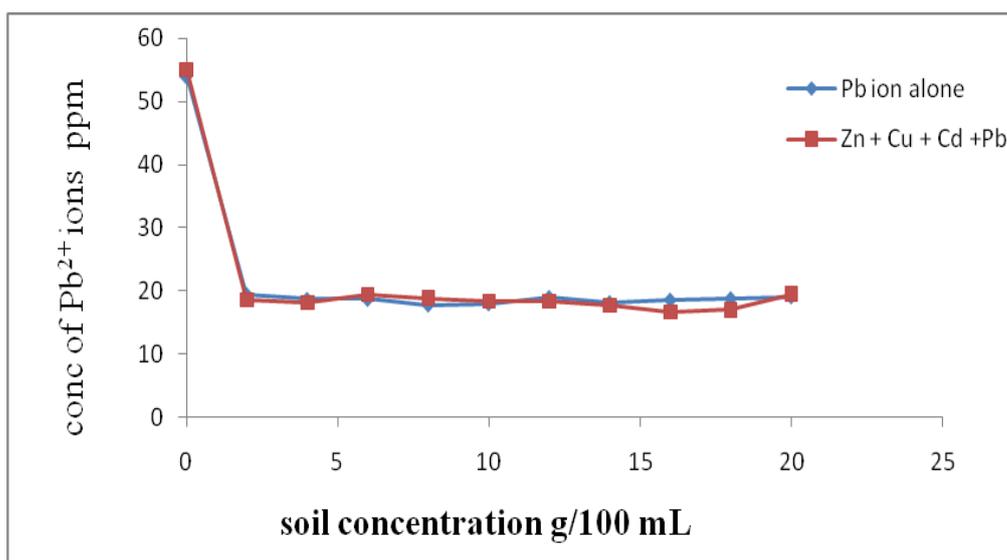


Figure 4.8 Adsorption of Pb^{2+} Ions on Red Soil from 100 mL of 50 ppm Pb^{2+} Ions and 100 mL of 50 ppm of Four Metal Ions ($Pb^{2+} + Cu^{2+} + Zn^{2+} + Cd^{2+}$) in Solution

Table 4.7 Adsorption of Lead Ions (50 ppm) on Red Soil With Single (Pb^{2+}) and Multi Metal Ions (Cu^{2+} , Cd^{2+} , Zn^{2+} and Pb^{2+}) at Soil Concentration Equal 1.0 gram/100mL.

Initial conc. of Pb^{2+} ions (ppm) in solution	Pb^{2+} ions (ppm) adsorbed on soil from Pb^{2+} solution	Pb^{2+} ions (ppm) adsorbed on soil from a solution containing four metal ions
10.0	9.4	8.9
20.0	18.0	15.6
40.0	33.2	25.6
75.0	60.0	41.2
150.0	105.0	52.5
300.0	136.0	58.3

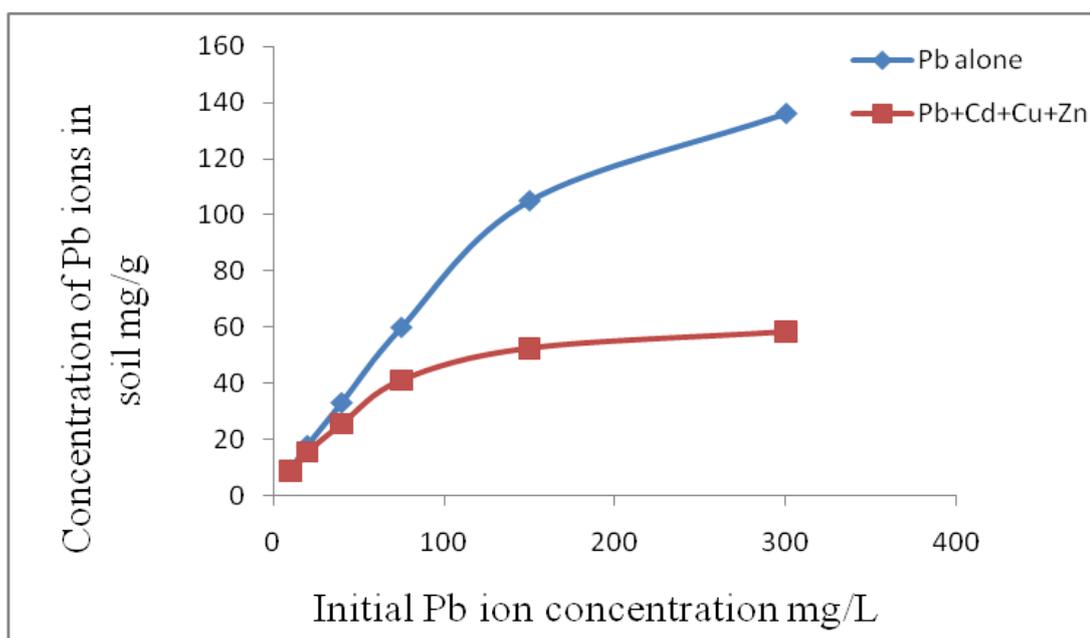


Figure 4.9 Adsorption of Lead Ions(50 ppm) on Red Soil With Single (Pb^{2+}) and Multi Metal Ions (Cu^{2+} , Cd^{2+} , Zn^{2+} and Pb^{2+}) at Soil Concentration Equal 1.0 gram/100mL.

Table 4.8 Adsorption of Copper Ions on Red Soil from 100 mL of 50 ppm Cu^{2+} Ions in Solution and 100 mL of 50 ppm of Four Metal Ions ($\text{Pb}^{2+} + \text{Cu}^{2+} + \text{Zn}^{2+} + \text{Cd}^{2+}$) in Solution

Soil conc. g/100mL	Cu^{2+} ions (ppm) remained in solution from a solution containing Cu^{2+} ions alone	Cu^{2+} ions (ppm) remained in solution from a solution containing four metal ions
0.0	38.0	39.3
2.0	6.5	1.9
4.0	1.8	0.5
6.0	1.1	0.5
8.0	0.7	0.4
10.0	0.6	0.4
12.0	0.5	0.3

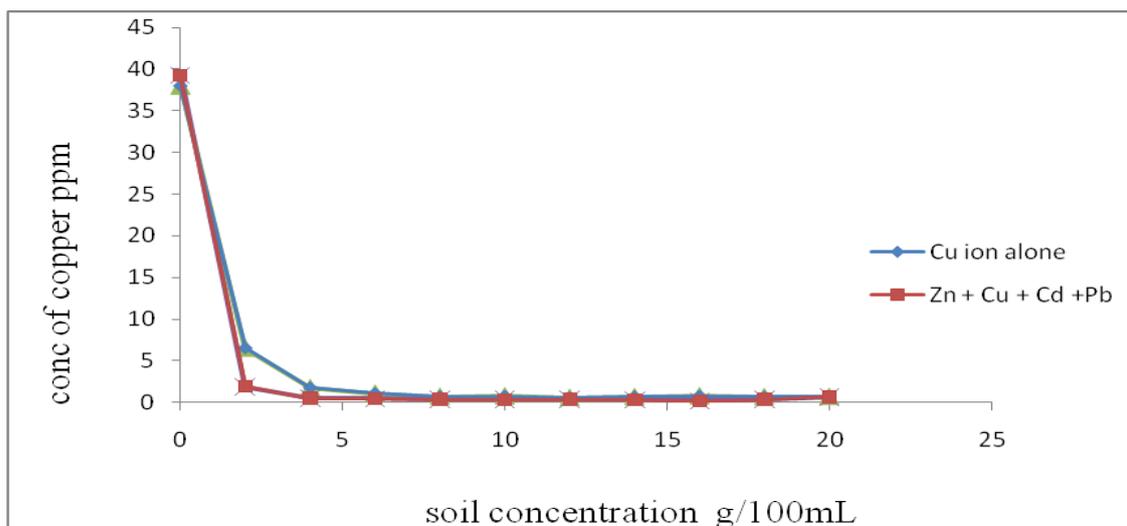


Figure 4.10 Adsorption of Copper Ions on Red Soil from 100 mL of 50 ppm Cu^{2+} Ions in Solution and 100 mL of 50 ppm of Four Metal Ions ($\text{Pb}^{2+} + \text{Cu}^{2+} + \text{Zn}^{2+} + \text{Cd}^{2+}$) in Solution

Table 4.9 Adsorption of Copper Ions (50 ppm) on Red Soil With Single (Cu^{2+}) and Multi Metal Ions (Cu^{2+} , Cd^{2+} , Zn^{2+} and Pb^{2+}) at Soil Concentration Equal 1.0 gram/100mL.

Initial conc. of Cu^{2+} ions (ppm) in solution	Cu^{2+} ions (ppm) adsorbed on soil from Cu^{2+} solution	Cu^{2+} ions (ppm) adsorbed on soil from a solution containing four metal ions
10.0	0.3	0.2
20.0	11.5	6.4
40.0	18.0	9.5
75.0	28.5	13.5
150.0	45.0	15.0
300.0	61.5	18.0

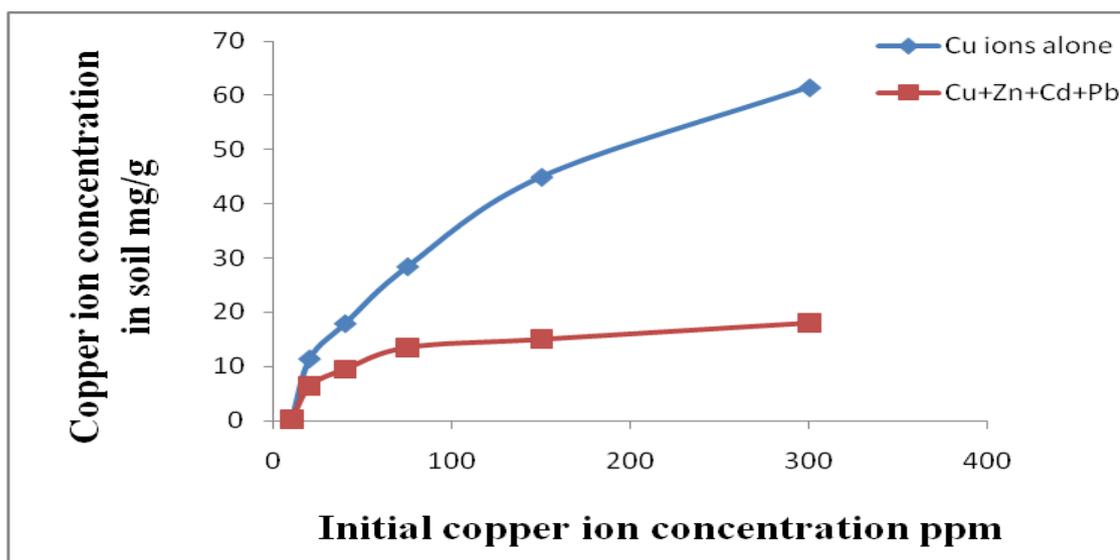


Figure 4.11 Adsorption of Copper Ions on Red Soil With Single (Cu^{2+}) and Multi Metal Ions (Cu^{2+} , Cd^{2+} , Zn^{2+} and Pb^{2+}) at Soil Concentration Equal to 1.0 gram/100mL.

Table 4.10 Adsorption of Zinc Ions on Red Soil from 100 mL of 50 ppm Zn^{2+} Ions in Solution and 100 mL of 50 ppm of Four Metal Ions ($\text{Pb}^{2+} + \text{Cu}^{2+} + \text{Zn}^{2+} + \text{Cd}^{2+}$) in Solution

Soil conc. g/100mL	Zn^{2+} ions (ppm) remained in solution from a solution containing Zn^{2+} ions alone	Zn^{2+} ions (ppm) remained in solution from a solution containing four metal ions
0.0	17.5	17.8
2.0	13.2	14.6
4.0	11.6	10.1
6.0	10.7	7.8
8	10.1	6.0
10.0	9.2	5.6
12.0	7.8	5.6

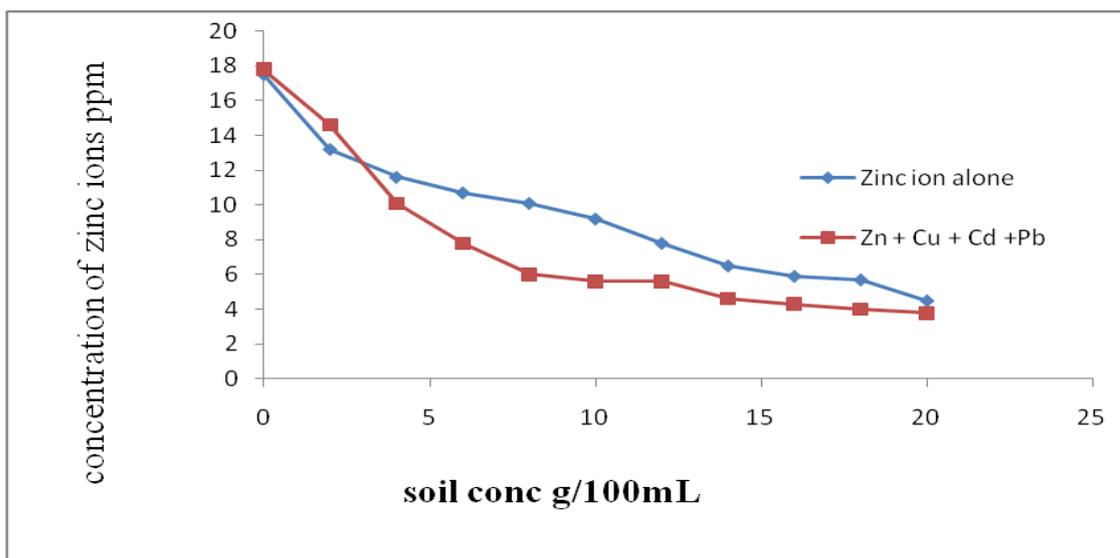


Figure 4.12 Adsorption of Zinc Ions on Red Soil from 100 mL of 50 ppm Zn^{2+} Ions in Solution and 100 mL of 50 ppm of Four Metal Ions ($Pb^{2+} + Cu^{2+} + Zn^{2+} + Cd^{2+}$) in Solution

Table 4.11 Adsorption of Zinc Ions on Red Soil With Single (Zn^{2+}) and Multi Metal Ions (Cu^{2+} , Cd^{2+} , Zn^{2+} and Pb^{2+}) at Soil Concentration Equal 1.0 gram/100mL.

Initial conc. of Zn^{2+} ions (ppm) in solution	Zn^{2+} ions (ppm) adsorbed on soil from Zn^{2+} solution	Zn^{2+} ions (ppm) adsorbed on soil from a solution containing four metal ions
10.0	7.3	4.7
20.0	11.2	7.2
40.0	19.2	8.3
75.0	30.1	17.0
150.0	57.3	27.1
300.0	136.0	54.2

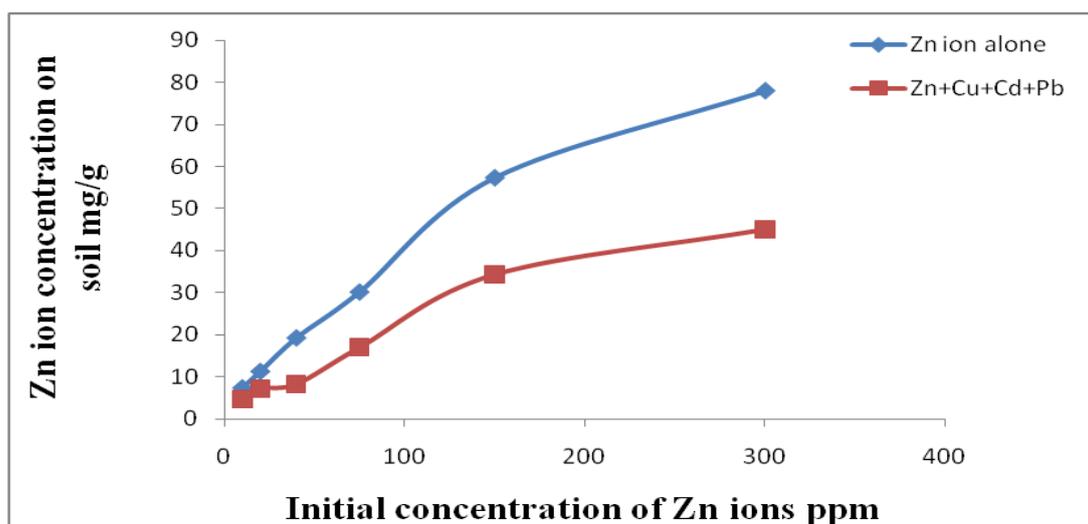


Figure 4.13 Adsorption of Zinc Ions on Red Soil With Single (Zn^{2+}) and Multi Metal Ions (Cu^{2+} , Cd^{2+} , Zn^{2+} and Pb^{2+}) at Soil Concentration Equal 1.0 gram/100mL.

Table 4.12 Adsorption of Cadmium Ions on Red Soil from 100 mL of 50 ppm Cd^{2+} Ions in Solution and 100 mL of 50 ppm of Four Metal Ions (Pb^{2+} + Cu^{2+} + Zn^{2+} + Cd^{2+}) in Solution

Soil conc. g/100mL	Cd^{2+} ions (ppm) remained in solution from a solution containing Cd^{2+} ions alone	Cd^{2+} ions (ppm) remained in solution from a solution containing four metal ions
0.0	26.0	27.0
2.0	20.0	19.4
4.0	5.4	11.8
6.0	2.2	8.3
8.0	0.0	6.1
10.0	0.0	5.9
12.0	0.0	5.5

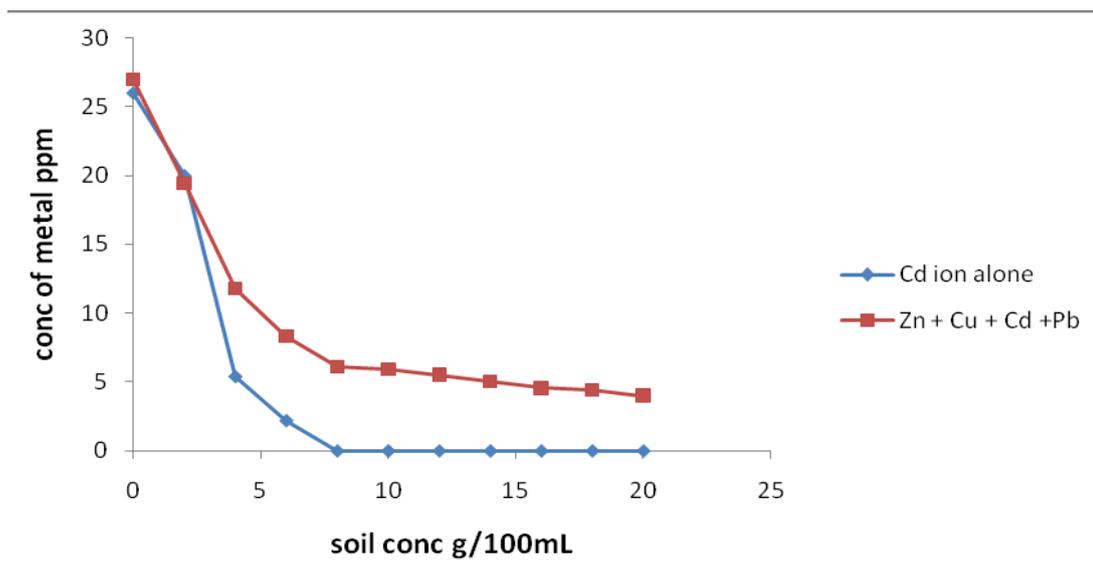


Figure 4.14 Adsorption of Cadmium Ions on Red Soil from 100 mL of 50 ppm Cd^{2+} Ions in Solution and 100 mL of 50 ppm of Four Metal Ions ($\text{Pb}^{2+} + \text{Cu}^{2+} + \text{Zn}^{2+} + \text{Cd}^{2+}$) in Solution

Table 4.13 Adsorption of Cadmium Ions on Red Soil With Single (Cd^{2+}) and Multi Metal Ions (Cu^{2+} , Cd^{2+} , Zn^{2+} and Pb^{2+}) at Soil Concentration Equal 1.0 gram/100mL.

Initial conc. of Cd^{2+} ions (ppm) in solution	Cd^{2+} ions (ppm) adsorbed on soil from Cd^{2+} solution	Cd^{2+} ions (ppm) adsorbed on soil from a solution containing ($\text{Cd} + \text{Cu} + \text{Pb} + \text{Zn}$) metal ions
10.0	7.3	5.3
20.0	14.4	8.2
40.0	24.3	12.0
75.0	45.2	21.3
150.0	81.2	45.0
300.0	136.0	58.3

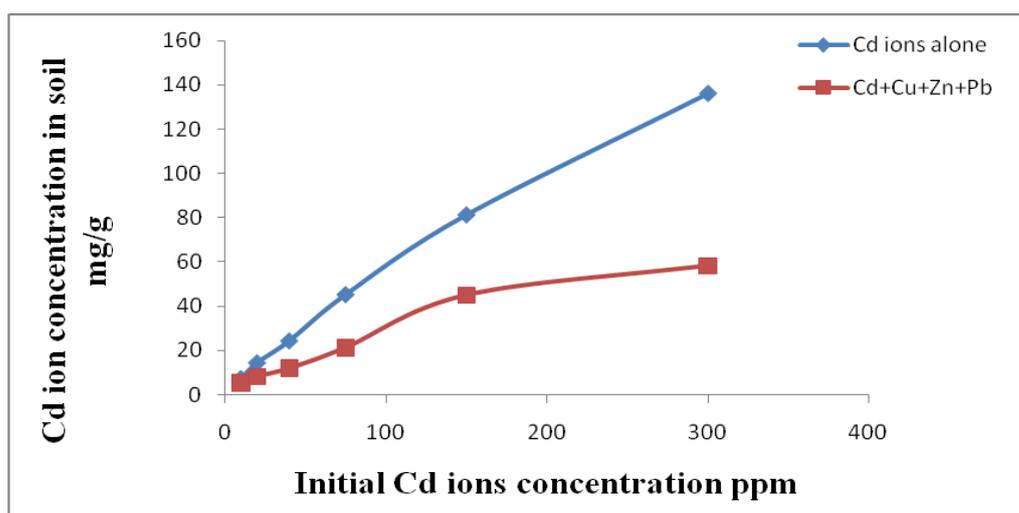
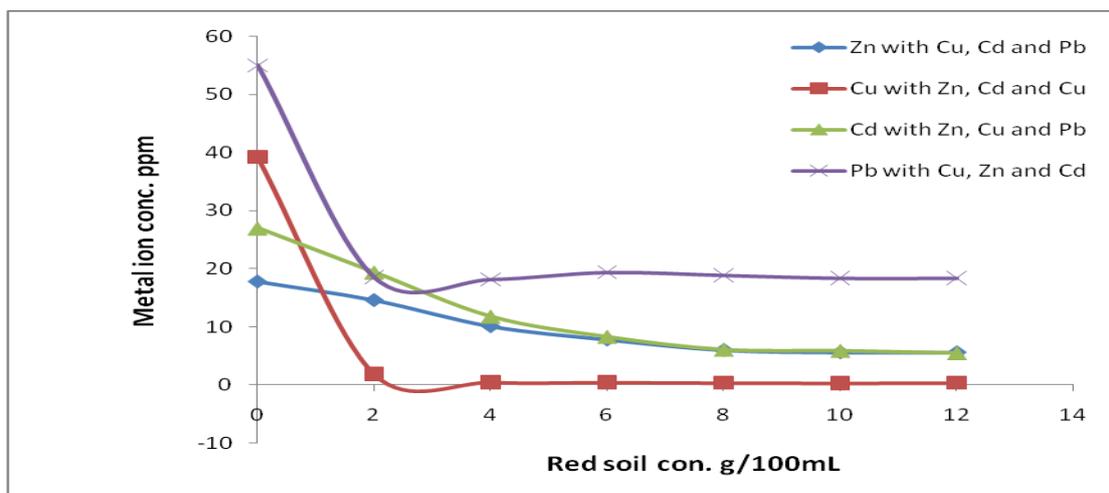


Figure 4.15 Adsorption of Cadmium Ions on Red Soil With Single (Cd^{2+}) and Multi Metal Ions (Cu^{2+} , Cd^{2+} , Zn^{2+} and Pb^{2+}) at Soil Concentration Equal 1.0 gram/100mL.

Finally, Figures (4.16, 4.17) shows the summing of four metals Copper, Zinc, Cadmium and Lead.

Table 4.14 Adsorption of Metal Ions on Red Soil from 100 mL of 50 ppm of Four Metal Ions ($\text{Pb}^{2+} + \text{Cu}^{2+} + \text{Zn}^{2+} + \text{Cd}^{2+}$) in Solution

Soil conc. g/100mL	Zn^{2+} ions (ppm) remained in solution from a solution containing four metal ions	Cu^{2+} ions (ppm) remained in solution from a solution containing four metal ions	Cd^{2+} ions (ppm) remained in solution from a solution containing four metal ions	Pb^{2+} ions (ppm) remained in solution from a solution containing four metal ions
0.0	17.8	39.25	27.0	55.0
2.0	14.6	1.9	19.4	18.6
4.0	10.1	0.48	11.8	18.2
6.0	7.8	0.46	8.3	19.4
8.0	6.0	0.37	6.1	18.9
10.0	5.6	0.34	5.9	18.4
12.0	5.6	0.37	5.5	18.4



FFigure 4.16 Adsorption of Metal Ions on Red Soil from 100 mL of 50 ppm of Four Metal Ions ($\text{Pb}^{2+} + \text{Cu}^{2+} + \text{Zn}^{2+} + \text{Cd}^{2+}$) in Solution

Table 4.15 Adsorption of Metal Ions on Red Soil From Different Concentrations of Four Metal Ions (Cu^{2+} , Cd^{2+} , Zn^{2+} and Pb^{2+}) in Solution at Soil Concentration Equal 1.0 gram/100mL

Initial conc. of four ions (ppm) in solution.	Pb^{2+} ions (ppm) adsorbed on soil from a solution containing four metal ions	Cu^{2+} ions (ppm) adsorbed on soil from a solution containing four metal ions	Zn^{2+} ions (ppm) adsorbed on soil from a solution containing four metal ions	Cd^{2+} ions (ppm) adsorbed on soil from a solution containing four metal ions
10.0	8.9	0.2	4.7	5.3
20.0	15.6	6.4	7.2	8.2
40.0	25.6	9.5	8.3	12.0
75.0	41.2	13.5	17.0	21.3
150.0	52.5	15.0	27.1	45.0
300.0	58.3	18.0	54.2	58.3

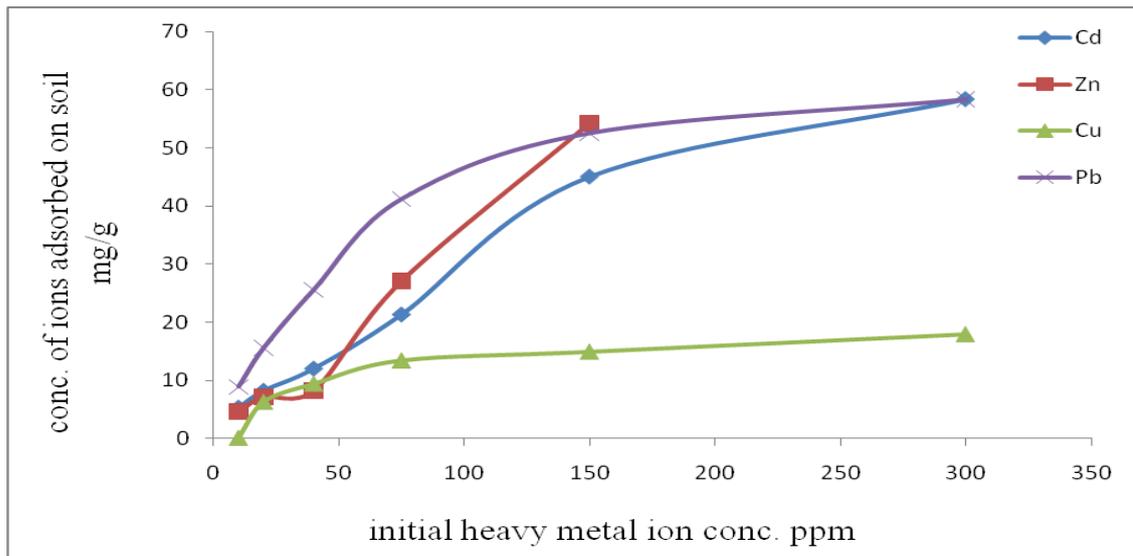


Figure 4.17 Adsorption of Metal Ions on Red Soil From Different Concentrations of Four Metal Ions (Cu^{2+} , Cd^{2+} , Zn^{2+} and Pb^{2+}) in Solution at Soil Concentration Equal 1.0 gram/100mL.

Concerning the main question of the competitive adsorption mechanism, the batch experiment results have clearly shown a different behavior of heavy metals in the four studied metals. In fact, for red soil Cu has clearly shown the highest adsorption rate as compared to Cd, Pb and Zn, Figure (4.16). A similar conclusion was reported by McBrib, 1995 and Alcacio et al., 2001. For adsorption isotherms, the selectivity sequence was $\text{Cu} > \text{Pb} > \text{Zn} = \text{Cd}$ in single-element systems and $\text{Pb} > \text{Zn} = \text{Cd} > \text{Cu}$ in multi-element systems Figures (4.16-17).

The extended constant-capacitance surface complexation model by Srivastava P., et al., 2005 proposed three kinds of possible reaction mechanism to explain the adsorption behavior.

At low pH, all these metals adsorb onto permanent charge sites by ion exchange reactions. Adsorption onto variable charge sites takes place

at higher pH by forming inner-sphere complexes at the crystal edges and octahedral alumina faces. The hydroxyl species of Cu and Pb adsorb by forming monodentate inner-sphere complexes, whereas adsorption of Cd and Zn on variable charges occurs by forming bidentate complexes.

Permanent-charge minerals such as montmorillonite carry a negative charge as a result of ion substitution during the formation of the minerals variable-charge minerals such as Fe, Mn, and Al oxides carry charges varying from negative to positive, depending on pH.

Adsorption and desorption of Cu^{2+} on soil are affected by the proportion of these two types of minerals. Moreover, the Fe, Al, and Mn oxides have a relatively strong affinity (pH dependent) for Cu^{2+} and other heavy metal cations and the adsorption of Cu^{2+} on these oxides is considered to be inner-sphere complex through a chemisorption process (Bertsch and Seaman, 1999). On the other hand, soil organic matter has a strong affinity for Cu^{2+} at low levels of Cu^{2+} (Buffle, 1988).

Recently, Alcacio et al. (2001) provided spectroscopic evidence for the hypothesis proposed by McBride (1994) for the possible binding configurations of Cu^{2+} on complexes of oxide minerals and organic matter: (i) Cu^{2+} is bonded to the mineral surfaces only (inner-sphere complex); (ii) Cu^{2+} is bonded to the organic matter that is adsorbed by the oxides at high levels; and (iii) Cu^{2+} acts as a bridge cation between the oxides and the organic matter that is adsorbed at low levels. Therefore, Fe,

Al, and Mn oxides and organic matter are considered to play a very important role in the adsorption–desorption of Cu^{2+} in the variable-charge soil.

4.3 The Effect of Competitive Ions on the Adsorption of Heavy Metals on White Chalk and on Sandy Soil

The effect of the presence of competing ions on the adsorption of metal ions on white chalk and on sandy soil was studied using the ions Pb, Cu, Zn and Cd.

The adsorption of each metal ion on white chalk and on sandy soil was examined with and without other ions. This study was done at constant metal ion concentration (50ppm) and variable white chalk and sandy soil concentration (0-12g/100mL). The results of these experiments are shown in Tables 4.16-4.225 and Figures 4.18-4.27.

The effect of the initial concentration on the adsorption of Pb, Cu, Zn and Cd on white chalk and sandy soil was examined and the results are shown in Table 4.16-4.25, Figures 4.18-4.27. When increasing the initial metal ion concentration from 0.0 to 14 g/100 mL resulted in an increase in the metal ion adsorbed of both single metal and multi-metal competitive adsorption. In general, the adsorption of Pb and Cu ions onto the chalk and sandy soil was not significantly different between single metal and multi-metal ion competitive adsorption at any concentration of soil as shown in Figures (4.18, 4.21, 4.23 and 4.26). This agrees with the

conclusions of K. G. Bhattacharyya et al., 2008. In contrast, there was a significant difference between single metal and multi-metal ion adsorbed on soil from Zn and Cd as shown in Figures (4.20, 4-24, 4.19 and 4.25).

The adsorption of these elements in single metal was more than twice in multi-metal ion competitive adsorption. It may be because a large number of the adsorption sites were available to the metal ion and the adsorption was independent of the initial concentration of the soil.

At higher pH values, the adsorption of Cd, Zn, Cu and Pb takes place onto variable charge sites by forming inner-sphere complexes at the crystal edges and octahedral alumina faces.

The hydroxyl species of Cu and Pb adsorb by forming monodentate inner-sphere complexes, whereas adsorption of Cd and Zn on variable charges occurs by forming bidentate complexes. A similar conclusion was reported by S. Yu, Z. L. He et al. 2002.

Finally, Figures (4.22, 4.27), shows the summing of four metals (Copper, Zinc, Cadmium and Lead).

Table 4.16 Adsorption of Lead Ions on White Chalk Soil from 100 mL of 50 ppm Pb²⁺ Ions in Solution and 100 mL of 50 ppm of Four Metal Ions (Pb²⁺ + Cu²⁺ + Zn²⁺ + Cd²⁺) in Solution

Soil conc. g/100mL	Pb ²⁺ ions (ppm) remained in solution from a solution containing Pb ²⁺ ions alone	Pb ²⁺ ions (ppm) remained in solution from a solution containing four metal ions
0.0	50.0	50.0
2.0	20.0	21.0
4.0	19.0	20.0
6.0	19.0	19.0
8.0	19.0	18.0
10.0	19.0	16.0

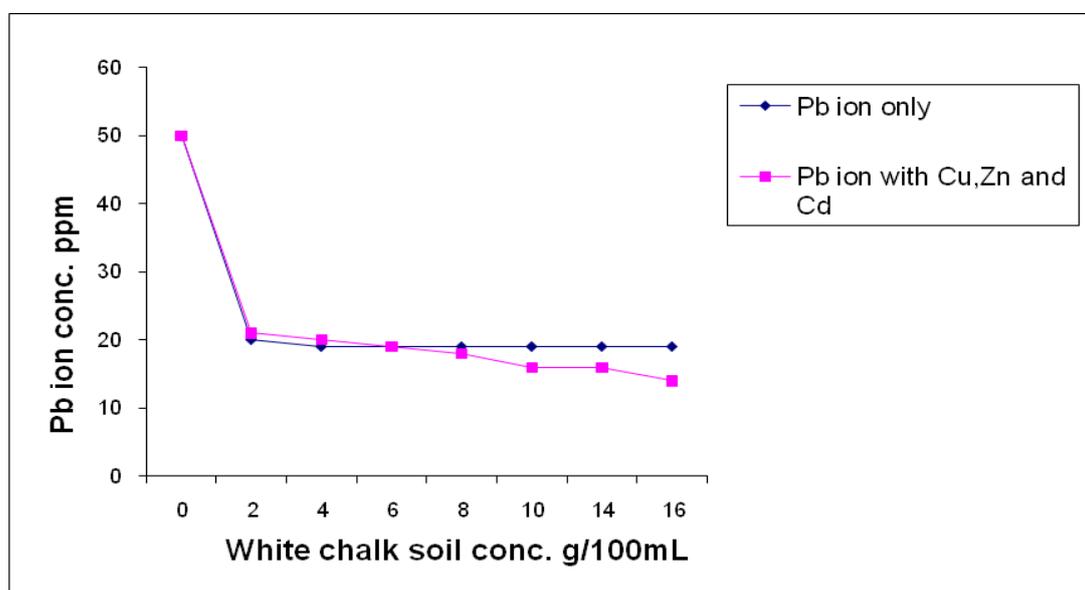


Figure 4.18 Adsorption of Lead Ions on White Chalk Soil from 100 mL of 50 ppm Pb²⁺ Ions in Solution and 100 mL of 50 ppm of Four Metal Ions (Pb²⁺ + Cu²⁺ + Zn²⁺ + Cd²⁺) in Solution

Table 4.17 Adsorption of Cadmium Ions on White Chalk Soil from 100 mL of 50 ppm Cd^{2+} Ions in Solution and 100 mL of 50 ppm of Four Metal Ions ($\text{Pb}^{2+} + \text{Cu}^{2+} + \text{Zn}^{2+} + \text{Cd}^{2+}$) in Solution

Soil conc. g/100mL	Cd^{2+} ions (ppm) remained in solution from a solution containing Cd^{2+} ions alone	Cd^{2+} ions (ppm) remained in solution from a solution containing four metal ions
0.0	50.0	50.0
2.0	3.0	35.0
4.0	0.0	20.0
6.0	0.0	15.0
8.0	0.0	0.0
10.0	0.0	0.0
14.0	0.0	0.0

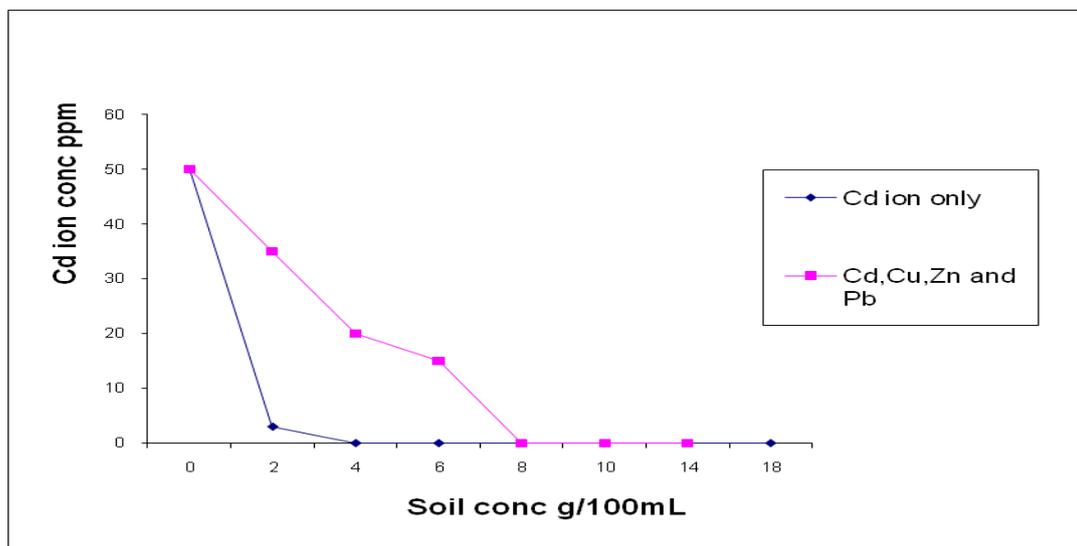


Figure 4.19 Adsorption of Cadmium Ions on White Chalk Soil from 100 mL of 50 ppm Cd^{2+} Ions in Solution and 100 mL of 50 ppm of Four Metal Ions ($\text{Pb}^{2+} + \text{Cu}^{2+} + \text{Zn}^{2+} + \text{Cd}^{2+}$) in Solution

Table 4.18 Adsorption of Zinc Ions on White Chalk Soil from 100 mL of 50 ppm Zn^{2+} Ions in Solution and 100 mL of 50 ppm of Four Metal Ions ($Pb^{2+} + Cu^{2+} + Zn^{2+} + Cd^{2+}$) in Solution

Soil conc. g/100mL	Zn^{2+} ions (ppm) remained in solution from a solution containing Zn^{2+} ions alone	Zn^{2+} ions (ppm) remained in solution from a solution containing four metal ions
0.0	50.0	50.0
2.0	8.0	40.0
4.0	5.0	30.0
6.0	5.0	26.0
8.0	4.5	20.0
10.0	4.5	16.0
12.0	4.0	16.0

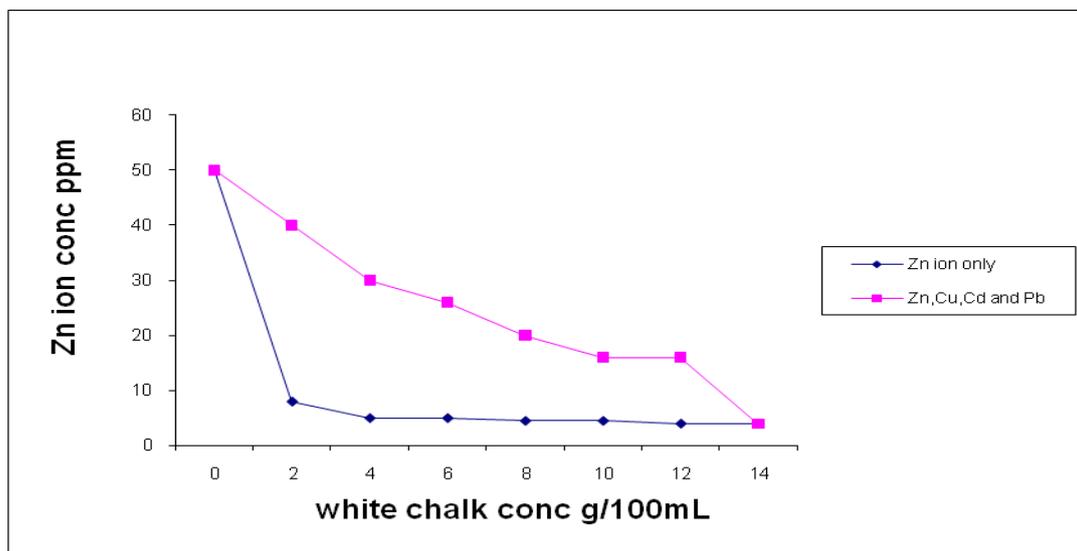


Figure 4.20 Adsorption of Zinc Ions on White Chalk Soil from 100 mL of 50 ppm Zn^{2+} Ions in Solution and 100 mL of 50 ppm of Four Metal Ions ($Pb^{2+} + Cu^{2+} + Zn^{2+} + Cd^{2+}$) in Solution

Table 4.19 Adsorption of Copper Ions on Red White Chalk from 100 mL of 50 ppm Cu^{2+} Ions in Solution and 100 mL of 50 ppm of Four Metal Ions ($\text{Pb}^{2+} + \text{Cu}^{2+} + \text{Zn}^{2+} + \text{Cd}^{2+}$) in Solution

Soil conc. g/100mL	Cu^{2+} ions (ppm) remained in solution from a solution containing Cu^{2+} ions alone	Cu^{2+} ions (ppm) remained in solution from a solution containing four metal ions
0.0	50.0	50.0
2.0	0.0	12.0
4.0	0.0	6.0
6.0	0.0	4.0
8.0	0.0	0.0
10.0	0.0	0.0
14.0	0.0	0.0

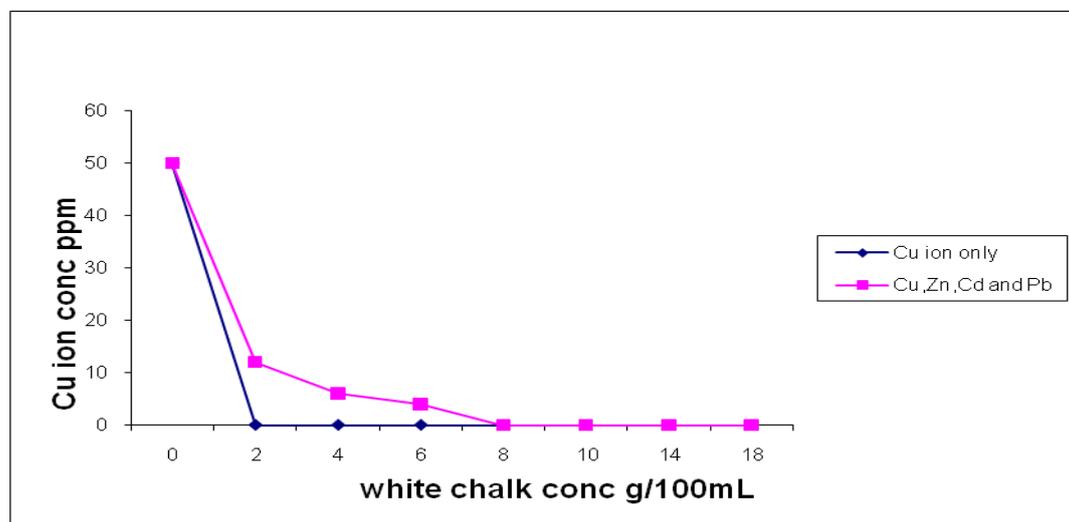


Figure 4.21 Adsorption of Copper Ions on White Chalk Soil from 100 mL of 50 ppm Cu^{2+} Ions in Solution and 100 mL of 50 ppm of Four Metal Ions ($\text{Pb}^{2+} + \text{Cu}^{2+} + \text{Zn}^{2+} + \text{Cd}^{2+}$) in Solution

Table 4.20 The Effect of Competing Ions on the Adsorption of Cu, Pb, Zn and Cd on White Chalk

Soil conc. g/100m L	Pb ²⁺ ions (ppm) remained in solution from a solution containing four ions	Cd ²⁺ ions (ppm) remained in solution from a solution containing four ions	Zn ²⁺ ions (ppm) remained in solution from a solution containing four ions	Cu ²⁺ ions (ppm) remained in solution from a solution containing four ions
0.0	50.0	50.0	50.0	50.0
2.0	26.0	35.0	40.0	12.0
4.0	20.0	20.0	30.0	6.0
6.0	18.0	15.0	26.0	4.0
8.0	15.0	6.0	20.0	0.0
10.0	12.0	0.0	16.0	0.0
14.0	12.0	0.0	16.0	0.0

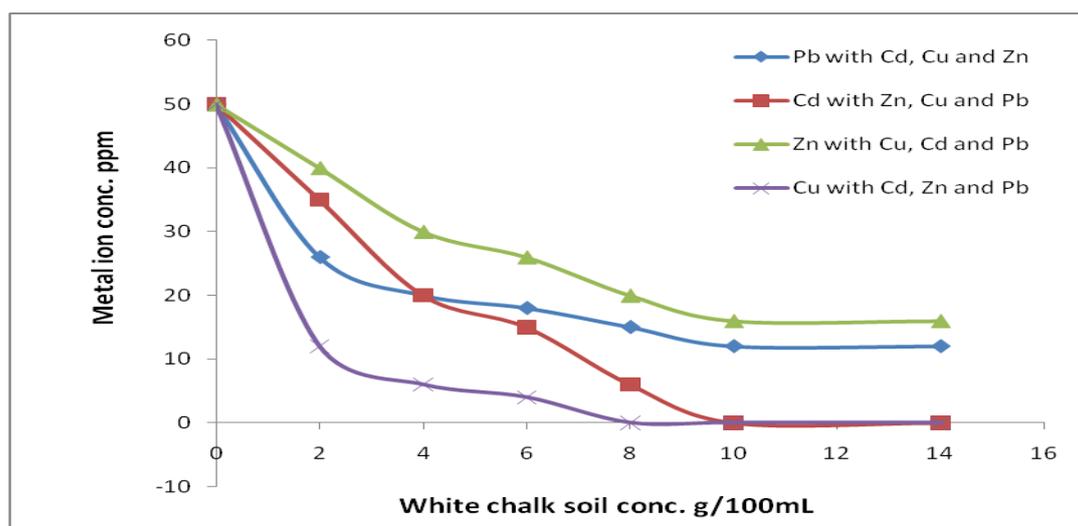


Figure 4.22 Adsorption of Metal Ions on White Chalk Soil from 100 mL of 50 ppm of Four Metal Ions (Pb²⁺ + Cu²⁺ + Zn²⁺ + Cd²⁺) in Solution

Table 4.21 Adsorption of Copper Ions on Sandy Soil from 100 mL of 50 ppm Cu^{2+} Ions in Solution and 100 mL of 50 ppm of Four Metal Ions ($\text{Pb}^{2+} + \text{Cu}^{2+} + \text{Zn}^{2+} + \text{Cd}^{2+}$) in Solution

Soil conc. g/100mL	Cu^{2+} ions (ppm) remained in solution from a solution containing Cu^{2+} ions alone	Cu^{2+} ions (ppm) remained in solution from a solution containing four metal ions
0.0	36.0	42.0
2.0	4.5	22.0
4.0	3.0	17.0
6.0	2.5	16.0
8.0	1.0	12.0
10.0	0.0	5.0
14.0	0.0	3.0

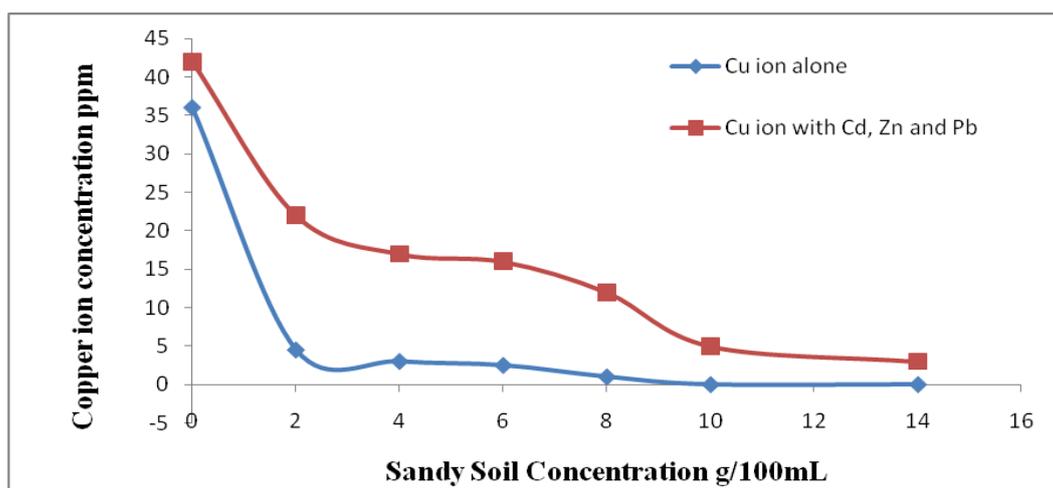


Figure 4.23 Adsorption of Copper Ions on Sandy Soil from 100 mL of 50 ppm Cu^{2+} Ions in Solution and 100 mL of 50 ppm of Four Metal Ions ($\text{Pb}^{2+} + \text{Cu}^{2+} + \text{Zn}^{2+} + \text{Cd}^{2+}$) in Solution

Table 4.22 Adsorption of Zinc Ions on Sandy Soil from 100 mL of 50 ppm Zn^{2+} Ions in Solution and 100 mL of 50 ppm of Four Metal Ions ($Pb^{2+} + Cu^{2+} + Zn^{2+} + Cd^{2+}$) in Solution

Soil conc. g/100mL	Zn^{2+} ions (ppm) remained in solution from a solution containing Zn^{2+} ions alone	Zn^{2+} ions (ppm) remained in solution from a solution containing four metal ions
0.0	50.0	50.0
2.0	18.0	45.0
4.0	9.0	40.0
6.0	8.0	40.0
8.0	6.6	40.0
10.0	6.0	37.0
14.0	5.8	35.0

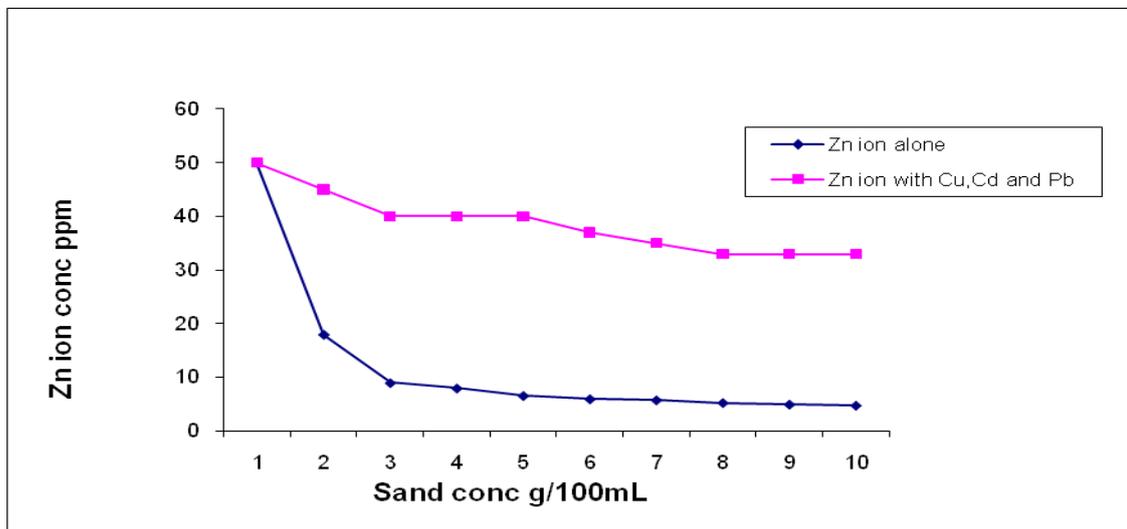


Figure 4.24 Adsorption of Zinc Ions on Sandy Soil from 100 mL of 50 ppm Zn^{2+} Ions in Solution and 100 mL of 50 ppm of Four Metal Ions ($Pb^{2+} + Cu^{2+} + Zn^{2+} + Cd^{2+}$) in Solution

Table 4.23 Adsorption of Cadmium Ions on Sandy Soil from 100 mL of 50 ppm Cd^{2+} Ions in Solution and 100 mL of 50 ppm of Four Metal Ions ($\text{Pb}^{2+} + \text{Cu}^{2+} + \text{Zn}^{2+} + \text{Cd}^{2+}$) in Solution

Soil conc. g/100mL	Cd^{2+} ions (ppm) remained in solution from a solution containing Cd^{2+} ions alone	Cd^{2+} ions (ppm) remained in solution from a solution containing four metal ions
0.0	37.0	50.0
2.0	0.0	48.0
4.0	0.0	44.0
6.0	0.0	40.0
8.0	0.0	38.0
10.0	0.0	33.0
14.0	0.0	30.0

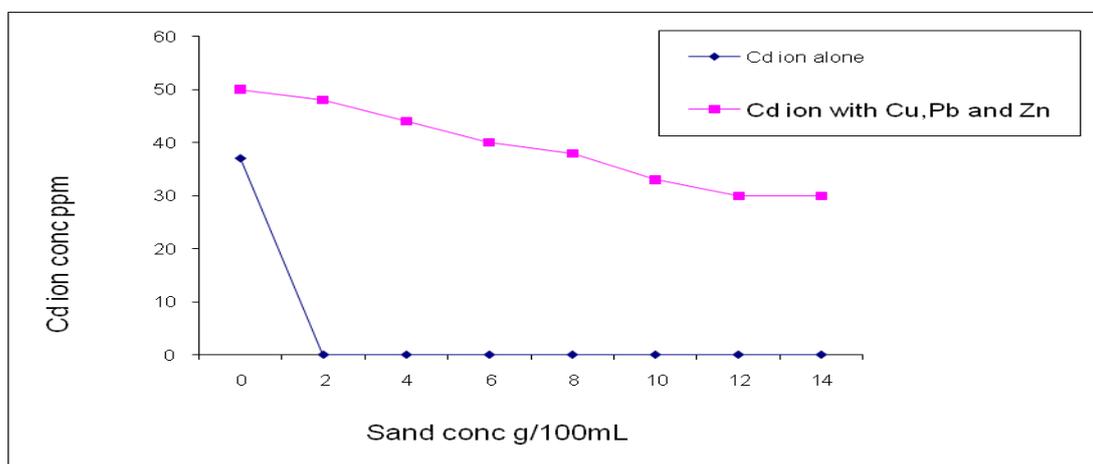


Figure 4.25 Adsorption of Cadmium Ions on Sandy Soil from 100 mL of 50 ppm Cd^{2+} Ions in Solution and 100 mL of 50 ppm of Four Metal Ions ($\text{Pb}^{2+} + \text{Cu}^{2+} + \text{Zn}^{2+} + \text{Cd}^{2+}$) in Solution

Table 4.24 Adsorption of Lead Ions on Sandy Soil from 100 mL of 50 ppm Pb^{2+} Ions in Solution and 100 mL of 50 ppm of Four Metal Ions ($Pb^{2+} + Cu^{2+} + Zn^{2+} + Cd^{2+}$) in Solution

Soil conc. g/100mL	Pb^{2+} ions (ppm) remained in solution from a solution containing Pb^{2+} ions alone	Pb^{2+} ions (ppm) remained in solution from a solution containing four metal ions
0.0	45.0	50.0
2.0	19.0	30.0
4.0	19.0	26.0
6.0	19.0	23.0
8.0	19.0	21.0
10.0	19.0	20.0
14.0	19.0	19.0

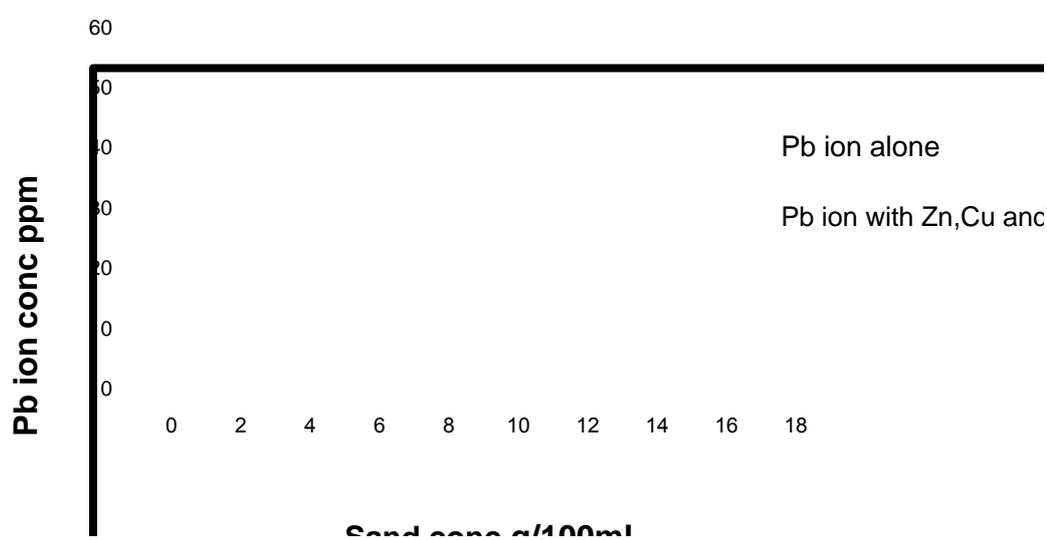


Figure 4.26 Adsorption of Lead Ions on Sandy Soil from 100 mL of 50 ppm Pb^{2+} Ions in Solution and 100 mL of 50 ppm of Four Metal Ions ($Pb^{2+} + Cu^{2+} + Zn^{2+} + Cd^{2+}$) in Solution

Table 4.25 Adsorption of Metal Ions on Sandy Soil from 100 mL of 50 ppm of Four Metal Ions ($\text{Pb}^{2+} + \text{Cu}^{2+} + \text{Zn}^{2+} + \text{Cd}^{2+}$) in Solution

Soil conc. g/100mL	Pb^{2+} ions (ppm) remained in solution from a solution containing four ions	Cd^{2+} ions (ppm) remained in solution from a solution containing four ions	Zn^{2+} ions (ppm) remained in solution from a solution containing four ions	Cu^{2+} ions (ppm) remained in solution from a solution containing four ions
0.0	50.0	50.0	50.0	42.0
2.0	30.0	48.0	45.0	22.0
4.0	26.0	44.0	40.0	17.0
6.0	23.0	40.0	40.0	16.0
8.0	21.0	38.0	40.0	12.0
10.0	20.0	33.0	37.0	5.0
14.0	19.0	30.0	35.0	3.0

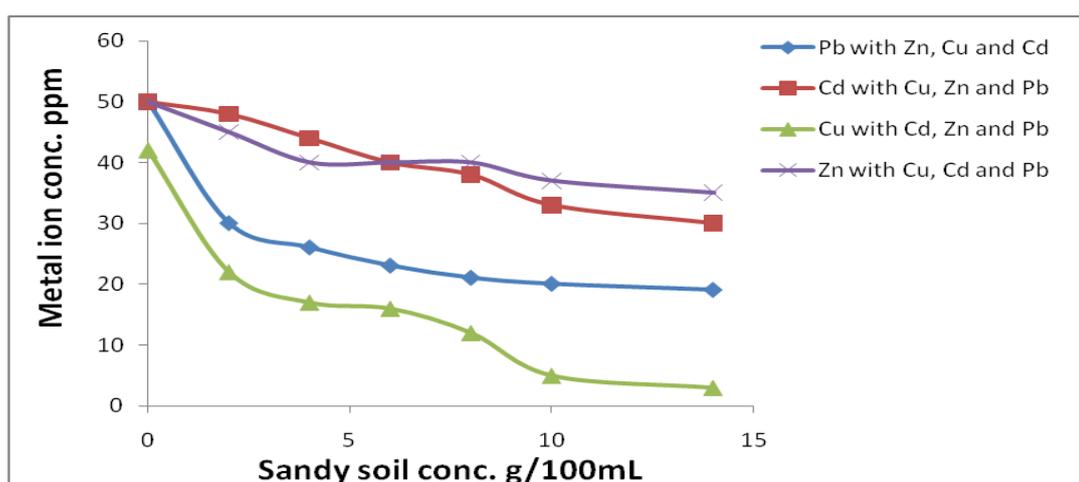


Figure 4.27 Adsorption of Metal Ions on Sandy Soil from 100 mL of 50 ppm of Four Metal Ions ($\text{Pb}^{2+} + \text{Cu}^{2+} + \text{Zn}^{2+} + \text{Cd}^{2+}$) in Solution

4.4 The Effect of pH on Adsorption of Copper Ions on Red Soil at Room Temperature (25 °C).

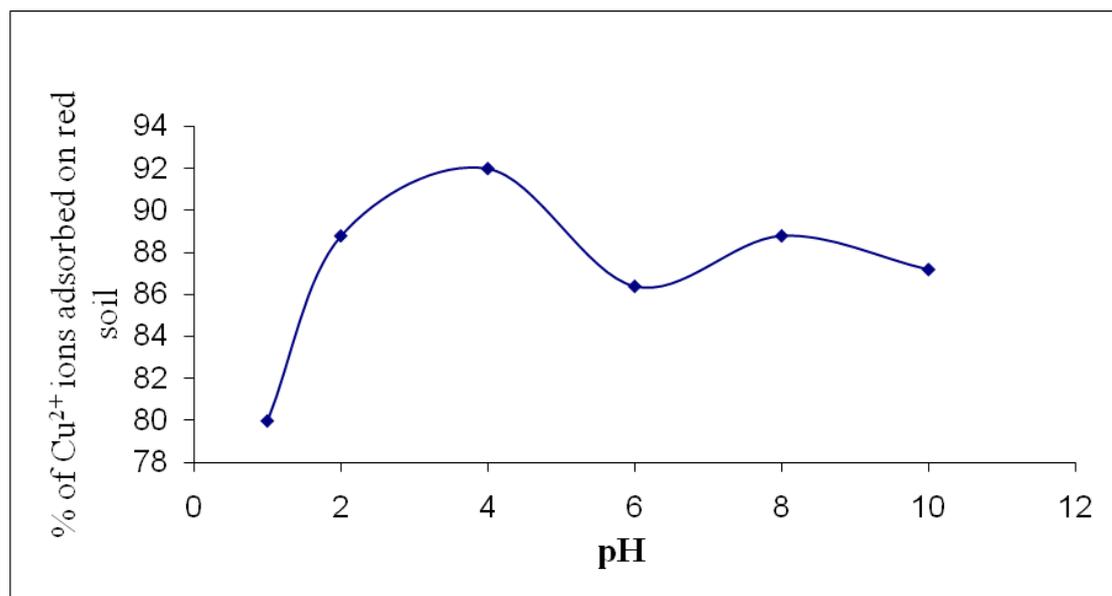
Soil pH is the most important parameter influencing metal-solution and soil-surface chemistry. The dependence of heavy metals adsorption on solution pH has been noticed early by H. B. Bradl. (2004), they concluded that the number of negatively charged sites on soil surface increases with pH.

In general, heavy metal adsorption is small at low pH values in which adsorption occurred onto permanent charge sites by ion exchange reactions. Adsorption onto variable charge sites takes place at higher pH by forming inner-sphere complexes at the crystal edges and octahedral alumina faces. The hydroxyl species of Cu^{2+} adsorb by forming monodentate inner-sphere complexes. Permanent-charge minerals such as montmorillonite carry a negative charge as a result of ion substitution during the formation of the minerals. Variable-charge minerals such as Fe, Mn, and Al oxides carry charges varying from negative to positive, depending on pH.

Adsorption increases at intermediate pH value (pH=4.0) over a relatively small pH range; this pH range is referred to as the pH-adsorption edge. At high pH values, the metal ions are completely removed from solution and precipitated as metal hydroxides. Figure (4.28) shows the pH dependence of copper ions adsorption onto a red soil which consists basically of Al-, Fe-, and Si-oxides.

Table 4.26 Adsorption of Copper on Red Soil at Different pH Values

pH	% of Cu ⁺² Ions Adsorbed on Red soil
1.0	80.0 %
2.0	88.8 %
4.0	92.0 %
6.0	86.4 %
8.0	88.8 %
10.0	87.2 %

**Figure 4.28 Adsorption of Copper on Red Soil at Different pH Values**

In general, adsorption of heavy metals onto oxide and humic constituents of soil follows the basic trend of metal-like adsorption, which is characterized by increased adsorption with pH as mentioned by Tessier A., et al., (1989) and Kooner Z. S., (1998).

4.5. Desorption of Copper from Artificially Contaminated Red Soil Using Different Types and Concentrations of Surfactants in the Absence of Ligands

The objective of this study was to measure the desorption rates of selected heavy metals from artificially contaminated red soil in the presence of various surfactants. Four surfactants were evaluated in this study; the anionic surfactant SDS, the nonionic surfactant Triton X-100, the nonionic surfactant Tween 80 and nonionic surfactant Tergitol. The surfactant concentrations used in the study were 0.2, 0.1, 0.05, 0.005 and 0.0005 mol / L.

The results of desorption of the four surfactants (Triton X-100, Tergitol, SDS and Tween 80) on artificially contaminated red soil in the absence of ligand is illustrated in Table (4.27) and Figure (4.29). The maximum amount of adsorbed copper on red soil found to be 330 mg/g. The control washed with pure distilled water adsorbed 42.8 mg/g which is 13% of the original amount of adsorbed copper on red soil and 0.1 M of Triton X-100 without ligands adsorbed 45.5 mg/g which is 14% of the original amount of adsorbed copper on red soil as shown in Table 4.30.

As shown in Table 4.27 Triton X-100 generally desorbed higher level of copper metals than the control which was only washed with distilled water. A gradual increase on desorption of copper was observed by Triton X -100, it was able to desorb 14% of copper ions from the original contaminated red soil. Triton X -100 (0.1 M) proved to be more

potent washing agent for red soil than distilled water and other surfactants; however its ability to desorb heavy metals remains limited.

Table 4.27 Desorption of Copper Ions (ppm) from Artificially Contaminated Red Soil by Surfactants in Absence of Ligands

Surfactant Conc. M	Triton X-100	Tergitol	Tween 80	S. D. S
	Desorbed Cu ²⁺ ions	Desorbed Cu ²⁺ ions	Desorbed Cu ²⁺ ions	Desorbed Cu ²⁺ ions
0.2	46.9	35.6	39.8	42.4
0.1	45.8	34.3	36.7	41.4
0.05	42.8	34.1	35.7	32.2
0.005	38.0	30.2	35.5	31.4
0.0005	31.0	32.5	31.8	25.2

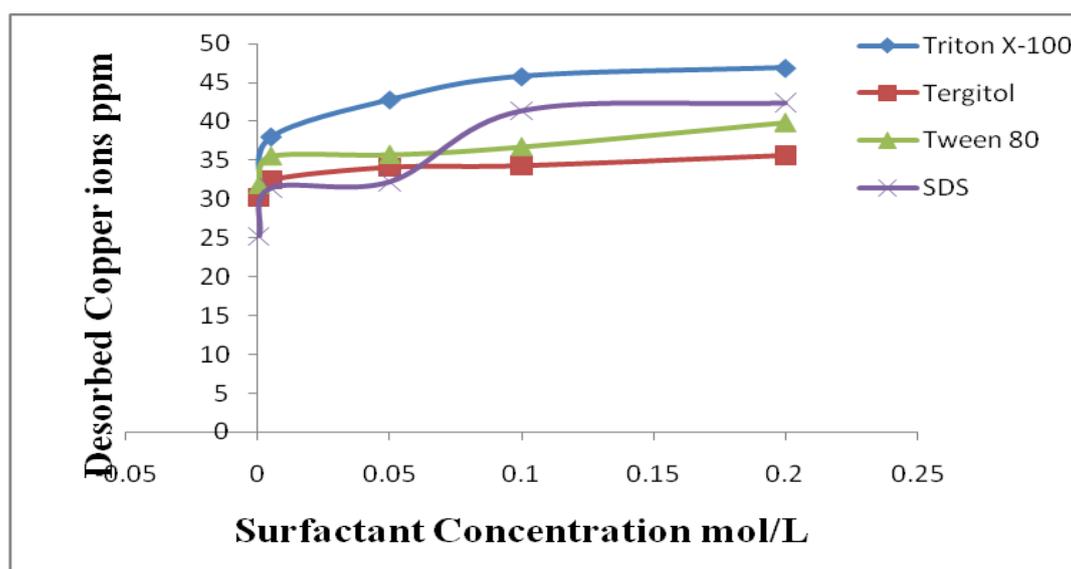


Figure 4.29 Desorption of Copper Ions From Artificially Contaminated Red Soil Using Surfactants in the Absence of Ligands

4.5.1. Desorption of Copper from Artificially Contaminated Sandy and White Chalk Soil Using Different Types and Concentrations of Surfactants in the Absence of Ligands

The results of desorption of the four surfactants mention in section 4.5 on artificially contaminated sandy soil in the absence of ligand are shown in Tables (4.28) and Figure (4.30). As shown in Table 4.28, Tween 80 generally desorbed a higher level of copper metals than the control washes with distilled water and surfactants. Results for all surfactants show that desorbed copper concentration increases with increasing surfactant concentration until the concentration of surfactant reach a value equal to two times the critical micelle concentration (CMC) value, above 0.1M surfactant concentration the removal of copper ions does not get altered very much (Figure 4.30).

The results suggest that the micelles indirectly cause the mobilization and removal of copper ions, as mentioned by Ramamurthy A. S. et al 2008. Bourbonais et al. (1995) expected anionic surfactants to exhibit better metal removal efficiency than nonionic surfactants, because amphoteric and cationic surfactants tend to form strong complexes with soil minerals. However, present results; indicate that significant differences in copper extraction using neutral and anionic surfactants were not present.

Similar results were obtained for white chalk results are summarized in Table (4.29) and Figure (4.31).

Table 4.28 Desorption of Copper Ions (ppm) from Artificially Contaminated Sandy Soil by Surfactants in the Absence of Ligands

Surfactant Conc.	Tween 80	Tergitol	Triton X-100	S. D. S
	Desorbed Cu ²⁺ ions			
0.2	71.4	15.4	7.9	52.3
0.1	54.4	12.2	2.4	35.9
0.05	52.5	8.1	3.2	20.3
0.005	67.0	3.0	4.728	3.3
0.0005	60.7	1.8	1.9	1.5

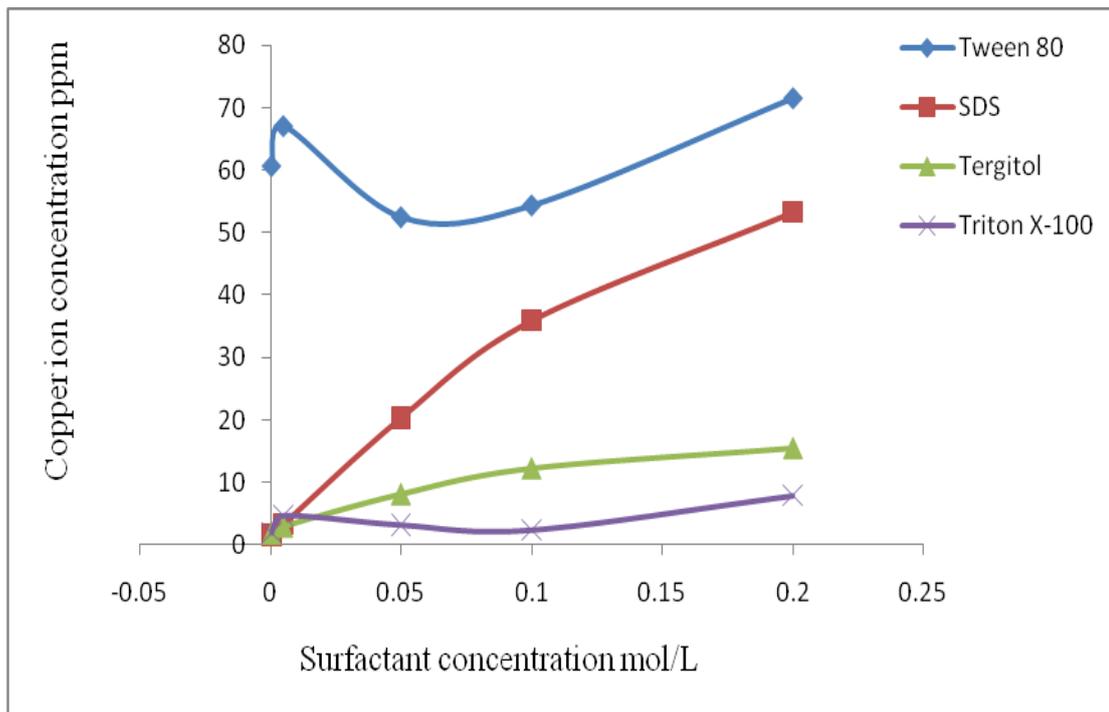


Figure 4.30 Desorption of Copper Ions (ppm) from Artificially Contaminated Sandy Soil by Surfactants in the Absence of Ligands

Table 4.29 Desorption of Copper Ions (ppm) from Artificially Contaminated White Chalk Soil by Surfactants in the Absence of Ligands

Surfactant Conc.	Tween 80	Tergitol	S. D. S
	Desorbed Cu^{2+} ions	Desorbed Cu^{2+} ions	Desorbed Cu^{2+} ions
0.2	16.7	3.2	7.3
0.1	8.8	1.6	3.5
0.05	5.1	0.8	1.3
0.005	3.8	0.6	0.8
0.0005	2.8	0.5	0.8

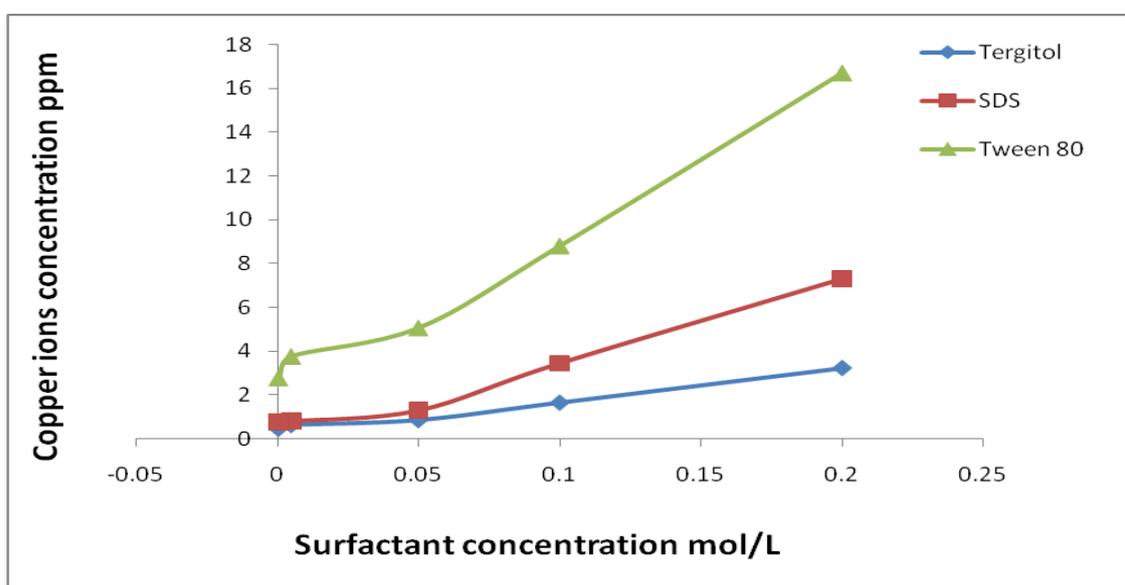


Figure 4.31 Desorption of Copper Ions (ppm) from Artificially Contaminated White Chalk Soil by Surfactants in the Absence of Ligands

4.6 Desorption of Copper from Artificially Contaminated Soil Using 0.1 M Triton X-100 with Different Concentrations of Ligands

The purpose of this study was to evaluate the effect of Triton X - 100 and different ligands like EDTA, Γ^- and SCN^- on desorption of copper ions from three artificially contaminated types of soil. The maximum amount of adsorbed copper on red soil found to be 330 mg/g.

The surfactant concentration used in the test was 0.1 mol/ L which is higher than the CMC level of Triton X-100 surfactant. Therefore, surfactant monomers are expected to form micelles in the experimental solution used, the same results was obtained by Chu and Chan, 2003.

4.6.1 Desorption of Copper from Artificially Contaminated Red Soil Using 100 mL of 0.1 M Triton X-100 with Different Concentrations of the Ligands Γ^- , SCN^- and EDTA

In the presence of Triton X-100, the heavy metal desorption efficiencies of the ligands Γ^- , SCN^- , and EDTA are presented in Tables (4.30, 4.31& 4.32) and in Figures (4.32, 4.33). The ligand Γ^- desorbed 18% Cu at the maximum tested ligand concentration of 0.4 mol/ L. From the results shown in Tables 4.30, 4.31, 4.32, the desorption efficiency for heavy metals increased with increasing ligand concentration, except for the lower ligand concentration of 0.05 M Γ^- and SCN^- , the desorption of copper was 35% higher than 0.1 M Γ^- , same thing happened in the case of 0.05 M SCN^- the desorption was 84% higher than 0.1 M SCN^- .

When 0.4 M solution of ligands I^- and SCN^- in the presence of Triton X-100, it desorbed 18 % and 15 % Cu, (Table 4.30). It is also shown that increasing ligand concentration will increase heavy metal mobilization.

Copper preferred the SCN^- -complex at very low concentrations but it preferred the I^- complex at high concentrations of ligand in presence of Triton X-100, Figure (4.33). Although both SCN^- and I^- complexes desorbed only limited quantities of copper proved to be relatively immobile as compared to other ligands like EDTA, because of its smaller hydrated ionic radius, and therefore its greater attraction for soil adsorption sites.

The results of these experiments were consistent with heavy metal complexation behavior in surfactant micellar suspension in aqueous media (Shin et al., 1997; Shin et al., 2000).

The micelle-solubilized ligand complex was therefore quite efficient at removing heavy metal from soil if the ligand selected had an appreciable affinity for the target heavy metal. Finally, the micelle-solubilized ligand complex did not require acidification of the soil to desorb the heavy metals, as is required for certain other soil washing agents. This is an appreciable major environmental advantage because of the adverse effects of acidic conditions on microbial populations and plant growth (Reed et al., 1996). Various chemical reagents including chelating and extracting agents have been evaluated for their effectiveness in

extracting heavy metals from soils (Abumaizar and Khan, 1996; Abumaizar and Smith, 1999; Allen and Chen, 1993; Chen et al., 1992). Most studies have focused on comparisons of various chelating and extracting agents in batch tests with the conclusion that metal desorption efficiency depends on the soil type and on the composition of the washing solution. One chelating agent, ethylenediaminetetraacetic acid (EDTA), is quite

effective in removing heavy metals. 0.1 M EDTA with 0.1 mol/L desorbs more than 98% of copper adsorbed in red soil as shown in Table (4.32) and Figure (3.32), but can potentially affect the permeability of the treated soil (Abumaizar and Khan, 1996).

Since micelles are composed of an inner hydrophobic core and a hydrophilic exterior surface, the surfactant micelles can solubilize both ionic and non-ionic compounds, such as heavy metals and PCBs. Many studies directed to the extraction of hydrophobic contaminants from soils using surfactant micelles (Huang et al., 1997; Noordman et al., 1998; Zhang et al., 1997) have demonstrated that solubilization can be attributed to the incorporation of hydrophobic contaminants within the hydrophobic core of the surfactant micelles in solution.

Table 4.30 Desorption of Copper Ions (ppm) From Artificially Contaminated Red Soil Using Different Γ^- (Ligand) Concentrations in 100 mL of 0.1 M Triton X-100 Solution.

Distilled Water(100mL)	Triton X-100 0.1M(100mL)	Concentration of Γ^- (M) in 100 mL of 0.1M Triton X-100				
		0.05	0.1	0.2	0.3	0.4
42.8	45.5	29.0	21.5	26.5	93.3	60.3

Table 4.31 Desorption of Copper Ions (ppm) From Artificially Contaminated Red Soil Using Different SCN^- (Ligand) Concentrations in 100 mL of 0.1 M Triton X-100 Solution.

Distilled Water(100mL)	Triton X-100 0.1M(100mL)	Concentration of Γ^- (M) in 100 mL of 0.1M Triton X-100				
		0.05	0.1	0.2	0.3	0.4
24.8	45.5	35.5	19.3	17.0	17.0	50.5

Table 4.32 Desorption of Copper Ions (ppm) From Artificially Contaminated Red Soil Using Different EDTA (Ligand) Concentrations in 100 mL of 0.1 M Triton X-100 Solution.

Distilled Water(100mL)	Triton X-100 0.1M(100mL)	Concentration of Γ^- (M) in 100 mL of 0.1M Triton X-100				
		0.05	0.1	0.2	0.3	0.4
24.8	45.5	188.5	301.0	325.5	324.0	270.5

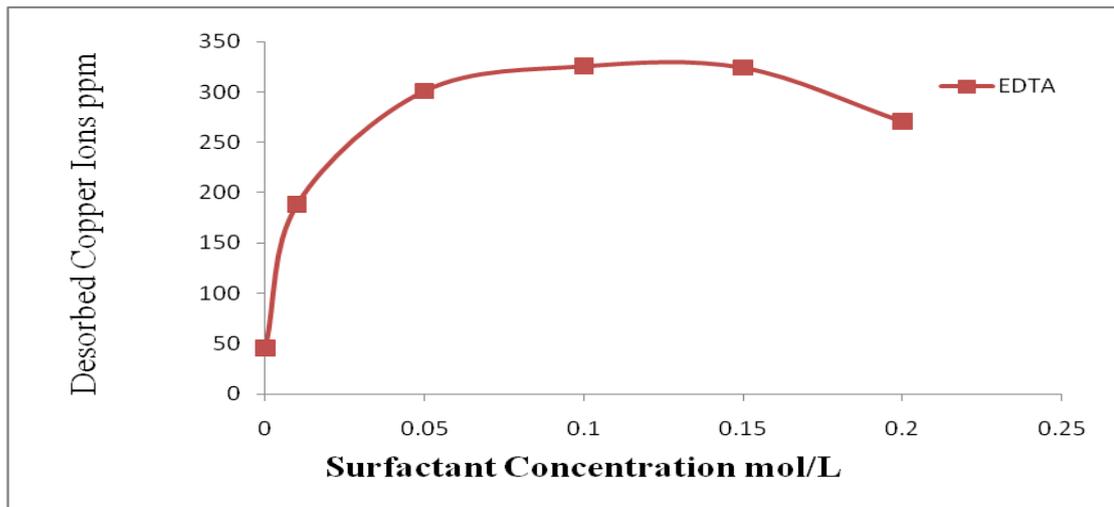


Figure 4.32 Desorption of Copper from Artificially Contaminated Red Soil Using Triton X-100 with Ligands

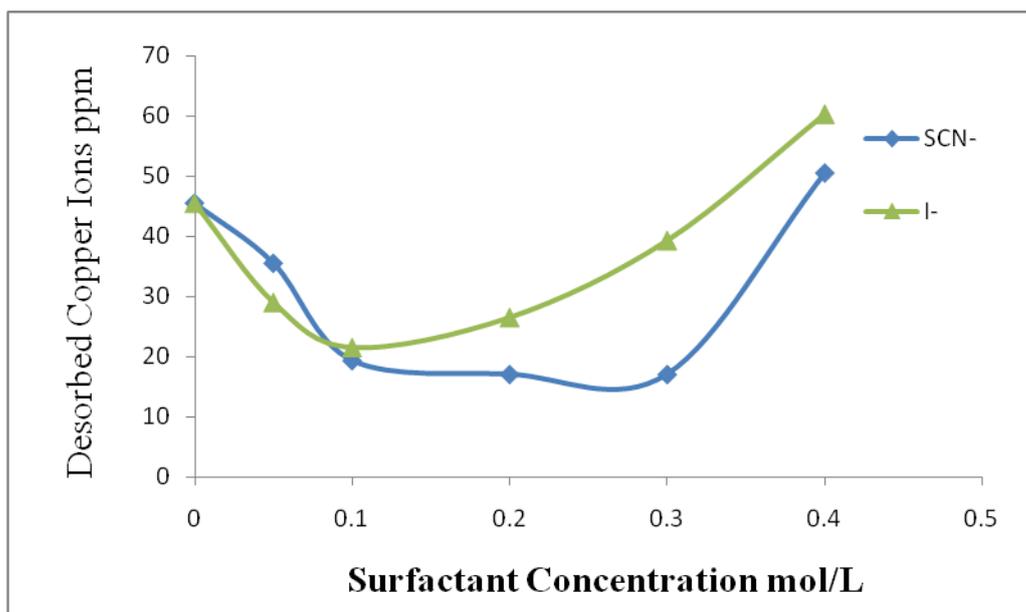


Figure 4.33 Desorption of Copper from Red Soil Using Triton X-100 with I⁻ and SCN⁻ Ligands

Some surfactants have been found to remove heavy metals from soils, under both acidic and alkaline conditions, through direct complexation followed by solubilization, this results were reported by Herman et al., 1995 and Mulligan et al., 1999. Without changing the soil pH, surfactants can extract heavy metals when coupled with a ligand that

forms a micelle-solubilized complex. The ligand interacts with the adsorbed metal where increases hydrophobic character of the product and results in preferential accumulation of the complex within the surfactant micelle. The results of these experiments were consistent with heavy metal complexation behavior in surfactant micellar suspension in aqueous media (Shin *et al.*, 1997; Shin *et al.*, 2000).

4.6.2 Desorption of Copper from Artificially Contaminated Sandy and White Chalk Soil Using Triton X-100 With Ligands

In Tables (4.33, 4.34 & 4.35) and Figures (4.34 and 4.35) we found that the concentration of Cu^{+2} in desorbed by distilled water from sandy soil was about 1.1 ppm which means that most of copper ions were desorbed in sandy soil. After addition of 100 mL of 0.1 M Triton X-100 to the contaminated sandy soil and analyzing Cu^{+2} in the aqueous solution, the concentration of Cu^{+2} in the aqueous phase found to be 1.4 ppm.

The experiment was done using Triton X-100 with different ligands like EDTA, I^- and SCN^- and the desorbed Cu^{+2} were as follow : 1.2 ppm for 0.05 M I^- , 195 ppm for 0.01 M EDTA, and 5.90 ppm for 0.05 M SCN^- see table (4.33). The other results observed as if we increase the concentrations of ligands from 0.05 M I^- to 0.4 M I^- the desorption of Cu^{+2} increases from 1.2 ppm to 13.7 ppm. The same observations occurred for both EDTA and SCN^- .

Increasing concentration of EDTA will increase the removal of Cu^{+2} ions. In the case of 0.15 M EDTA more than 98% Cu^{+2} removed

while using 0.01 M EDTA only 68% Cu^{+2} removed. These results agree with previous research (Abumaizar et al. 1999, Palma et al. 2003 and Ramamurthy et al., 2008). Soil flushing tests performed (Palma et al. 2003) on a sandy loam showed that complete lead and copper removal can be achieved by using a solution containing 0.01 M EDTA.

The excess dosage would insure that there were always sufficient molecules of chelating agents available to these heavy metals, even though some molecules of the chelating agents might be participated, adsorbed by the soil, or might form complexes with other cations (Ca, Mg, Fe, Al, and other trace heavy metals) that originally present in the soil.

Table 4.33 Desorption of Copper Ions (ppm) From Artificially Contaminated Sandy Soil Using Different I^- (Ligand) Concentrations in 100 mL of 0.1 M Triton X-100 Solution.

Distilled Water(100mL)	Triton X-100 0.1M(100mL)	Concentration of I^- (M) in 100 mL of 0.1M Triton X-100				
		0.01	0.05	0.1	0.15	0.2
1.1	1.4	1.2	2.1	5.2	8.7	13.7

Table 4.34 Desorption of Copper Ions (ppm) From Artificially Contaminated Sandy Soil Using Different SCN^- (Ligand) Concentrations in 100 mL of 0.1 M Triton X-100 Solution.

Distilled Water(100mL)	Triton X-100 0.1M(100mL)	Concentration of SCN^- (M) in 100 mL of 0.1M Triton X-100				
		0.01	0.05	0.1	0.15	0.2
1.1	1.4	5.9	10.8	28.3	28.9	74.0

Table 4.35 Desorption of Copper Ions (ppm) From Artificially Contaminated Sandy Soil Using Different EDTA (Ligand) Concentrations in 100 mL of 0.1 M Triton X-100 Solution.

Distilled Water(100mL)	Triton X-100 0.1M(100mL)	Concentration of I ⁻ (M) in 100 mL of 0.1M Triton X-100			
		0.01	0.05	0.1	0.15
1.1	1.4	195.0	241.0	249.0	281.0

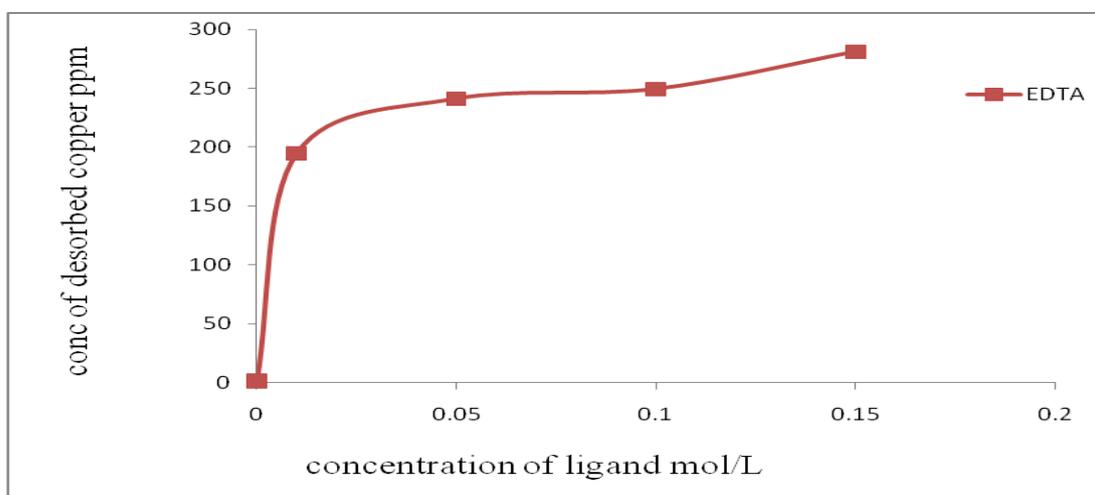


Figure 4.34 Desorption of Copper from Sandy Soil Using Triton X-100 with EDTA as a Ligand.

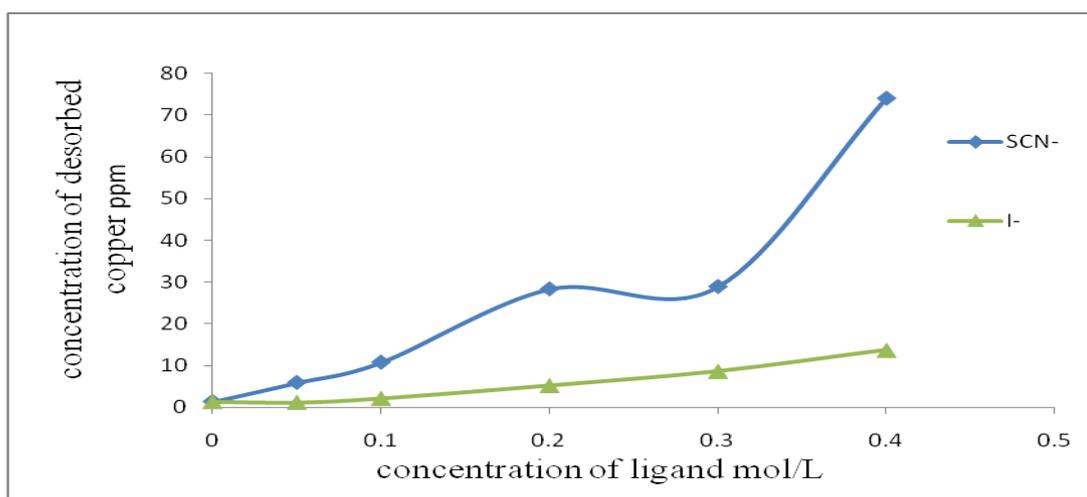


Figure 4.35 Desorption of Copper from Sandy Soil Using Triton X-100 with I⁻ and SCN⁻ Ligands

When this study was done on white chalk soil (Tables 4.36,4.37and 4.38) and Figures (4.36, 4.37) we found the same behavior of surfactant and ligands on desorbing copper from it as in sandy soil.

Table 4.36 Desorption of Copper Ions (ppm) From Artificially Contaminated White Chalk Soil Using Different Concentrations of I⁻ (Ligand) in 100 mL of 0.1 M Triton X-100 Solution.

Distilled Water(100mL)	Triton X-100 0.1M(100mL)	Concentration of I ⁻ (M) in 100 mL of 0.1M Triton X-100				
		0.05	0.1	0.2	0.3	0.4
2.5	3.5	11.0	18.4	33.3	48.0	63.0

Table 4.37 Desorption of Copper Ions from Artificially Contaminated White Chalk Soil Using Different Concentrations of SCN⁻ (Ligand) in 100 mL of 0.1 M Triton X-100 Solution.

Distilled Water(100mL)	Triton X-100 0.1M(100mL)	Concentration of SCN ⁻ (M) in 100 mL of 0.1M Triton X-100				
		0.05	0.1	0.2	0.3	0.4
2.5	3.5	38.0	59.0	67.0	75.0	82.0

Table 4.38 Desorption of Copper Ions (ppm) from Artificially Contaminated White Chalk Soil Using Different Concentrations of EDTA (Ligand) in 100 mL of 0.1 M Triton X-100

Distilled Water(100mL)	Triton X-100 0.1M(100mL)	Concentration of EDTA (M) in 100 mL of 0.1M Triton X-100				
		0.01	0.05	0.1	0.15	0.2
2.5	3.5	157.0	472.0	532.0	538.0	537.0

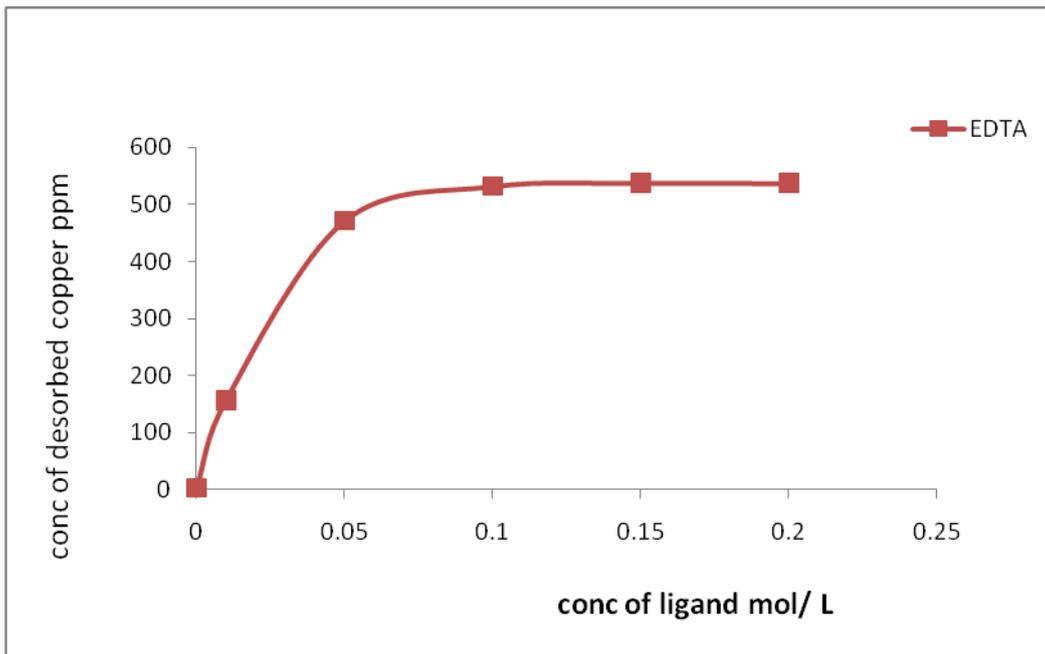


Figure 4.36 Desorption of Copper from White Chalk Soil Using Triton X-100 with EDTA Ligand

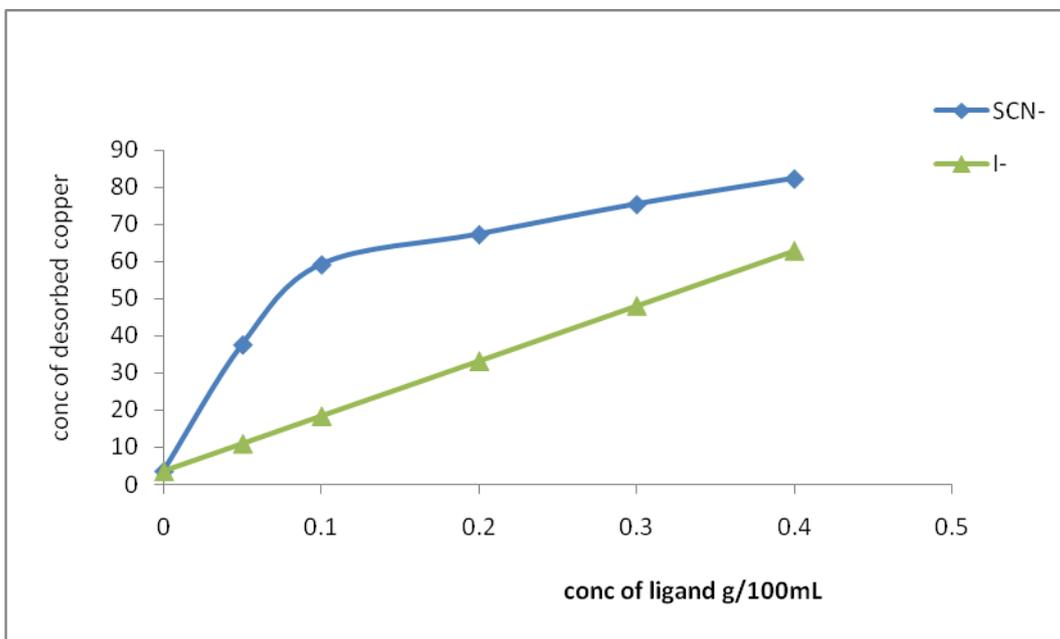


Figure 4.37 Desorption of Copper from White Chalk Soil Using Triton X-100 with I⁻ and SCN⁻ ligands

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

Adsorption of Cu^{2+} in three types of Palestinian soil was studied and the results were obtained:

- 1- The uptake of copper from red soil was increased by increasing soil concentration.
- 2- The order of adsorption of heavy metals on soil was first order reaction with respect to copper ions.
- 3- Our results agree with Freundlich and Langmuir Isotherms indicating a low coverage of copper on red soil.
- 4- The competition of the studied heavy metals on adsorption on red, sandy and white chalk soil is not present at low concentrations of target metals, but at higher concentrations the main factor control the competition of heavy metals is electronegativity.
- 5- The best pH for adsorption study of heavy metals is four.
- 6- Triton X-100 was found to be the best surfactant between the four surfactants under our study to desorb copper from red soil.
- 7- Tween 80 was found to be the best surfactant that desorbs copper ions from sandy and white chalk.
- 8- EDTA was found to be the best ligand with Triton X-100 to desorb copper from contaminated red sandy and white chalk soil.

5.2. Recommendations for Further Work

- 1- The soil can be replaced by olive jef after chemical treatments.
- 2- This technique can be used for other different heavy metals and toxic anions like nitrates.

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جامعة النجاح الوطنية

كلية الدراسات العليا

تأثير مسيلات السطوح على امتصاص ايونات العناصر الثقيلة بواسطة
المركبات المتصلة الغير عضوية على عينات مختارة من تورب ملوثة في
فلسطين

إعداد

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إشراف

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قدمت هذه الأطروحة استكمالاً لمتطلبات درجة الدكتوراه في الكيمياء
بكلية الدراسات العليا في جامعة النجاح الوطنية في
نابلس - فلسطين

2010

ب

تأثير مسيلات السطوح على امتصاص ايونات العناصر الثقيلة بواسطة المركبات المتصلة الغير

عضوية على عينات مختارة من تورب ملوثة في فلسطين

إعداد

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د. شحدة جودة

الملخص

إن العناصر الثقيلة مثل النحاس والرصاص والزنك و الكاديوم من أهم ملوثات البيئة.

وعملية تنظيف هذه العناصر من التربة تصاحبها مشاكل كثيرة لذا فهي تحتاج إلى

التحسين والتطوير دائماً حتى تصبح أكثر كفاءة وسهولة وشمولية .

تم عمل مجموعة من التجارب لمعرفة كفاءة تأثير مسيلات السطوح مع المركبات

العضوية الغير متصلة على تنظيف ايونات هذه العناصر الثقيلة وهي (من ثلاثة أنواع من تربة

فلسطين : التربة الحمراء , والتربة البيضاء , والتربة الرملية) التي تم تلويثها بهذه العناصر في

المختبر .

إن أفضل درجة حموضة (pH) لامتصاص هذه العناصر هي 4.

إن عملة امتصاص هذه العناصر وجدت على الترتيب التالي $Cd \approx Zn > Pb > Cu$ ، يمكن

تفسير هذا الترتيب حسب درجة الكهروسالبية للعناصر .

أثبتت مسيلات السطوح (TritonX-100 و SDS و Tergitol و Tween 80) فعاليتها على

تنظيف التربة من العناصر الثقيلة.

ج

إن زيادة تركيز مسيلات السطوح تزيد من قدرتها على تنظيف العناصر الثقيلة من التربة حتى نصل الى الدرجة الحرجة التي لا يفيد بعدها زيادة التركيز (CMC) .

إن هو الأقدر على تنظيف التربة الحمراء من العناصر الثقيلة **TritonX-100**.

إن هو الأقدر على تنظيف التربة الرملية والتربة البيضاء من العناصر الثقيلة **Tween 80**.

تمت دراسة وجود مركبات متصلة غير عضوية مثل EDTA , SCN⁻ , I⁻ وبتراكيز

مختلفة وقد وجد أن 0.1 مول لكل لتر من **TritonX-100** مع 0.1 مول من EDTA له القدرة الفائقة على امتصاص العناصر الثقيلة .