HEAVY METAL, SURFACTANT, LIGAND INTERACTIONS IN SOIL REMEDIATION

by
Hanife Tunç
B.S. in Chem., Uludağ University, 2002

Submitted to the Institude for Graduate Studies in
Science and Engineering in partial fulfillment of
the requirements for the degree of
Master of Science

Graduate Program in Chemistry
Boğaziçi University
2007

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to Assoc. Prof. Neylan Dirilgen and Prof. Zeynep Atay for their invaluable guidance, support, encouragement and help in every stage of this project.

I also would like to thank all the members of Chemistry Department who helped me in the all stage of the experiments.

I wish to thank to Hülya Metiner, always willing to help and share the problems.

I would like to thank Fatma Melis Çağdaş for her support and help during the voltammetric analysis.

I wish to thank to Duygu Güneş, Dilek Yılmaz, Tuğba Furuncuoğlu, and Pırıl Ertem who helped me during my experiments.

I also thank to Gülhan Kocasakal and Özge Yılmaz for their endless support and friendship.

I also would to express my special thanks to Rıza Dervişoğlu for his help during the AAS analysis.

Finally, I owe great thanks to my husband and my family for their encouragement, support and endless love through my life.

This project has been supported by Boğaziçi University Research fund (BAP) with 06S102 project number.

ABSTRACT

HEAVY METAL, SURFACTANT, LIGAND INTERACTIONS IN SOIL REMEDIATION

In this study, heavy metal-surfactant-ligand interactions and the effects of anionic and nonionic surfactants alone, two ligands alone, and combinations of these surfactants and ligands in the removal of heavy metals from soil were investigated.

Soil was taken from Tekirdağ region. 2 g soil samples were polluted with cadmium and lead at different concentration values and V/m = 20 and 40 mL g^{-1} ratios. The soil samples were polluted with 4, 6, and 8 mg L^{-1}cadmium solutions for 48 hours, the other samples were polluted with 2, 4, 6, 8, and 12 mg L^{-1} lead solutions for 72 hours and 16 and 20 mg L^{-1} lead solution for 96 hours which were determined as the equilibrium time of the interaction between the pollutant ions and soil.

The study showed the results from a number of washing treatments using two surfactants, anionic SDS and nonionic Triton X-100 and two chelating agents, iodide and citric acid and the combination of the surfactant-ligand systems aiming at the remediation of artificially heavy metal-contaminated soil. The soil samples were shaken for 25 hours on a shaker at a temperature of 25±2°C and the supernatant fraction was determined by Atomic Absorption Spectroscopy (AAS) and Differential Pulse Anodic Stripping Voltammetry (DPASV).

The most efficient Cd desorption values were obtained using combination of Triton X100-citric acid up to 100 percent, SDS-iodide up to 95 percent, and Triton X100-iodide almost 85 percent.

In the removal of lead studies, the best results were obtained with the combination of SDS-iodide and Triton X100-iodide systems which were up to 80 percent with SDS-iodide, 90 percent with Triton X100-iodide.

ÖZET

TOPRAK TEMİZLENMESİNDE AĞIR METAL-YÜZEY AKTİF MADDE-LİGAND ETKİLEŞİMLERİ

Bu çalışmada, ağır metal-yüzey aktif madde-ligand etkileşimleri ve ağır metallerin topraktan temizlenmesinde yalnızca yüzey aktif maddelerin, yalnızca ligandların ve yüzey aktif madde ve ligand birleşimleri etkileri araştırılmıştır.

Toprak Tekirdağ bölgesinden alınmıştır. 2 g ağırlığındaki toprak örnekleri değişik derişimlerde ve 20 mL g^{-1}, 40 mL g^{-1} oranlarındaki kadmiyum ve kurşun iyon çözeltileriyle yapay olarak kirletilmiştir. Toprak örnekleri 4, 6, and 8 mg L^{-1} kadmiyum çözeltileriyle 48 saat, 2, 4, 6, 8, and 12 mg L^{-1} kurşun çözeltileriyle 72 saat ve 16, 20 mg L^{-1} kurşun çözeltileriyle 96 saat kirletilmiştir. Kirletme zamanları, önceden yapılan deneylerle, kirletme iyonları ile toprağın dengeye gelmesi için gerekli zaman olarak belirlenmiştir.

Bu çalışmada iki farklı yüzey aktif madde; anyonik yüzey aktif madde olarak SDS, noniyonik yüzey aktif madde olarak Triton X-100, ve iki farklı ligand; iyot ve sitrik asit, ve bu yüzey aktif maddeler ile ligandların kombinasyonları kullanılmıştır. Yapay olarak kirletilen toprak örnekleri temizleme çözeltileriyle 24 saat süreyle mekanik çalkalayıcıda 25±2 °C'de etkileşime sokuldu ve çözeltideki kadmiyum derişimi AAS ve DPASV yöntemleri ile ve kurşun konsantrasyonu AAS yöntemi ile belirlenmiştir.

Topraktaki kadmiyum temizleme çalışmalarında en iyi sonuçları yüzde 100 oranı ile Triton X100-citric acid birleşimi, yüzde 95 oranı ile SDS-iyot birleşimi ve yüzde 85 oran ile Triton X100-iyot birleşimi sağlamıştır.

Kurşun temizleme çalışmalarında, en iyi sonuçları SDS-iyot ve Triton X100-iyot birleşimleri ile sırasıyla yüzde 80 ve yüzde 90 oranlarında temizleme elde edilmiştir.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS/ABBREVIATIONS

EPA	Environmental Protection Agency
CMC	Critical Micelle Concentration
SLS	Sodium lauryl sulfate
SLES	Sodium laury ether sulfate
PO	Propylene oxide
EO	Ethylene oxide
CTAB	Cetyl trimethylammonium bromide
q_i	Quantity of an adsorbate I adsorbed
c_i	Equilibrium solution concentration of the adsorbate
K	Affinity of the adsorbate for the surface
b	The upper limit for q_i
a	Adsorption equilibrium constant
n	Adsorption equilibrium constant
M_T	Total adsorbed metal concentration
M_S	Dissolved metal concentration
AAS	Atomic Absorption Spectrophotometer
CEC	Cation Exchange Capacity
E	Applied Potential
i	Resulting current
t	Time
T	Absolute temperature
R	Molar gas constant
F	Faraday constant
E_0	Standard reduction potential
DPASV	Differential Pulse Anodic Stripping Voltammetry
DME	Dropping mercury electrode
MFE	Mercury film electrode
RE	Reference electrode
WE	Working electrode

OMC	Organic matter content
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Occupied Molecular Orbital
CO	Carbon monoxide
HPLC	High Performance Liquid Chromatography

1. INTRODUCTION

The soil is the primary supplier of trace metals to the soil-plant-animal system and the soil-foodstuff / water-human system. In these systems, the metals and metalloids do not occur in isolation, and a number of interactions are recognized at both deficiency and excess concentration. The total concentration of trace metals and metalloids in soils, their chemical forms, mobility and availability to the food chain, provide the basis for a range of problems in crop, animal and human health. In large concentrations, many of the trace metals may be toxic to plants and animals, or may affect the quality of foodstuffs for human consumption [1].

Cadmium, copper, lead, mercury, nickel and zinc are considered the most hazardous metals and are included on the Environmental Protection Agency's (EPA) list of priority pollutants. The sources of metals include domestic and industrial effluents, the atmosphere, runoff and lithosphere [2].

Once metals are allowed to pass through the municipal waste treatment facility, the heavy ones return to the environment where they are persistent, cannot be biodegraded and can thus follow a number of different pathways. The metals can adsorb onto the soil, they can runoff into rivers or lakes or leach in the groundwater. Exposure to the heavy metals through ingestion or uptake by drinking water (particularly where water is reused) and foods can lead to accumulation in animals, plants and humans. This phenomenon can lead to extinction or alteration of plants and animals. Metals can accumulate in the following order: river sediments, bacteria and then fish and man if one consumes these fish [3].

The development of effective and low-cost remediation methods to treat contaminated soils has been the focus of many environmental remediation professionals during the last decade. Soil washing, solidification/stabilization, electrokinetics, bioremediation and phytoremediation are the remediation technologies that are applicable to treat metal contaminated soils. Soil washing is the most commonly used treatment technology for the remediation of metal-contaminated soils. This technique is an *ex situ* treatment method and is less expensive than many traditional or innovative treatment technologies, especially when smaller soil volumes are to be treated. In this method, the contaminated soil is excavated and mixed with an extractant solution. The extractant solution may be water, acid, oxidizing agent, chelating agent, or surfactant, depending on the type of contaminant. The soil and the extractant solution are mixed thoroughly for a specified time, and the soil is dewatered to separate the soil and liquids [4].

As far as metal mobilization from solid particles is concerned, the degree of extraction by chelating agents, in terms of both kinetics and removal efficiency, depends on a number of factors, including metal type, concentration and speciation in the solid material, sorption bond strength, selectivity of the chelating agent used towards the target metals, as well as washing solution conditions (pH, chelant concentration, ionic strength, presence of competing species). The degree of extraction of the target contaminants by chelating agents is affected by the presence of major cations which, due to their larger amounts in the solid matrix, compete with trace metals for chelant-based complex formation [5].

Application of surfactants for heavy metal remediation has gained popularity in recent years. Some surfactants have been found to remove heavy metals from soils, under both acidic and alkaline conditions, through direct complexation followed by solubilization. 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 that increases hydrophobic character of the product and results in preferential accumulation of the complex with in the surfactant micelle. Such metal complexes are formed extensively within the micellar phase rather than in the aqueous phase [6].

Plants have been used for decades for stabilization of disturbed and contaminated sites, and plant-based remediation technologies are receiving broad acceptance. One of the mechanisms by which plants are able to reduce toxicity from heavy metals in soils is the exudation of organic acids. Specific organic acids can sequester heavy metals and protect the roots from toxicity effects. The most commonly reported organic acids produced by plants are citric, succinic, malic acids. The presence of soluble organic ligands in soil may significantly influence metal adsorption through the formation of stable complexes [7].

In this study, soil is contaminated artificially with $Cd^{2+}$and Pb^{2+} at different concentration levels. The pollutant levels were determined according to the parameters taken from Turkish Ministry of Environment.

The objectives of this study were to evaluate the capacity of i) anionic surfactant SDS and non-ionic Triton X-100, ii) ligands iodide and citric acid ($C_6H_8O_7$), iii) surfactant-ligand pairs such as SDS- iodide , SDS-citric acid, and Triton X-100 - iodide , and Triton X-100 - citric acid to desorb Cd^{2+} and Pb^{2+} from the artificially contaminated soil samples. For this purpose, two different analytical methods were used; i) Voltammetry, ii) Atomic Absorption Spectroscopy (AAS).

Concentrations of SDS and Triton X-100 used in contact with the initially contaminated soil were below, above, and at the critical micelle concentrations (CMC) of the corresponding surfactants. CMC of SDS and Triton X-100 have been reported as 8 mM and 0.24 mM, respectively [8].

Studies of the polluted soil and ligand interactions were carried out at concentrations varying between 50 mM to 400 mM and 2.5 mM to 20 mM for iodide and citric acid, respectively.

Studies of the polluted soil-ligand-surfactant interactions were carried out only above the CMC of both surfactants, SDS and Triton X-100.

2. SOIL

2.1. Definition of Soil

Soil is a mass of inorganic material that holds inorganic and organic colloids, dead and living plant and animal material, water, and gases in variable but balanced proportions.

2.2. Properties of Soil

Many soil properties result from certain physical and chemical reactions which are conditioned not only by the rocks or rock materials from which soils are derived but also by the factors of climate, vegetation, topography, and time of reaction.

Soil is concerned with tracing the changes that have occurred and that are still taking place as a consequence of the action of meteorological, geological, and biological agencies on the rocks. The resulting soils, by reason of the great variation in the composition of the rocks and minerals of which they are the residue and the wide diversity in the nature and the mode of operation of the several agencies affecting their formation, are variable products.

To obtain chemical and mineralogical data that could be used for evaluating soil profile development most accurately, the techniques to be employed in soil analyses should yield results which would differentiate the three main types of inorganic substances in soils (a) the primary minerals, inherited from the original igneous and metamorphic rocks, (b)the secondary minerals, formed from the primary minerals – such as the clay minerals, and (c) the uncombined oxides and carbonates – such as Fe_2O_3, Al_2O_3, SiO_2, $CaCO_3$.

As a rule, the largest proportion of the primary minerals is confined to the coarser fractions of the soil- those with a diameter larger than about 2 micron. The secondary minerals are confined mainly to the finer fractions of the soil- those with a diameter smaller than 2 micron- the clay fraction [9].

2.2.1. Physical Properties of Soil

2.2.1.1. Mechanical Analysis. When a soil is taken apart and each part studied, the process is called a mechanical analysis.

When scientists take a soil sample apart, they usually find that it is composed of:

- Large pebbles and stones
- Coarse sand
- Fine sand
- silt
- Lumps or clods of varying sizes which consist of clusters of soil particles which are cemented by organic matter and clay
- A dark substance spread throughout the soil mass, called humus
- Dead leaves and twings
- Ants, earthworms, and other forms of animal life

After the soil sample has been screened through a two-millimeter sieve and the humus destroyed, a particle size-distribution analysis can be made. The purpose of a mechanical analysis is to determine the amounts of individual soil grains of the various sizes.

2.2.1.2. Soil Separates. To bring order to soil separates, the U.S. Department of Agriculture has established limits of variations among the soil separates and assigned a textural name to each group. For example, soils containing a large amount of sand are sandy, those with a high content of silt are silty, and soils containing a high percentage of clay are clayey. When the soil does not exhibit the properties of sand, silt, or clay, it is called a loam [10].

Natural soils are comprised of soil particles of varying sizes. As shown in the Figure 2.1 the soil particle-size groups, called soil separates, are sand (the coarsest), silts, and clays (the smallest). The relative proportions of soil separates in a particular soil determine its texture.

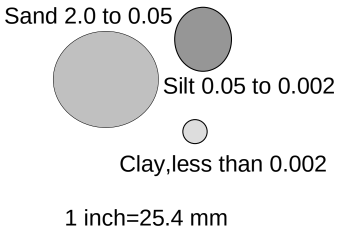


Figure 2.1. Particle size of the soil [11]

<u>2.2.1.3. Soil Texture</u>. Soil texture refers to the relative percentages of sand, silt, and clay in a soil. To determine the textural name of a soil from the mechanical analysis, an equilateral triangle has been adapted for his purpose. Figure 2.2 is a guide for a textural classification. The left angle represents 100 per cent sand, the right 100 per cent silt, and the top angle 100 per cent clay.

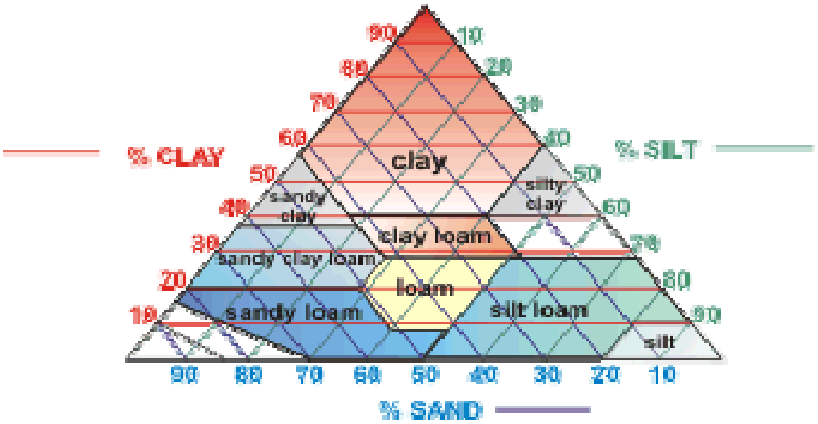


Figure 2.2. Soil texture triangle [12]

The textural name of a soil may be obtained from the results of a mechanical analysis in this way. Assume that the mechanical analysis of a soil is as follows: Sand; 40 percent, Silt; 40 percent, Clay; 20 percent. To find the textural name of this soil, locate the 40 along the bottom of the triangle, then the right side of the triangle labeled per cent silt until you come to 40. Follow down and to the right along the heavy line until this line intersects the 40 per cent line of the sand. Check this point of intersection by locating the 20 per cent point along the left side of the triangle. Follow this 20 per cent line to the right; it should intersect at the same point where the 40 per cent sand line and the 40 per cent silt line intersected. This point is the midpoint of the textural name loam [10].

2.2.1.4. Organic Soil. The preceding textural names are used for designating only the mineral particles. When the surface soil is mostly organic matter, the term muck or peat is used. Muck is the name used when the organic surface, to approximately a foot in depth, is so well decomposed that the plant remains are not recognizable. With less decomposition the soil is called peat.

2.2.1.5. Particle Density. One assumption necessary in making a mechanical analysis is that all soil particles have the same density. Although the assumption is fairly accurate for this purpose, the differences in particle density are important in the determination of other soil constants, such as pore space. Particle density is expressed as grams per cubic centimeter. The particle density of mineral soils over the world varies from approximately 2.60 to 2.80, with an average of approximately 2.65. Soils with a large amount organic matter will have average particle densities of approximately 2.5 or below.

2.2.1.6. Bulk Density. Bulk density is the density or weight of a given bulk (unit volume) of soil. The grams per cubic centimeter of soil, including the pores, are the bulk density. The bulk density can be calculated by dividing the oven-dry weight in grams by the volume of the soil in cubic centimeters.

2.2.1.7. Soil Structure. The relative proportion of primary (individual) particles in a soil mass is known as texture: how these particles are grouped together into aggregates is structure. Natural aggregates are called peds and are fairly water-stable: the word clod is restricted to an artificially formed aggregate that is usually not water-stable.

Soil structural terms for peds are divided into three categories: type (shape and arrangement of peds), class (size of peds), and grade (degree of distinctness of peds). Soil structure influences many important properties of the soil, such as the rate of infiltration of water. Both granular and single-grain soils have rapid infiltration rates; blocky and prismatic soils have moderate rates; and platy and massive soil result in slow infiltration rates.

2.2.1.8. Soil Consistence. Consistence refers to the attribute of cohesion or resistance of soil to rapture or deformation. Although structure and consistence are interrelated, structure deals with the shape, size, and distinctness of natural aggregates (peds), whereas consistence has reference to the force required to rapture soil material or to the properties of a deformed soil mass [10].

2.2.1.9. Soil Color. When soil is examined, color is one of the first things noticed. It indicates extremely important soil conditions. In general, color is determined by: (1) organic matter content, (2) drainage conditions, and (3) degree of oxidation (extent of weathering).

Surface soil colors vary from almost white, through shades of brown and gray, to black. Light colors indicate a low organic matter content and dark colors can indicate a high content. Light or pale colors in the surface soil are frequently associated with relatively coarse texture, highly leached conditions, and high annual temperatures. Dark colors may result from high water table conditions (poor drainage), low annual temperatures, or other conditions that induce high organic matter content and, at the same time, slow the oxidation of organic materials. However, soil coloration may be due to the colors imparted by the parent material. Shades of red or yellow, particularly where associated with relatively fine textures, usually indicate that subsoil material has been incorporated in the surface layer [11].

2.2.2. Chemical Properties of Soil

Soils are chemically different from the rocks and minerals from which they are formed in that soils contain less of the water soluble weathering products, calcium, magnesium, sodium, and potassium, and more of the relatively insoluble elements such as iron and aluminum. Old, highly weathered soils normally have high concentrations of aluminum and iron oxides.

The organic fraction of a soil, although usually representing much less than 10% of the soil mass by weight, has a great influence on soil chemical properties. Soil organic matter is composed chiefly of carbon, hydrogen, oxygen, nitrogen and smaller quantities of sulfur and other elements. The organic fraction serves as a reservoir for the plant essential nutrients, nitrogen, phosphorus, and sulfur, increases soil water holding and cation exchange capacities, and enhances soil aggregation and structure.

The most chemically active fraction of soils consists of colloidal clays and organic matter. Colloidal particles are so small (< 0.0002 mm) that they remain suspended in water and exhibit a very large surface area per unit weight. These materials also generally exhibit net negative charge and high adsorptive capacity. Several different silicate clay minerals exist in soils, but all have a layered structure. Montmorillonite, vermiculite, and micaceous clays are examples of 2:1 clays, while kaolinite is a 1:1 clay mineral. Clays having a layer of aluminum oxide (octahedral sheet) sandwiched between two layers of silicon oxide (tetrahedral sheets) are called 2:1 clays. Clays having one tetrahedral sheet bonded to one octahedral sheet are termed 1:1 clays [13].

2.2.2.1. Cation Exchange Capacity. Many of the nutrient elements are cations. These include NH^{4+}, Ca^{2+}, Mg^{2+}, K^{+}, Fe^{3+}, Mn^{2+}, Zn^{2+}, Cu^{2+}. Other cations of importance are H^{+} and Al^{3+}. Cations are attracted to negatively charged surfaces of small clay and organic (humus) particles called colloids. This attraction is called adsorption. Generally, cations are held tightly enough on adsorption sites to restrict their loss through leaching. These cations can move from the adsorption sites on colliods into the soil water solution (and vice versa) where they are available for root uptake and are also subject to leaching. Cation exchange capacity (CEC) is a measure of the number of adsorption sites in a soil and is an important indicator of the soil's ability to retain and supply cations for plant use. CEC is reported as mili-equivalents per 100 grams of soil (meq/100 g). The CEC of agricultural soils ranges from below 5 in sandy soils with little organic matter to over 20 in certain clay soils and those high in organic matter. A soil with a low CEC has little ability to store nutrients and is susceptible to nutrient loss through leaching [14].

2.2.2.2. Soil pH. Soil pH is a measure of alkalinity and acidity. Most plants grow best in the range of 6.5 to 7.0, which is acidic, but only slightly. The so-called acid-loving plants prefer lower pH, in the range of 4.0 to 6.0. Under 4.0, a few plants are able to survive. Slightly alkaline soil is not harmful to most plants (except acid lovers). In strongly alkaline soils, however, nutrient-availability problems related to pH result.

The parent material of soils initially influences soil pH. For example, granitic soils are acidic and limestone-based soils are alkaline. However, soil pH can change over time. Soils become acidic through natural processes as well as human activities. Rainfall and irrigation control the pH of most soils. In humid climates, heavy rainfall percolates through the soil. When it does, it leaches basic ions such as calcium and magnesium and replaces them with acidic ions such as hydrogen and aluminum. In arid regions (less than 20 inches of rain per year), soils tend to become alkaline, the rainfall is not heavy enough to leach basic ions from soils in these areas.

Other natural processes that increase soil acidity include root growth and decay of organic matter by soil microorganisms. Whereas the decay of organic matter gradually will increase acidity, adding sources of organic matter with high pH values (such as some manures and composts) can raise soil pH.

Human activities that increase soil acidity include fertilization with ammonium-containing fertilizers and production of industrial by-products such as sulfur dioxide and nitric acid, which ultimately enter the soil via rainfall. Irrigating with water high in bicarbonates gradually increases soil pH and can lead to alkaline conditions.

In most cases, changes in soil pH, whether natural processes or human activities cause them, occur slowly. This is due to the tremendous buffering capacity (resistance to change in pH) of most mineral soils. An exception to this is high-sand-content soils, where buffering tends to be low.

Soils with a high buffering capacity require a great deal of amendment to alter pH. This is good if the soil already has a desirable pH, but it can be a problem if the soil needs pH modification. Normally, soils high in clay or organic matter (those that have high CECs) have high buffering capacities. Calcareous soils often have high buffering capacities because lime effectively neutralizes acid—a great deal of acidification may be necessary to eliminate the lime before you can realize a significant drop in pH. Conversely, in lime-free soils, acid treatment can drop pH significantly. Soils also can resist upward changes in pH, depending on their composition.

Nutrient availability varies markedly according to pH. This, in fact, is the main reason why pH is so critical. The best pH for overall nutrient availability is around 6.5, which is one reason why this is an optimal pH for most plants.

Calcium, magnesium and potassium are cation nutrients, meaning they are available to plants in a form with a positive charge. As we discussed earlier, these nutrients adsorb to soil particles, especially clay particles. Soils high in clay or organic matter have high CECs. Thus, these soils act as reservoirs for these nutrients and plants growing in them seldom are deficient in the cation nutrients.

Cations do not adsorb permanently to particles. Other compounds that are more strongly attracted to the cation exchange sites can replace them. This is one way that pH affects nutrient availability. Low-pH soils, by definition, have many of their cation-exchange sites occupied by H^+ ions. By default, exchange sites holding H^+ ions cannot hold other cations. Therefore, low-pH soils are more likely to be deficient in nutrients such as magnesium, calcium or potassium. If cations are not held by particles, they can leach out of the soil.

Soil-solution pH also affects the solubility of other nutrients in the soil. In fact, pH affects the availability of all nutrients one way or another. Therefore, maintaining pH close to the ideal level—6.0 to 7.0 for most plants—is important [15].

3. HEAVY METALS

3.1. General Information

The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. Examples of heavy metals include mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), and lead (Pb).

Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. 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. Heavy metal poisoning could result, for instance, from drinking-water contamination (e.g. lead pipes), high ambient air concentrations near emission sources, or intake via the food chain.

Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted.

Heavy metals can enter a water supply by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and groundwater [16].

3.2. Common Toxic Heavy Metals

3.2.1. Cadmium

Cadmium is a chalcophile, associating geochemically with Zn in the sulfide minerals of rocks. Cadmium cation is even more soluble than Zn^{2+} in acidic oxidizing solutions, and is related as having medium to high mobility in well-drained acid soils. The high mobility is attributable to the fact that Cd^{2+} adsorbs rather weakly on organic matter, silicate clays, and oxides unless the pH is higher than 6. Above pH 7, Cd^{2+} can co-precipitate with $CaCO_3$ or precipitate as $CdCO_3$, and Cd phosphates may limit solubility as well. Therefore, mobility and bioavailabilty of Cd in neutral to alkaline soils is low. Liming acid soils is an effective means of limiting uptake of Cd by plants.

Cadmium concentration in soil exceeding 0.5 μgg^{-1} is considered to be evidence of soil pollution from one of a number of possible sources: industry (mining, metallurgy, etc.), proximity to high ways, high- Cd phosphates fertilizers, or sewage sludge application. Nevertheless, natural geochemical processes have been known to concentrate Cd in surface soils. Like Hg, Cd tends to accumulate in peaty soils by precipitation in sulfide minerals, and Cd levels may also be high in poorly drained soils or soils of arid and semiarid climates [17].

Among heavy metals, Cd and its fate in soil have received a great attention because it is easly taken up by plants, making it more toxic than other heavy metals and consequently imposing harmful effects on human and other animals by entering food chain. Therefore, knowledge about the factors affecting Cd availability and conversion of its chemical forms in soil is important [18].

3.2.2. Lead

Lead is a common contaminant of soil and considered to be a risk to human health when soil concentration exceed 400-500 mg Pb/kg soil (US EPA, 2001).Lead may contaminate soil through vehicle exhausts, sewage-sludge biosolids, mining, and smelting [7].

Lead exists principally in the +2 oxidation state in soils.It is strongly chalcophilic, occuring primarily as PbS in rocks and becoming very insoluble in reduced soils because of its precipitation by sulfide generated from sulfide reduction. Sulfhydryl groups, if they present in humus, strongly complex the Pb^{2+} cation. Under oxidizing conditions, the Pb^{2+} ion becomes less soluble as soil pH is raised. Complexation with organic matter, chemisorption on oxides and silicate clays, and precipitation as the carbonate, hydroxide, or phosphate are all favored at higher pH. In alkaline soils, solubility may increase by formation of soluble Pb- organic and Pb- hydroxy complexes. The Pb^{2+} ion has a particularly high affinity for Mn oxides, a fact perhaps explained by Mn oxidation of Pb^{2+} to Pb^{4+}, a very insoluble ion. Lead is the least mobile heavy metals in soils, especially under reducing or nonacid conditions [17].

4. SURFACE-ACTIVE-AGENTS (SURFACTANTS)

4.1. Properties of Surfactants

Surfactants are surface-active agents that reduce surface tension and exhibit a tendency to form micelles in solvents as illustrated in Figure 4.1. They concentrate at interfaces such as polar water and nonpolar oil and act as emulsifying or foaming agents. This mode of action is directly related to their chemical structure. All surfactants have in common an asymmetric skeleton with a hydrophobic and a hydrophilic moiety. The hydrophobic part generally consists of a linear or a branched alkyl chain, which is then linked to a hydrophilic group. Due to this bifunctionality both parts of the surfactant molecule interact differently with water, the most commonly used solvent. The hydrophilic group is surrounded by water molecules which results in good solubility. On the other hand, the hydrophobic moieties are repulsed by strong interactions between the water molecules. Hence the molecules are repelled out of the inner phase and accumulate at the interfaces. These are the fundamentals for one of the most important uses of surfactants, at least the most popular one, as key ingredients in detergent and cleaning preparations that benefit from these properties in order to formulate all types of household, industrial and institutional products as well as cosmetic and body-care applications [19].

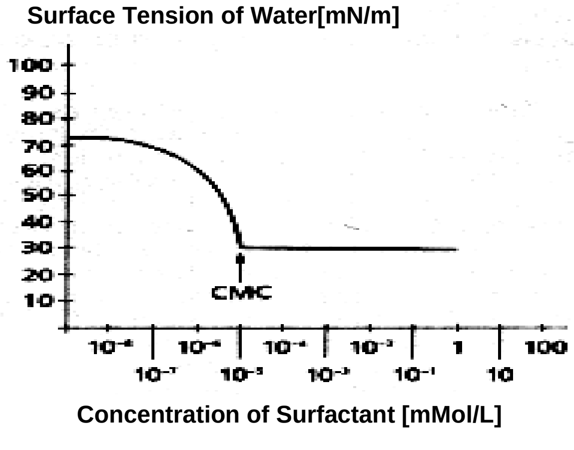


Figure 4.1. Typical decrease of the surface tension of water by surfactants

Surfactants have been used industrially as adhesives, flocculating, wetting and foaming agents, de-emulsifiers and penetrants [20]. Petroleum users have traditionally been the mojor users, as in enhanced oil removal applications. In this application, surfactants increase the solubility of petroleum. They have also been used for mineral flotation as well as the pharmaceutical industries. Typical desirable properties include solubility enhancement, surface tension reduction, wett-ability and foaming capacty [21].

Application of surfactants for heavy metal remediation has gained popularity in recent years. At concentrations in excess of the critical micelle formation (CMC) in aqueous solution, the surfactant molecules aggregate to form clusters called micelles that enhance the remediation capability of surfactant suspensions. 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 organic contaminants. Many studies directed to the extraction of hydrophobic contaminants from soils using surfactant micelles have demonstrated that solubilization can be attributed to the incorporation of hydrophobic contaminants within the hydrophobic core of the surfactant micelles in solution. Some surfactants have been found to remove heavy metals from soils, under both acidic and alkaline conditions, through direct complexation followed by solubilization [6].

The two distinctive affinities in the surfactant molecule mentioned above serve as the basis for the commonly accepted definition of surfactant groups. According to the charge of their hydrophilic moiety, surfactants can be classified into four categories: anionic, non-ionic, cationic and amphoteric [19].

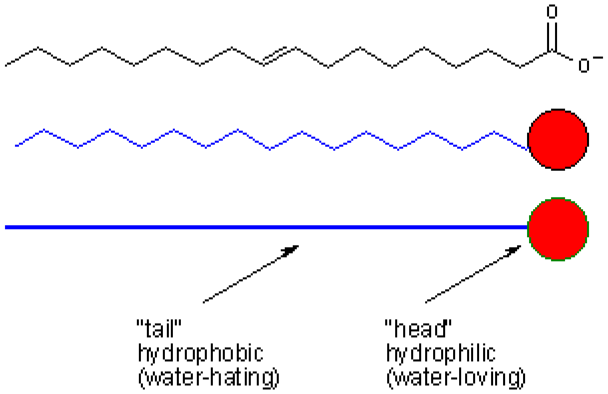


Figure 4.2. Schematic representation of surfactant molecule

Surfactants are said to have a "head" and a "tail". The head is hydrophilic which means that it is water loving, and it is generally depicted as a circle. The tail is generally a long hydrocarbon chain and is hydrophobic, which means water-hating (therefore oil-loving). The tail may be depicted either as a straight line or a wavy tail.

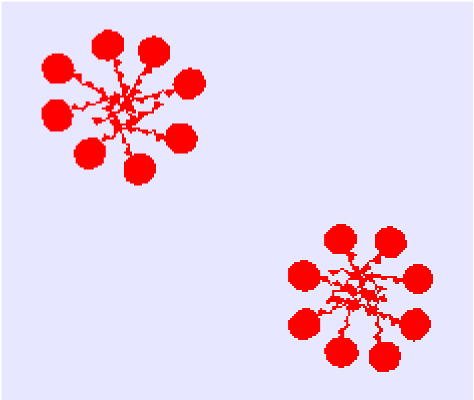


Figure 4.3. The mechanism of micelle formation

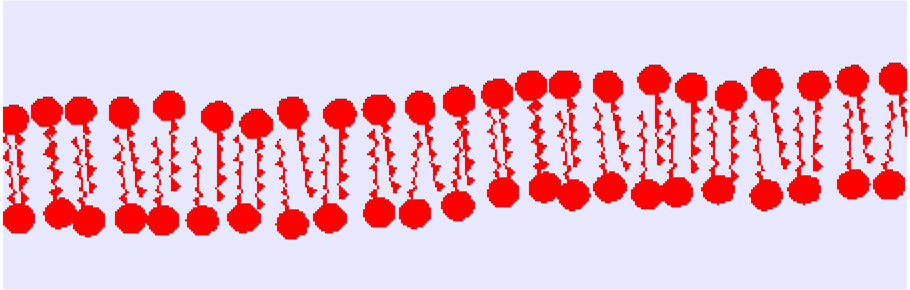


Figure 4.4. The mechanism of surfactant bilayer formation

Surfactants can aggregate to form micelles. Forming a micelle allows the hydrophobic tails to get out of the water but still allows the hydrophilic heads to stay in the water. There is usually between a few dozen to a couple of hundred surfactant molecules in a micelle.

Surfactants also aggregate to form extended structures in water, such as the surfactant bilayer depicted here [22].

4.2. Anionic Surfactants

4.2.1. General Information

Anionic surfactants are known as the products having one or more functional groups that ionize in water to produce negatively charged surface-active organic ions. The anionic surfactants constitute the most important group in terms of consumption on a worldwide basis [19].

In solution, the head is negatively charged. This is the most widely used type of surfactant for laundering, dishwashing liquids and shampoos because of its excellent cleaning properties and high. The surfactant is particularly good at keeping the dirt away from fabrics, and removing residues of fabric softener from fabrics. Anionic surfactants are particularly effective at oily soil cleaning and oil/clay soil suspension.

The most commonly used anionic surfactants are alkyl sulphates, alkyl ethoxylate sulphates and soaps [22].

4.2.2. Sodium Dodecyl Sulfate

Sodium dodecyl sulfate (SDS) ($C_{12}H_{25}NaO_4S$), also known as sodium lauryl sulfate (SLS), is an ionic surfactant that is used in household products such as toothpastes, shampoos, shaving foams and bubble baths for its thickening effect and its ability to create a lather. The molecule has a tail of 12 carbon atoms, attached to a sulfate group as shown in the Figure 4.5, giving the molecule the amphiphilic properties required of a detergent.

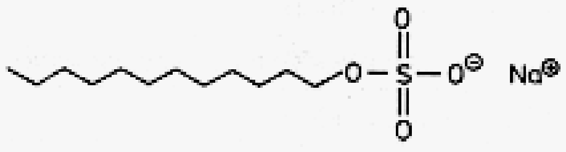


Figure 4.5. Chemical composition of Sodium Dodecyl Sulfate

Table 4.1. Chemical Composition of Sodium Dodecyl Sulfate

Chemical formula	$NaC_{12}H_{25}SO_4$
Molecular mass	288.38 g mol^{-1}
Density	1.01 g/cm^3
Melting point	206 °C

It is prepared by sulfonation of dodecanol (lauryl alcohol, $C_{12}H_{25}OH$) followed by neutralization with sodium carbonate. It is used in both industrially produced and home-made cosmetics. Like all detergent surfactants (including soaps), it removes oils from the skin, and can cause skin irritation. It is also irritating to the eyes.

SDS can be converted by ethoxylation to sodium laureth sulfate (also called sodium lauryl ether sulfate; SLES), which is less harsh on the skin, probably because it is not as much of a protein denaturant as is the unethoxylated substance. It is probably the most researched anionic surfactant compound [23].

4.3. Non-Ionic Surfactants

4.3.1. General Information

The non-ionic surfactants do not produce ions in aqueous solution. The solubility of non-ionic surfactants in water is due to the presence of functional groups in the molecules that have a strong affinity for water. Similarity to any other group of surfactants, they also reduce the surface tension of water.

This is a very important group of products and most of them are adducts of long-chain alcohols or alkylphenols with a number of ethylene oxide (EO) units. Adducts with propylene oxide (PO) and copolymers of ethylene and PO are also used although they are less important in terms of usage volume than the pure ethoxylate derivatives.

The most representative non-ionic surfactants are the alkyl (alcohol) ethoxylates. These are adducts of a long chain alcohol (12- 18) with a variable number of EO units (3-11). Other non-ionic surfactants are derived from carbohydrates, fatty alcohols, and amines.

4.3.2. Triton X-100

Triton X-100 ($C_{14}H_{22}O(C_2H_4O)_n$) is a nonionic surfactant which has a hydrophilic polyethylene oxide group (on average it has 9.5 ethylene oxide units) and a hydrocarbon lipophilic or hydrophobic group. The hydrocarbon group is a 4-(1,1,3,3-tetramethylbutyl)-phenyl group. It is related to the Pluronic range of detergents. The pluronics are triblock copolymers of ethylene oxide and propylene oxide. The part formed from ethylene oxide is more hydrophilic than the part from propylene oxide. It is very viscous at room temperature and is thus easiest to use after being gently warmed [24]

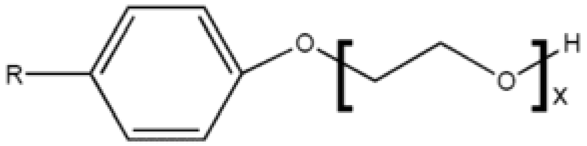


Figure 4.6. Chemical Composition of Triton X-100

4.4. Cationic Surfactants

Cationic surfactants are surface-active compounds with at least one hydrophobic alkyl chain and a hydrophilic group carrying a positive charge. Cationic surfactants are positively charged in aqueous solutions. Of the cationic surfactants especially the quaternary ammonium compounds are used in commercial products. The quaternary ammonium compounds are characterized by a positively charged quaternary nitrogen atom. Commercial raw materials are normally derived from natural oils which implies that homologous mixtures of surfactants with different alkyl chain lengths are used in the products. In household products, the cationic surfactants are primarily applied in fabric softeners, hair conditioners, and other hair preparations. Other applications of cationic surfactants include disinfectants and biocides, emulsifiers, wetting agents, and processing additives. By volume, the most important cationic surfactants in household products are the alkyl ester ammonium salts that are used in fabric softeners [25].

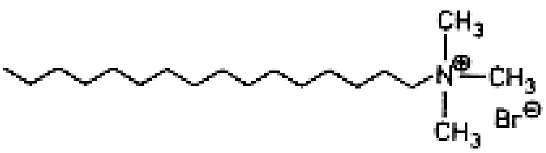


Figure 4.7. Chemical structure of CTAB as an example of cationic surfactant

4.5. Amphoteric Surfactants

Amphoteric Surfactants have two or more functional groups which, depending on the conditions of the medium, can be ionised in aqueous solutions to give the compound the characteristics of either an anionic or a cationic surfactant. By choosing the right conditions they can be compatible with either anionic or cationic surfactants in detergent preparetions. The most significant amphoteric surfactants are derivatives of betaine.

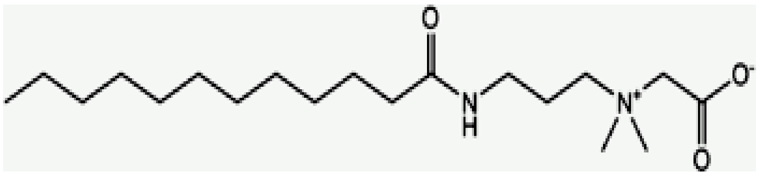


Figure 4.8. Chemical composition of Cocamidopropyl betaine as an example of amphoteric surfactant

5. ADSORPTION

5.1. Introduction

Adsorption can be simply defined as the preferential concentration of one component of a system at an interface, where the local concentration of one or more components of one or both phases is different from those in the bulk phases. Adsorption can occur at any type of interface, although the distinct characteristics of solid versus liquid interfaces make the analysis of each case somewhat different. For that reasons, the discussion of each situation is best presented in the context of specific interfaces.

Interfaces containing only liquids and vapors generally exhibit simpler adsorption characteristics than containing solid surfaces, because in liquid surfaces, the complications arising from specific structures and surface heterogeneities can be ignored. In addition, multilayer adsorption can usually be ruled out.

When adsorption occurs on a solid, the solid is referred to as the adsorbent and the adsorbed material the adsorbate. In some cases absorption may also occur. It can be difficult to separate the effects of the two phenomena if they occur together. In fact, it is likely that one will affect the other and produce a situation even more difficult to analyze than that produced by one alone [26]. As the retention mechanism of metal ions at soil surfaces is often unknown, the term “sorption” is preferred, which in general involves the loss of a metal ion from an aqueous to a contiguous solid phase and consists of three important processes: adsorption, surface precipitation, and fixation [27].

5.2. Adsorption Types

Various types of attractive forces exist between solute molecules and the molecules of adsorbing surfaces, and all of these have their origins electromagnetic interactions of nuclei and electrons. It can be identified some of these forces, three defined categories are: (i) chemical, (ii) electrostatic, and (iii) physical.

5.2.1. Chemical Adsorption

Chemical adsorption involves solute-sorbent interactions having the characteristics of true chemical bonds. Such sorptive phenomena are thus characterized by large heats of adsorption, typically 100 to 400 kJ/mol. Substantial activation energies may be involved in chemisorption reactions.

5.2.2. Electrostatic Adsorption

Electrostatic adsorption also involves high-energy forces, just as electrostatic bonds between charged chemical species involve high-energy bonds. They relate directly to Coulombic forces of attraction between oppositely charged species, and their differential heats of adsorption may be as large as 200 kJ/mol. Such forces are particularly strong in ion exchange process and engineering process.

Physical Adsorption

Physical adsorption results from the action of Van der Waals forces, comprised by London dispersion forces and classical electrostatic forces. Physical adsorption is a rapid and reversible process, it can be considered to occur to some extend on almost all solid surfaces except under extreme conditions of high temperature and high vacuum [28].

5.3. Parameters Influencing Adsorption

Adsorption of heavy metal ions on soils and soil constituents is influenced by a variety of parameters, the most important ones being pH, type and speciation of metal ion involved, heavy metal competition, soil composition and aging.

5.3.1. Soil pH

Soil pH is the most important parameter influencing metal-solution and soil-surface chemistry. The dependence of heavy metal adsorption on, e.g., clays on solution pH has been noticed early. The number of negatively charged surface sites increases with pH. In general, heavy metal adsorption is small at low pH values. Adsorption then increases at intermediate pH from near zero to near complete adsorption over a relatively small pH range [27].

Heavy-metal adsorption seem to be related to a balance between the predominance of the metals in their unhydrolyzed (M^{2+}) form in soils with lower pH and the hydrolyzed (MOH^{+}) form in the soils with higher pH. In the first case, the larger metal electronegativity the easier the dissociation of the H from the functional groups of the soil mineral and organic particles, forming covalent bonding. Electronegativity and cation affinity for oxygen should play more roles in the order of adsorption of heavy metals in acidic soils whereas pH and hydrolyzed forms of metal cations should be more important in the less acidic younger soils [29].

Metal Ion

Universally consistent rules of metal selectivity cannot be given as it depends on a number of factors such as the chemical nature of the reactive surface groups, the level of adsorption (i.e., adsorbate/adsorbent ratio), the pH at which adsorption is measured, the ionic strength of the solution in which adsorption is measured, which determines the intensity of competition by other cations for the bonding sites, and the presence of soluble ligands that could complex the free metal. All these variables may change the metal adsorption isotherms. Competition from monovalent metal in background electrolytes has relatively little effect on adsorption on heavy metals, although presence of Ca ions does suppress adsorption on Fe oxide.

5.3.3. Soil Type

The soil type and composition plays an important role for heavy metal retention. In general, coarse-grained soils exhibit lower tendency for heavy metal adsorption than fine-grained soils. The fine-grained soil fraction contents soil particles with large surface reactivities and large surface areas such as clay minerals, iron and manganese oxyhydroxides, humic acids, and others and display enhanced adsorption properties. Clays are known for their ability to effectively remove heavy metals by specific adsorption and cation exchange as well as metal oxyhydroxides. Soil organic matter exhibits a large number and variety of functional groups and high CEC values, which results in enhanced heavy metal retention ability mostly by surface complexation, ion exchange, and surface precipitation. Also aging may play an important role for heavy metal retention as stable surface coatings are formed as a function of time and heavy metal retention onto aged soils acquires a more irreversible character [27].

Clay particles are usually negatively charged. This is a very important factor influencing sorption properties of the soil. There are at least two major possibilities as to how these charges are formed. Firstly the hydroxyl groups which exist on the edges and on the outer layers of minerals can dispose of hydrogen which is bonded with oxygen probably covalently, not very tight. This is a pH-dependent process and the ability to split the hydrogen atom decreases when pH decreases. When pH is above 6 hydrogen may easily by replaced by other ions like Ca^{2+}, Al^{3+}, Pb^{2+}, Cd^{2+}. The second process of creating negative charges is connected to the isomorphous ion replacement in the minerals. In the silica tetrahedral Al^{3+} can replace the silicon ion Si^{4+} because these two have a similar ionic radius, whereas Mg^{2+}, Fe^{2+} can exist in the octahedral layers instead of Al^{3+}. The negative charge, which appears as a result of isomorphous ion replacement, is pH-independent and therefore quite persistent [30].

5.4. Adsorption Isotherms

The simplest model of adsorption on a surface is that in which localized adsorption takes place on an energetically uniform surface without any interaction between adsorbed molecules.

The most commonly used isotherm is the Langmuir isotherm, which has been originally derived for adsorption of gases on plane surfaces such as glass, mica, and platinum. It is applied for adsorption of heavy metal ions onto soils and soil components in the form.

$$q_i = b(Kc_i /1+Kc_i) \tag{5.1}$$

where the quantity q_i of an adsorbate i adsorbed is related to the equilibrium solution concentration of the adsorbate c_i by the parameters K and b. The steepness of the isotherm is determined by K. K can be looked upon as a measure of the affinity of the adsorbate for the surface. The value of b is the upper limit for q_i and represents the maximum adsorption of i determined by the number of reactive surface adsorption sites. The parameters b and K can be calculated from adsorption data by converting into the linear form:

$$q_i/c_i=bK-Kq_i \qquad (5.2)$$

Then the ratio q_i/c_i (the so-called distribution coefficient K_d) can be plotted against q_i. If the Langmuir equation can be applied, the measured data should fall on a straight line with slope of $-K$ and x intercept of bK.

The Freundlich equation has the form:

$$q_i=ac^n{}_i \qquad (5.3)$$

where a and n are adjustable positive valued parameters with n ranging only between 0 and 1. The parameters are estimated by plotting logq_i against logc_i with the resulting straight line having a y intercept of log$a$ and a slope of n. The Freundlich equation will fit data generated from the Langmuir equation. Converting the Freundlich equation to the logarithmic form, the equation becomes:

$$logq_i=loga+nlogc_i \qquad (5.4)$$

Considering the adsorption of heavy metals by soils, q_i is equated to the total adsorbed metal concentration (M_T in mg kg^{-1}) and c_i is equated to the dissolved metal concentration (M_S in mg L^{-1}) in the batch solution at equilibrium with the solid. Defining log$a$ as a constant, the equation becomes

$$logM_T=C+nlogM_S \qquad (5.5)$$

This form of the equation can be used to relate the amount of heavy metal adsorbed on specific soils to the dissolved concentration of free metal ions. A generalized Langmuir and Freundlich isotherms can also be used as a model base for the interpretation of competitive adsorption isotherms.

The Langmuir equation for adsorption of heavy metal ions in soils and clays has been derived and applied in many studies. Also deviations between experimental data and calculated behavior have been observed, which has been explained by the presence of competition of different adsorbates for the adsorption sites on the surface. Consequently, the original Langmuir equation had to be modified to include competitive effects and can be expressed as the so called competitive Langmuir equation:

$$q_1=bK_1/(1+K_1c_1+K_2c_2) \tag{5.6}$$

5.5. Metal Sorption Mechanisms in Soils

Heavy metal adsorption is often described in the scientific literature in terms of two basic mechanisms: specific adsorption, which is characterized by more selective and less reversible reactions including chemisorbed inner-sphere complexes, and nonspecific adsorption (or ion exchange), which involves rather weak and less selective outer-sphere complexes. Specific adsorption brings about strong and irreversible binding of heavy metal ions with organic matter and variable charge minerals while nonspecific adsorption is an electrostatic phenomenon in which cations from the pore water are exchanged for cations near the surface. Cation exchange is a form of outer-sphere complexation with only weak covalent bonding between metals and charged soil surfaces. It is reversible in nature and occurs rather quickly as it is typical for reactions which are diffusion-controlled and of electrostatic nature.

Specific adsorption can be described by a surface complexation model which defines surface complexation formation as a reaction between functional surface groups and an ion in a surrounding solution, which form a stable unit. Functional surface groups can be silanol groups, inorganic hydroxyl groups, or organic functional groups. Specific adsorption is based upon adsorption reactions at OH-groups at the soil surfaces and edges, which are negatively charged at high pH. The adsorbing cation bonds directly by an inner sphere mechanism to atoms at the surface. As a consequence, the properties of the surface and the nature of the metal constituting the adsorption site influence the tendency for adsorption. These reactions depend largely on pH, are equivalent to heavy metal ion hydrolysis and can be described as follows for a metal cation Me and a surface S:

$$\text{S---OH+Me}^{2+}\text{+H}_2\text{O} \rightleftharpoons \text{S---O---MeOH}_2{}^{+}\text{+H}^{+} \qquad (5.1)$$

In contrast to adsorption, surface precipitation is characterized by the growth of a new solid phase, which repeats itself in three dimensions and forms a 3-D network. Metals may precipitate as oxides, hydroxides, carbonates, sulfides, or phosphates onto soils. Surface precipitation is mainly a function of pH and the relative quantities of metals and anions present. It has been reported that surface precipitation of hydrous oxide-type soil constituents occurs at pH values lower than those required for metal hydroxide precipitation in pure aqueous solutions without soil suspension.

The surface precipitation model can be described by two reactions: first a surface complex formation of a metal cation Me and a surface S as described by Equation 5.2 and second the precipitation of Me at the surface S:

$$\text{S---O---MeOH}_2{}^{+}\text{+Me}^{2+}\text{+H}_2\text{O} \rightleftharpoons \text{S---O---MeOH}_2{}^{+}\text{+Me(OH)}_2\text{(s)+2H}^{+} \qquad (5.2)$$

This model results in a Langmuir type isotherm at low metal concentration and in a Freundlich type isotherm for increasing metal concentrations. If the metal concentration increases further solid solution precipitation predominates. There is often a continuum between surface complexation and surface precipitation [27].

5.6. Surfactant Sorption Mechanisms in Soils

Surfaces possessing charged groups in aqueous solvents are especially sensitive to environmental conditions such as electrolyte content and the pH of the aqueous phase. In the presence of high electrolyte concentrations, the surface of solid may possess high degree of bound counterions that ion exchange is the only mechanism of adsorption available other than dispersion or hydrophobic interactions. The attraction between the unlike charge groups on the surface and the surfactant, and repulsion between the like charges of the surfactant molecules, will be suppressed.

An increase in electrolyte content will generally cause a decrease in adsorption of surfactants onto surfaces of opposite charge and an increase in adsorption of like charged molecules (Figure 5.1). An important exception to that rule is the case of ionic surfactants in which the added cation has a specific interaction with the adsorbing solute that reduces its solubility in the solution leading to enhance adsorption.

The presence in the solution of polyvalent cations such as Ca^{+2} or Al^{+3} generally increase the adsorption of anionic surfactants onto like-charged surfaces. Such ions characteristically tightly bound to a negatively charged surface, effectively neutralizing charge repulsions. They also can serve as an efficient bridging ion by association with both the negative surface and the anionic surfactant head group (Figure 5.1) [26].

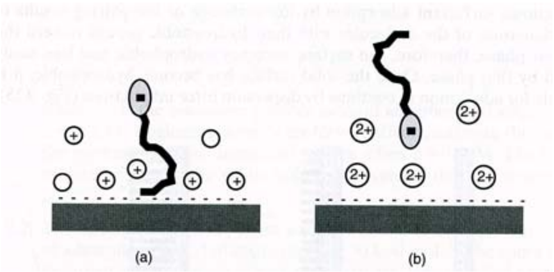


Figure 5.1. Schematic representation of surfactant adsorption

The shape of surfactant molecules has an effect on the sorption behavior of the surfactants. On soil surfaces, anionic surfactants are expected to adsorp in a tail-on fashion due to electrostatic repulsion between the headgroup and negative charge the surface would acquire when in contact with the aqueous solution. This is also known as ‘hydrophobic bonding’. In the case of cationic surfactants, however, ‘cation-exchange’ between the cationic surfactants in the solution and the positively charged counter ions closely bound to the surface on the surafe is expected to take place. A cationic surfactant would then adsorb in a head-on manner. At low concentration of cationic surfactants, sorption is known to be by cation-exchange mechanisms only [31].

The development of technologies for the decontamination of soils and waters polluted by hydrophobic organic compounds has encouraged research into the use of anionic and non-ionic surfactants as potential agents for the enhanced solubilization and removal of contaminants from soils and sediments. However, the effectiveness of a surfactant is attenuated if this is adsorbed by the soil, since the amount available for solubilizing the contaminant decreases, and its mobility through the medium to which it is applied is reduced. Furthermore, surfactant adsorption will increase the organic carbon content of the soil, favoring the adsorption of hydrophobic organic compounds. The adsorption of surfactants by soil components may lead to a significant reduction in their effectiveness to remove the contaminats from the soil. In this sense, in the selection of a surfactant, as well as its capacity to solubilize the contaminant it is important to consider its tendency to be adsorbed by the soil or sediment to be contaminated [31].

Type of clay, nature of exchangeable ions and the ion strength of the aqueous solution are also the determining factors for the sorption of surfactants [31]. This means that the behavior of surfactants in the soil is not well known [8].

6. LIGANDS

6.1. Definition of Ligands

In chemistry, a ligand is an atom, ion, or molecule that generally donates one or more of its electrons through a coordinate covalent bond to, or shares its electrons through a covalent bond with, one or more central atoms or ions (these ligands act as a Lewis base). Fewer examples exist where a molecule can be described as a ligand that accepts electrons from a Lewis base (hence, the ligand acts as a Lewis acid) [34].

Most commonly the central atom is a metal or metalloid in inorganic chemistry. But in organic chemistry ligands are also used to protect functional groups (e.g. borane BH_3 as ligand for the protection of phosphine PH_3), or to stabilize reactive compounds (tetrahydrofuran THF as a ligand for BH_3 to make BH_3 easier to handle). The molecule resulting from the coordination of a ligand (or an array of ligands) to a central atom is termed a complex.

Factors that characterize the ligands are their charge, size (bulk), and of course the nature of the constituent atoms.

The ligands in a complex:

- stabilize the central atom, and
- dictate the reactivity of the central atom

6.2. Ligands in metal complexes

The ligands that are directly bonded to the metal are called "inner sphere" ligands. If the inner-sphere ligands do not balance the charge of the central atom, this may be done by simple ionic bonding with another set of counter ions (the "outer-sphere" ligands). The complex of the metal with the inner sphere ligands is then called a complex ion (which can be either cationic or anionic). The complex, along with its counter ions, is called a coordination compound. The size of a ligand is indicated by its cone angle.

6.3. Donation and Back-Donation

In general, ligands donate electron density to central atom ; that is, they overlap between the highest occupied molecular orbital (HOMO) of the ligand with the lowest unoccupied molecular orbital (LUMO) of the central atom. The ligand thus acts as a Lewis base by donating electron density (in general electron pairs) to the central atom, acting as a Lewis acid. In some cases ligands donate only one electron from a singly occupied orbital (the donating atom in these ligands is a radical).

Some metal centers in combination with certain ligands (e.g. carbon monoxide (CO)) can be further stabilised by donating electron density back to the ligand in a process known as back-bonding. In this case a filled, central-atom-based orbital donates density into the LUMO of the (coordinated) ligand.

In coordination complexes, several Lewis bases "donate"(an electron donor or giver) their "free" pairs of electrons to a metal cation (an electron acceptor), which acts as a Lewis acid and "accepts" the electrons. Coordinate bonds form and the resulting compound are called a coordination complex, and the electron donors are called ligands.

Many chemical compounds can serve as ligands, often these contain oxygen, sulfur, nitrogen, and halide ions. The most common ligand is water (H_2O), which forms coordination complexes with metal ions (like the hexaaquacopper(II) ion, $[Cu(H_2O)_6]^{2+}$). Ammonia (NH_3) is also a common ligand, as well as anions, especially fluoride (F^-), chloride (Cl^-), iodide (I^-) and citrate ($C_6H_5O_7{}^{3-}$) [32].

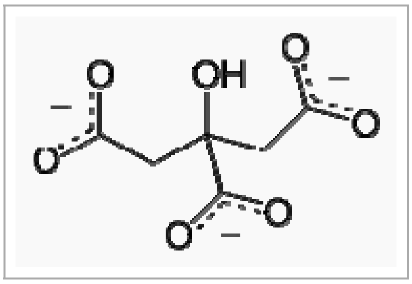


Figure 6.1. Chemical composition of citrate which is an example of ligand

6.4. Complexation of a Ligand with a Surfactant Micelle

Surfactants (surface active agents) possess a hydrophilic functionality, increasing solubility in aqueous media, and a hydrophobic moiety, enabling them to adsorb to hydrophobic organic compounds. At concentrations in excess of the critical micelle formation (CMC) in aqueous solution, the surfactant molecules aggregate to form clusters called micelles. 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 organic contaminants. Some surfactants have been found to interact with heavy metals, under both acidic and alkaline conditions, through direct complexation followed by solubilization. Without changing the soil pH, surfactants can solubilize metals when coupled with a ligand that forms a micelle-solubilized complex as shown in Figure 6.1. The ligand interacts with the metal that increases hydrophobic character of the product and results in preferential accumulation of the complex within the surfactant micelle. Such metal complexes are formed extensively within the micellar phase rather than in the aqueous phase. For example, Cd also complexed with I^- favorably in micellar phase as $[CdI_4]^{2-}$ with the larger negative enthalpy value of -15 kJ mol^{-1} than the value of -5 kJ mol^{-1} in aqueous phase. The anionic complexes of metal-ligand may form ion pairs in micelles such as $Na_2[CdI_4]$ to keep electric neutrality and be stabilized in the hydrophobic environment of micelle [6].

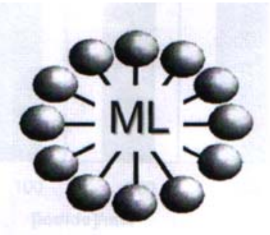


Figure 6.2. Micellar formation for heavy metal-ligand complex

7. ANALYTICAL TECHNIQUES

7.1. Voltammetry

7.1.1. Fundamentals of Voltammetry

The common characteristic of all voltammetric techniques is that they involve the application of a potential (E) to an electrode and the monitoring of the resulting current (i) flowing through the electrochemical cell. In many cases the applied potential is varied or the current is monitored over a period of time (t). Thus, all voltammetric techniques can be described as some function of E, i, and t. They are considered active techniques (as opposed to passive techniques such as potentiometry) because the applied potential forces a change in the concentration of an electroactive species at the electrode surface by electrochemically reducing or oxidizing it.

The analytical advantages of the various voltammetric techniques include excellent sensitivity with a very large useful linear concentration range for both inorganic and organic species (10^{-12} to 10^{-1} M), a large number of useful solvents and electrolytes, a wide range of temperatures, rapid analysis times (seconds), simultaneous determination of several analytes, the ability to determine kinetic and mechanistic parameters, a well-developed theory and thus the ability to reasonably estimate the values of unknown parameters, and the ease with which different potential waveforms can be generated and small currents measured.

Analytical chemists routinely use voltammetric techniques for the quantitative determination of a variety of dissolved inorganic and organic substances. Inorganic, physical, and biological chemists widely use voltammetric techniques for a variety of purposes, including fundamental studies of oxidation and reduction processes in various media, adsorption processes on surfaces, electron transfer and reaction mechanisms, kinetics of electron transfer processes, and transport, speciation, and thermodynamic properties of solvated species. Voltammetric methods are also applied to the determination of compounds of pharmaceutical interest and, when coupled with HPLC, they are effective tools for the analysis of complex mixtures [33].

The voltammetric measurement is made in a cell filled with electrolyte in which three electrodes are immersed, the working electrode, the reference electrode, and the auxiliary (or counter) electrode. A potential is applied to the working electrode with respect to the reference electrode. The solution may or may not be stirred depending on the analytical technique. At some potential the redox reaction will occur, the current is measured and plotted against potential. The potential at which the reaction occurs is characteristic of the analyte, the amount of current that is measured is related to concentration. For a reversible or Nernstian process, the reduction of an electroactive analyte may be represented by:

$$\mathrm{Ox} + n\,e^{-} \rightleftharpoons \mathrm{Red} \qquad (7.1)$$

Resulting in an equation similar to the Nerst equation:

$$E = E^{0} + (RT / nF)ln([\mathrm{Ox}]/[\mathrm{Red}]) \qquad (7.1)$$

where [Ox] is the concentration of oxidized analyte at the electrode surface, and [Red] the concentration of reduced analyte. R is the molar gas constant (8.3144 J $\mathrm{mol^{-1}K^{-1}}$), T is the absolute temperature (K), n is the number of electrons transferred, F is the Faraday constant (96,485 C/equiv), and E_0 is the standard reduction potential for the redox couple. In order to be reduced or oxidized, the analyte must be at the electrode surface. If the potential is made more negative the ratio becomes larger (that is, Ox is reduced) and, conversely, if the potential is made more positive the ratio becomes smaller (that is, Red is oxidized). Migration, diffusion, or convection the routes by which the analyte travels to the electrode surface. Migration is minimized by the use of an electrolyte and the convection is controlled by stirring, and monitoring temperature effects.

Migration is the movement of a charged ion in the presence of an electric field. In voltammetry, the use of a supporting electrolyte at concentrations 100 times that of the species being determined eliminates the effect of migration. Convection is the movement of the electroactive species by thermal currents, by density gradients present in the solution, or by stirring the solution or rotating the electrode. Convection must be eliminated or controlled accurately to provide controlled transport of the analyte to the electrode.

Many voltammetric techniques have their own unique laws and theoretical relationships that describe and predict in greater detail the various aspects of i–E behavior (such as curve shape, peak height, width, and position) [33].

In voltammetry, the voltage of the working electrode is varied systematically while the current response is measured. Several different voltage-time functions, called excitation signals, can be applied to the electrode. The simplest of these is a linear scan, in which the potential of the working electrode is varied linearly with time. Other waveforms that can be applied are pulsed waveforms and triangular waveforms. The waveforms of four of the most common excitation signals used in voltammetry are shown in Figure 7.1. The classical voltammetric excitation signal is the linear scan, in which the dc voltage applied to the cell increases linearly as a function of time. The current that develops in the cell is then measured as a function of the applied potential.

Two pulse-type excitation signals are shown in Figure 7.1. Currents are measured at various times during the lifetimes of these pulses. With the triangular waveform, the potential is varied linearly between a maximum and minimum value. This process may be repeated numerous times while the current is recorded as a function of potential [34].

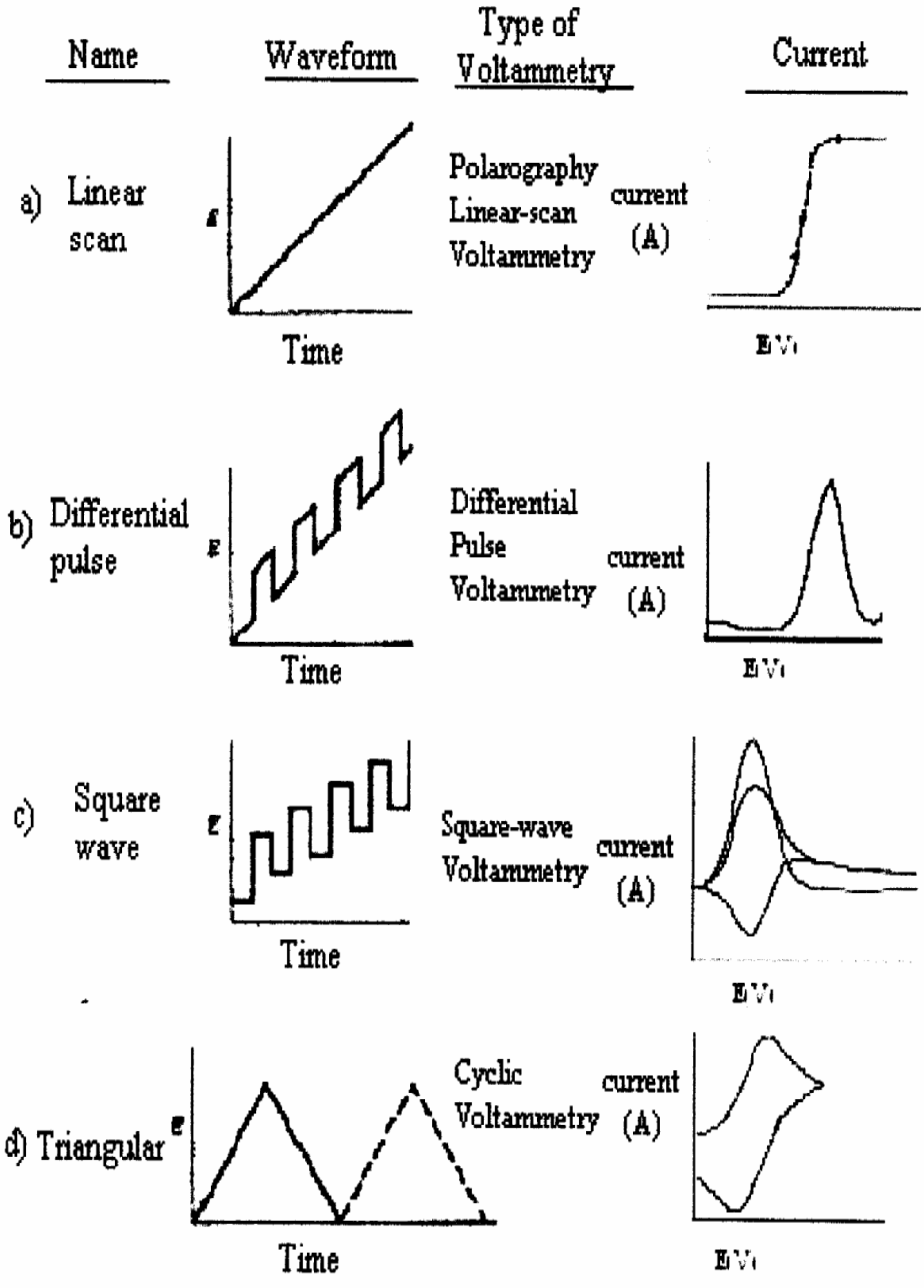


Figure 7.1. Excitation Signal Waveforms in Voltammetry [34]

In this study, our technique is differential-pulse voltammetry combined with anodic stripping analysis.

Differential-pulse voltammetry is an extremely useful technique for measuring trace levels of organic and inorganic species. In differential-pulse voltammetry, fixed magnitude pulses-superimposed on a linear potential ramp-are applied to the working electrode at a time just before the end of the drop. The current is sampled twice, just before the pulse application and again late in the pulse life (after ~40 ms, at 2, when the charging current has decayed). The first current is instrumentally subtracted from the second, and this current difference is plotted versus the applied potential. Figure 7.2 illustrated excitation signal for Differential Pulse Voltammetry. The resulting differential pulse voltammogram consists of current peaks as shown in Figure 7.3, the height of which is directly proportional to the concentration of the corresponding analytes [35].

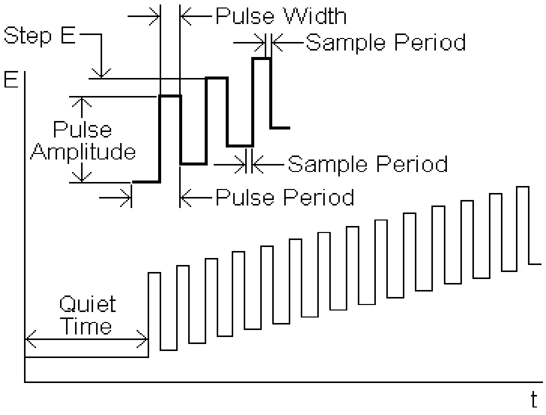


Figure 7.2. Excitation signal for differential-pulse voltammetry

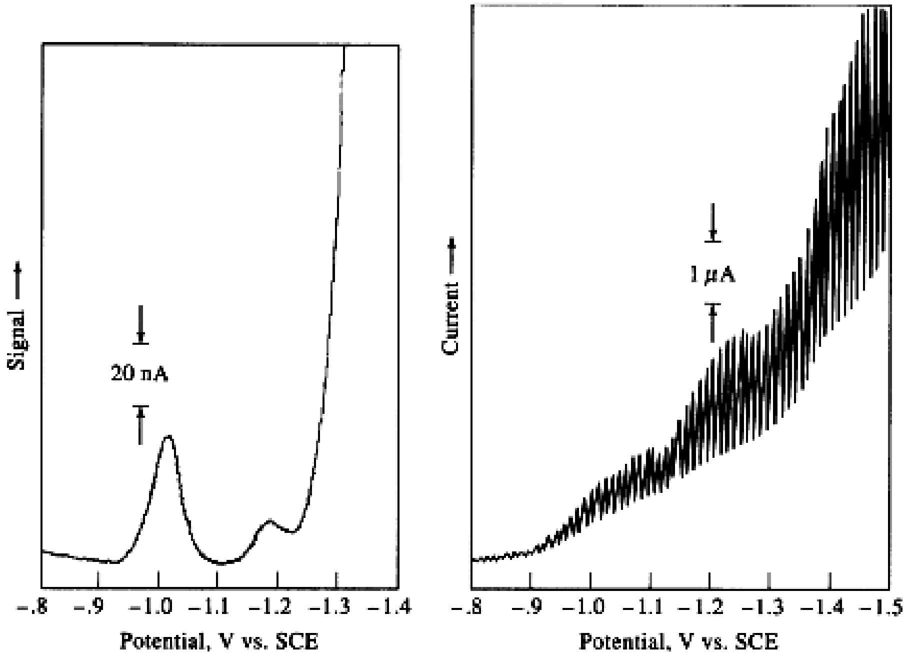


Figure 7.3. Differential pulse voltammogram

Stripping analysis is an analytical technique that utilizes a bulk electrolytic step to preconcentrate the analyte from the sample solution into or onto the working electrode. In this case the preconcentration step can be viewed as an effective electrochemical extraction in which the analyte is preconcentrated in the mercury phase to a much higher level than it exist in solution [36].

There are three important parts in an anodic stripping experiment: Deposition, quiet time, and stripping. During the deposition step, the potential applied to the mercury electrode is held at a constant value (deposition potential) at which the metal ions are reduced and formed metal-amalgam complex for a pre-determined time period (deposition time). The effect of this amalgamation is to concentrate the metal in the mercury electrode, so the deposition step is often called the preconcentration or accumulation step. The efficiency of the deposition can be increased by stirring the solution in the presence of working mercury electrode.

After the deposition step, the stirring is stopped, and the system is allowed to reach equilibrium. This is the quiet time, which is typically 10 - 15 s.

During the stripping step, the applied potential is scanned in a positive direction, and the metal in the mercury electrode is oxidized back to metal ions in solution; that is, the metal is "stripped" from the electrode. The potential at which the stripping occurs is related to the redox potential of the analyte, and hence the potential of the current peak on the stripping step can be used to identify the analyte. The magnitude of the current of the stripping peak is proportional to the concentration of the analyte in the mercury electrode. Since the concentration of the analyte in the electrode is related to its concentration in solution, the stripping peak current is therefore proportional to the solution concentration.

The corresponding reactions for anodic stripping voltammetry are summarized as:

Deposition: $Mn^{+} + ne^{-} \rightarrow M(Hg)$ (7.2)

Stripping: $M(Hg) \rightarrow Mn^{+} + ne^{-}$ (7.3)

7.1.2. Instrumentation

The basic components of a modern electroanalytical system for voltammetry are a voltage source, voltammetric cell, and voltammetric data (voltommogram) as shown Figure 7.4.

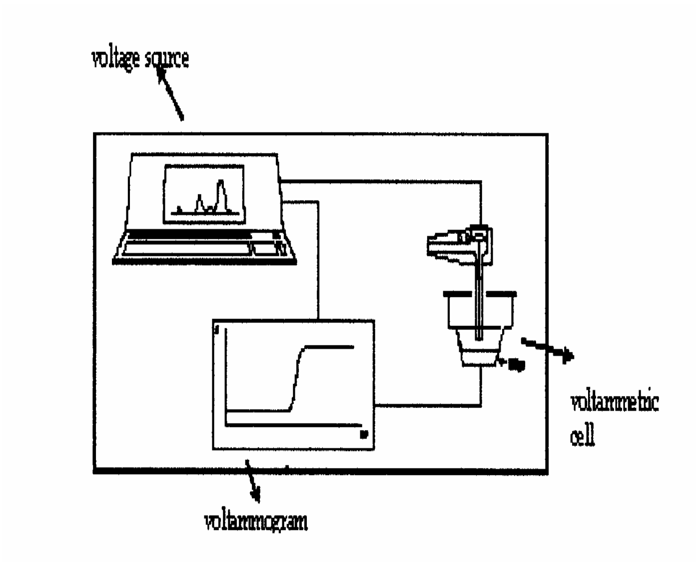


Figure 7.4. Voltammeetric Instrument Components

7.1.3. The Electrodes and Cell

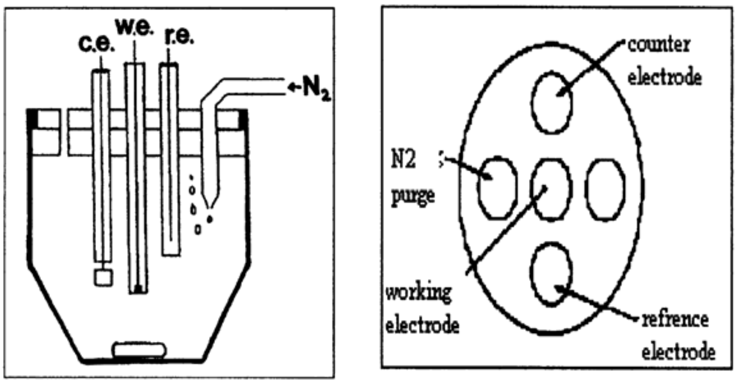


Figure 7.5. Voltammetric Cell Components

A typical electrochemical cell consists of the sample dissolved in a solvent, an ionic electrolyte, and three (or sometimes two) electrodes as illustrated in Figure 7.5. Cells (that is, sample holders) come in a variety of sizes, shapes, and materials. The type used depends on the amount and type of sample, the technique, and the analytical data to be obtained. The material of the cell (glass, Teflon, polyethylene) is selected to minimize reaction with the sample. In most cases the reference electrode should be as close as possible to the working electrode; in some cases, to avoid contamination, it may be necessary to place the reference electrode in a separate compartment. The unique requirements for each of the voltammetric techniques are described under the individual techniques.

Working Electrodes (WE); the performance of the voltammetric procedure is strongly influenced by the material of the working electrode. The WE should provide high signal-to-noise characteristics, as well as reproducible response. Thus, its selection depends primarily on two factors: the redox behavior of the target analyte and the background current over the potential region required for the measurement. The most popular WEs are mercury, carbon, or noble metals (particularly platinum and gold). Figure 7.7 displays accessible potential window of these electrodes in various solutions.

Mercury is a very attractive choice of electrode material because it has a high hydrogen overvoltage that greatly extends the cathodic potential window and possesses a high reproducible, readily renewable, and smooth surface. Disadvantage of the use of mercury are its limited anodic range (due to the oxidation of mercury) and its toxicity.

There are several types of mercury electrodes. Of these, the dropping mercury (DME), the hanging mercury drop electrode (HMDE), and mercury film electrode (MFE) are the most frequently used [34]. Figure 7.6 illustrates a typical working electrode. The electrode consists of a very fine capillary tube connected to a mercury-containing reservoir. The metal is forced out of the capillary by a piston arrangement driven by a micrometer screw. The micrometer permits formation of drops with surface areas that are reproducible to 5 percent or better [35].

Accessible potential window of a working mercury electrode in various supporting electrolytes are given in Figure 7.7.

Reference Electrode (RE); the RE should provide a reversible half-reaction with Nernstian behavior, its potential should be constant over time, and it should be easy to assemble and maintain. The most commonly used REs for aqueous solutions are,

a) The calomel electrode, with potential determined by the reaction:

$$Hg_2Cl_{2(s)} + 2e^- \rightleftharpoons 2Hg_{(l)} + 2Cl^- \tag{7.4}$$

b)The silver/silver chloride electrode (Ag/AgCl), with potential determined by the reaction:

$$AgCl_{(s)} + e^- \rightleftharpoons Ag_{(s)} + Cl^- \tag{7.5}$$

These electrodes are commercially available in a variety of sizes and shapes [33].

Auxiliary (Counter) Electrode; In most voltammetric techniques the analytical reactions at the electrode surfaces occur over very short time periods and rarely produce any appreciable changes in bulk concentrations of Reductant or Oxidant. Thus, isolation of the counter electrode from the sample is not normally necessary. Most often the counter electrode consists of a thin Pt wire, although Au and sometimes graphite have also been used [33].

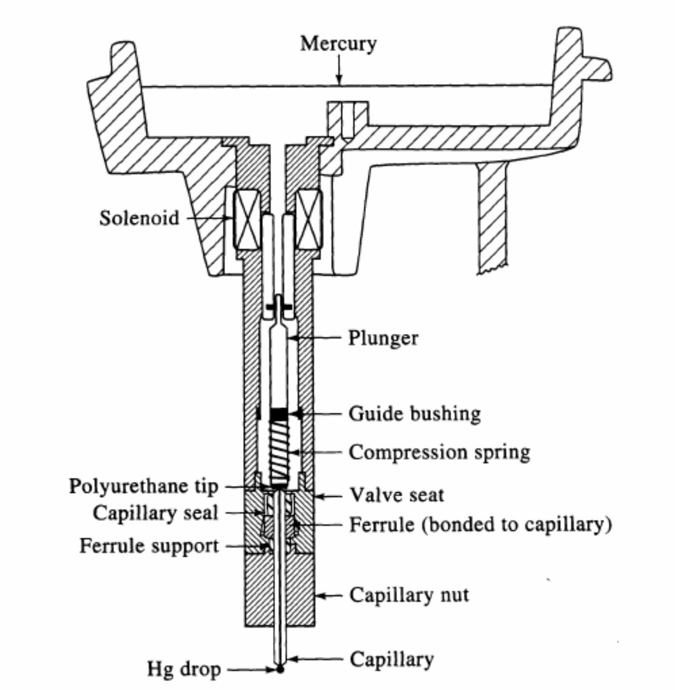


Figure 7.6. Figures of Mercury Microelectrode

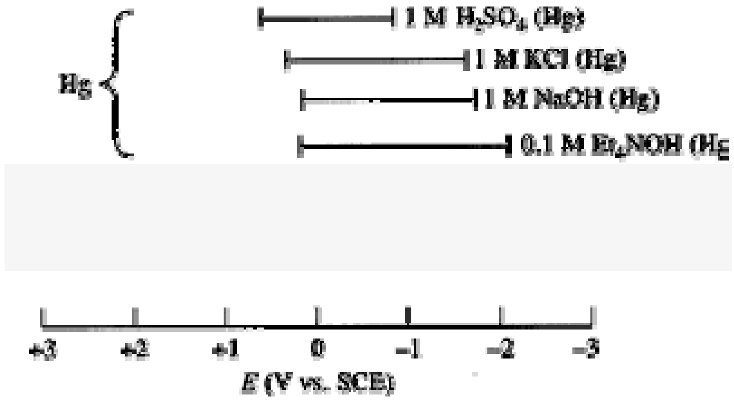


Figure 7.7. Accessible potential window of mercury electrode in various supporting electrolytes

Supporting Electrolyte; electrochemical measurements are commonly carried out in a medium that consists of solvent containing electrolyte. The choice of the solvent is dictated primarily by the solubility of the analyte and its redox activity, and by solvent properties such as the electrical conductivity, electrochemical activity, and chemical reactivity. The solvent should not react with the analyte (or products) and should not undergo electrochemical reactions over a wide potential range [34].

Supporting electrolytes are required in controlled-potential experiments to decrease the resistance of the solution, to eliminate electromigration effects, and to maintain a constant ionic strength. The inert supporting electrolyte may be an inorganic salt, a mineral acid, or a buffer. The composition of the electrolyte may affect the selectivity of voltammetric measurements. The supporting electrolyte should be prepared from highly purified reagents, and should not be easily oxidized or reduced. The usual electrolyte concentration range is 0.1-1.0 M, in other words, in large excess of the concentration of all electroactive species [34].

Oxygen Removal; dissolved oxygen is readily reduced at various electrodes; an aqueous solution saturated with air exhibits two distinct oxygen waves as shown Figure 7.8. The firts results from the reduction of oxygen to peroxide

$$O_2\,(g) + 2H^+ + 2e^- \rightleftharpoons 2H_2O \qquad (7.6)$$

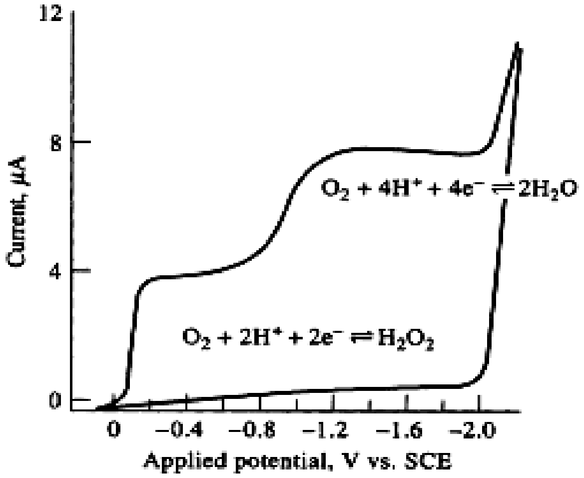


Figure 7.8. Voltammogram for the reduction of oxygen in an air-saturated 0.1 M KCl solution

The second correspond to the further reduction of the hydrogen peroxide:

$$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O \qquad (6.7)$$

Figure 6.8 illustrates the two waves are of equal height, the sum of the two process near the second wave.

In voltammetric measurements, oxygen often interferes with the measurements. Thus oxygen removal is ordinarily the first step in most voltammetric procedures. Usually, the solution is deaerated for several minutes by bubbling a high-purity inert gas through it. During the analysis, a stream of the same gas, usually nitrogen is passed over the surface to prevent oxygen from re-entering the solution [34].

7.2. Atomic Absorption Spectroscopy (AAS)

7.2.1. Fundamentals of AAS

Atomic-absorption (AA) spectroscopy uses the absorption of light to measure the concentration of gas-phase atoms. Since samples are usually liquids or solids, the analyte atoms or ions must be vaporized in a flame. The atoms absorb ultraviolet or visible light and make transitions to higher electronic energy levels. The analyte concentration is determined from the amount of absorption. The technique makes use of the wavelengths of light specifically absorbed by an element. They correspond to the energies needed to promote electrons from one energy level to another, higher, energy level [37].

An atomic absorption spectrometer needs the following three components: a light source; a sample cell to produce gaseous atoms; and a means of measuring the specific light absorbed.

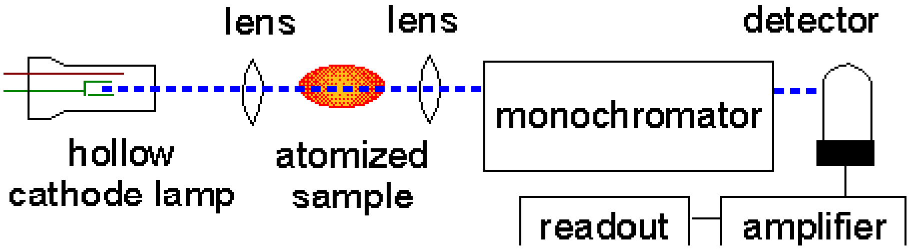


Figure 7.9. Schematic Representation of an Atomic-Absorption

7.2.2. Light Source

The common source of light is a 'hollow cathode lamp' (Fig. 7.9). This contains a tungsten anode and a cylindrical hollow cathode made of the element to be determined. These are sealed in a glass tube filled with an inert gas (e.g. neon or argon) at a pressure of between 1 Nm and 5 Nm. The ionisation of some gas atoms occurs by applying a potential difference of about 300-400 V between the anode and the cathode. These gaseous ions bombard the cathode and eject metal atoms from the cathode in a process called sputtering. Some sputtered atoms are in excited states and emit radiation characteristic of the metal as they fall back to the ground state. The shape of the cathode concentrates the radiation into a beam which passes through a quartz window, and the shape of the lamp is such that most of the sputtered atoms are redeposited on the cathode.

A typical atomic absorption instrument holds several lamps each for a different element. The lamps are housed in a rotating turret so that the correct lamp can be quickly selected.

7.2.3. Optical System and Detector

A monochromator is used to select the specific wavelength of light which is absorbed by the sample, and to exclude other wavelengths. The selection of the specific light allows the determination of the selected element in the presence of others. The light selected by the monochromator is directed onto a detector that is typically a photomultiplier tube. This produces an electrical signal proportional to the light intensity (Fig. 7.9).

7.2.4. Sample Atomization

Two systems are commonly used to produce atoms from the sample. Aspiration involves sucking a solution of the sample into a flame; and electrothermal atomization is where a drop of sample is placed into a graphite tube that is then heated electrically.

Some instruments have both atomization systems but share one set of lamps. Once the appropriate lamp has been selected, it is pointed towards one or other atomization system.

7.2.5. The optical system and detector

A monochromator is used to select the specific wavelength of light which is absorbed by the sample, and to exclude other wavelengths. The selection of the specific light allows the determination of the selected element in the presence of others. The light selected by the monochromator is directed onto a detector that is typically a photomultiplier tube. This produces an electrical signal proportional to the light intensity.

7.2.6. Calibration

A calibration curve is used to determine the unknown concentration of an element in a solution.

The instrument is calibrated using several solutions of known concentrations. A calibration curve is produced which is continually rescaled as more concentrated solutions are used. The calibration curve shows the concentration against the amount of radiation absorbed. The sample solution is fed into the instrument and the unknown concentration of the element is then displayed on the calibration curve [37].

8. REAGENTS AND INSTRUMENTS

8.1. Reagents

8.1.1. Surfactants

8.1.1.1. Sodium Dodecyl Sulfate (SDS). Anionic surfactant SDS ($NaC_{12}H_{25}SO_4$) was obtained from Sigma Chemicals Company. It was found in white powdered form with 99 per cent purity. Concentration levels of SDS were kept 6, 8, 12, 20, 50, and 100 mM in soil remediation experiments.

8.1.1.2. Triton X- 100. Non-ionic surfactant Triton X- 100 ($C_{14}H_{22}O(C_2H_4O)n$) was obtained from Merck with 98 - 100 per cent purity. Concentration levels of Triton X-100 were 0.24, 0.60, 50, and 100 mM in soil remediation experiments.

8.1.2. Citric Acid ($C_6H_8O_7$)

Ligand, citric acid was obtained from Merck. It was used in soil remediation experiments, at 2.5 mM, 5 mM, 10 mM, and 20 mM concentration levels.

8.1.3. Potassium Iodide (KI)

Ligand, potassium iodide was obtained from Sigma Chemical Company. It was used at 50, 100, 200, and 400 mM concentration values.

8.1.4. Acetate Buffer Solution

Acetate buffer solution was prepared by using acetic acid (CH_3COOH) and aqueous ammonia (NH_3) which were both obtained from Merck. It was prepared by mixing a 11.76 mL of acetic acid with a 7.47 mL of aqueous ammonia and diluting to 100 mL in a volumetric flask. The final pH value was registered between 4.60 and 4.80.

8.1.5. Cadmium (Cd) Standart Solution

$Cd(NO_3)_2$ solution of a 1000 mg L^{-1} concentration was supplied from Merck. Cadmium test solutions were prepared from this stock solution at 4, 6, and 8 mg L^{-1} levels to pollute the soil artificially. Also, cadmium standart solutions between 10 and 40 mg L^{-1} were prepared for the application of addition method in voltammetric measurements.

8.1.6. Lead (Pb) Standart Solution

$Pb(NO_3)_2$ solution of a 1000 mg L^{-1} concentration was supplied from Merck. A series of lead solutions at 2, 4, 6, 8, 12, 16, and 20 mg L^{-1} levels were prepared from this stock solution to pollute the soil artificially. Also, lead standart solutions between 10 and 50 mg L^{-1} were prepared for the standard addition method in voltammetric measurements.

8.1.7. Potassium Chloride Solution (KCl)

Potassium Chloride (KCl) solution (3 M) was supplied from Metrohm. It was used in the voltammetric measurements to keep the electrolyte concentration constant.

8.1.8. Hydrochloric Acid (HCl)

10 percent hydrochloric acid (HCl), which was used supplied from Merck, was used in cleaning the glasswares and analyte cell during the voltammetric measurements.

8.2. Instruments

8.2.1. pH-meter

The pH-meter WTW Inolab pH/Cond 720 was used. The instrument was calibrated by using buffer solutions of pH 4.00 and 7.00.

8.2.2. Mechanical Shaker

Two mechanical shakers of MRC Water Bath Shaking BT-350 were used to equilibrate the soil and the reactants. Temperature was kept at 25±1°C.

8.2.3. Voltammetric Analyzer

Voltammetric measurements were carried out by using Metrohm 757 VA Computrace Voltammetric Analyzer. The instrument had the three electrode system: 1) WE, 2) auxiliary electrode, and 3) DME was used as the WE, where a Glassy Carbon and Ag/AgCl electrodes served as the auxiliary and reference electrodes, respectively.

DPASV was used to determine the heavy metal content in the sample solution.

The analytes were prepared by taking a 10 mL of sample solution, 0.5 mL of acetate buffer solution and a 0.1 mL of 3 M KCl solution for the voltammetric measurements. The instrument was operated by a computerized program where the method parameters were optimized prior to the determination step. The analyzer was connected to a nitrogen tank at a pressure of 2 bar. Working conditions for the DPASV Method are given in Table 10.1 and 10.2 in section 10.6.

8.2.4. Atomic Absorption Spectrophotometer (AAS)

AAS method was used to confirm the results of the voltammetric measurements. The instrument was a Varian model SpectrAA 250 Plus. Working conditions for AAS are given in Table 8.3 and 8.4 in section 8.6.

9. EXPERIMENTAL METHODS

9.1. Soil Characterization

Soil used in the experiments was taken from Trakya, Tekirdağ region. It was collected from rocky regions of the mountains and also used as a filling soil for the bottom layer in the flower pots. Air dried samples were processed by a mechanical sieve no 60, sieve 0.25mm.

Soil characterization analysis was carried out in the previous study which included its pH value, texture, water content and the organic matter content, and the cation exchange capacity. Results of the soil characterization analysis are given in Table 9.1, 9.2, and 9.3 [38].

Table 9.1. pH values of the soil samples according to the soil:water (1:5) suspension procedure [38]

	Soil (Sample 1)	**Soil (Sample 2)**	**Average pH**
pH	5.28	5.23	5.25

These results showed that the soil samples were all acidic and also had very close pH values.

Table 9.2. Soil texture percentages

Soil Texture	**Percentage (%)**
Gravel	10.96
Sand	85.71
Silt + Clay	3.33

Table 9.3. Results of Soil Analysis

Water Content (percent)	2.39
Organic Matter Content (OMC) (percent)	2.73
Cation Exchange Capacity (CEC)(cmol/kg) (percent)	22.81

9.2. Methodology for Heavy Metal-Soil Interaction

9.2.1. Cadmium-Soil Interaction

Cadmium (Cd)-soil interactions were investigated in the previous study to determine the time needed to establish the equilibrium between the soil and cadmium. The method of analysis was the same as in Pb-soil interaction studies except that experiments were carried out at 4, 6, and 8 mg L^{-1} of Cd^{+2} with varying V/m ratios of 20, 30, and 40 mL g^{-1}. According to this study, the equilibrium time was found to be 25 hours for 4, 6, and 8 mg L^{-1} of cadmium.

9.2.2. Lead (Pb)-Soil Interactions

Lead (Pb)-soil interactions were investigated to determine the time needed to establish the equilibrium between the soil and the pollutant, lead. The samples were prepared according to (V/m) ratio where V represents the volume of Pb^{2+} solution added to the soil sample at 2, 4, 6, 8, 12, 16 and 20 mg L^{-1} concentration levels and m stands for the mass of soil sample used. Experiments were carried out using 2-g soil samples. To determine the equilibrium time, samples with a (V/m) ratios of 20, and 40 mL g^{-1} were prepared and placed on a mechanical shaker for 2, 6, 12, 20, 25, 30, 50, and 72 hours. Amount of lead that was not retained by the soil was determined by DPASV technique. The data obtained by voltammetry were plotted versus the experiment time and the equilibrium time between the soil and the pollutant Pb^{2+} was determined. According to these experiments, the equilibrium time was found to be 72 hours for 2, 4, 6, 8, and 12 mg L^{-1} concentration levels of lead, and the equilibrium time was found to be 96 hours for 16 and 20 mg L^{-1} concentration levels of lead. Results of the experiments were given in section 10.2.

9.2.3. Effect of Contact Area on the Soil Adsorption

In order to investigate the effect of the contact area on the adsorption of lead by the soil, two different volumes of plastic erlens (100 and 250 mL) were used in the experiment.

2 g soil samples were contaminated with 20 mg L^{-1} of Pb^{+2} solutions with V/m = 40 mL g^{-1} in the 100 and 250 mL of erlen flasks for 96 hours on a mechanical shaker. The polluted soil were filtered out and dried in the oven at 100 °C. Amount of lead that was not retained by the soil was determined by DPASV technique.

It was concluded that as the contact area of the soil increased, the amount of lead retained by the soil did not change. The results are given in section 10.3.

9.2.4. Competitive Sorption of Cadmium and Lead in Soil

In this part of the study, soil samples were contaminated with 4, 6, and 8 mg L^{-1} of Pb^{2+} and Cd^{2+} solutions together with V/m ratio of 20 mL g^{-1} for 24 hours on a mechanical shaker. The polluted soil were filtered out and dried in the oven at 100 °C. Amount of lead and cadmium that were not retained by the soil was determined by a DPASV technique.

The results showed that cadmium sorption by the soil was affected in the presence of lead, lead sorption by the soil was also affected in the presence of cadmium. The results are given in section 9.4.

9.3. Soil Remediation Studies with Surfactant

Some surfactants have been found to remove heavy metals from soils, under both acidic and alkaline condition, through direct complexation followed by solubilization. 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 that increases hydrophobic character of the product and result in preferential accumulation of the complex within the surfactant micelle. Such metal complexes are formed extensively within the micellar phase rather than in the aqueous phase [6].

9.3.1. Polluted Soil with Cadmium (Cd^{+2}) and SDS Interaction

Soil samples (2 g) were polluted with 4, 6, and 8 mg L^{-1} of Cd^{2+} solutions with V/m ratios of 20 and 40 mL g^{-1} and they were placed on the mechanical shaker for 48 hours .The polluted soil samples were filtered and dried in the oven at 100°C.Then, they were put into contact with SDS at 20, 50, and 100 mM concentration levels for 24 hours on a mechanical shaker. The previous experimental results with 6-10 mM of SDS showed about 12 percent soil remediation. Hence, much higher concentration levels above the CMC of SDS were tested in this study. Amount of cadmium that was released back to the solution in the presence of SDS was determined by both DPASV and AAS. Results are given in section 10.5.1 [38].

9.3.2. Polluted Soil with Lead (Pb^{+2}) and SDS Interaction

Soil samples were treated as described in section 9.2.2. Then, the dried soil samples were put into contact with SDS at varying concentration levels between 6 mM and 100 mM with V/m ratios of 20 and 40 mL g^{-1} for 24 hours on a mechanical shaker. The experimental results with 6, 8, and 12 mM of SDS made it necessary to go up to much higher values of SDS. It was only then the cleansing effect of SDS was observed for the polluted soil samples. Amount of Pb^{2+} removed from soil by SDS was determined by both DPASV and AAS. Results are given in section 10.5.2.

9.4. Soil Remediation with Ligand

9.4.1. Polluted Soil with Cadmium (Cd^{2+}) and Ligand Interactions

Soil samples were polluted initially with cadmium as described in section 8.3.1. Then, they were put into contact with ligand iodide at 50, 100, 200, and 400 mM concentration levels with V/m ratios of 20 and 40 mL g^{-1}on a mechanical shaker for 24 hours. Also, another set which was composed of the polluted soil samples and the ligand, citric acid at 2.5, 5, 10, and 20 mM concentration levels were prepared.

To compare the effect of surfactant-inorganic ligand and surfactant-organic ligand, commonly used organic acid, citric acid was used. The V/m ratios and the contact time were exactly the same as in the experimental set with the ligand, iodide.

The presence of soluble organic ligands in soil may significantly influence metal adsorption through formation of stable complexes [7]. Thus, quantifying the sorption process is a critical aspect chemical behavior of a metal in soil. Results are given in section 10.6.1.

9.4.2. Polluted Soil with Lead (Pb^{2+}) and Ligand Intractions

Polluted soil samples as described in section 9.2.2 were put into contact with ligand iodide at 50, 100, 200, and 400 mM concentration levels with V/m ratios of 20 and 40 mL g-1 on a mechanical shaker for 24 hours. Also, a parallel set of initially polluted soil samples together with the ligand citric acid were put a mechanical shaker for 24 hours. Test concentrations for citric acid were the same as given for cadmium in section 9.4.1.

Soil samples were filtered and the supernatant was analyzed by AAS. Results are given in section 10.6.2.

9.5. Soil Remediation with Surfactant Micelle-Solubilized Ligand

Combined effects of surfactant-ligand interactions were studied in this section. The experiments were run to evaluate heavy metal-SDS-iodide, heavy metal-SDS-citric acid, heavy metal-Triton-X 100-iodide, and heavy metal-Triton-X 100-citiric acid interactions.

The concentration levels of SDS were set at 50, and 100 mM values with iodide ligand, SDS concentration values were kept 20, 50, and 100 mM with citric acid ligand. The concentration levels for Triton X-100 were set 50 and 100 mM values with both of the ligands, iodide and citric acid. The ligands, iodide and citric acid were kept at the same concentration levels as they were in the polluted soil-ligand interaction studies as described in section 9.4.1 and 9.4.2.

In this part of the study, initially polluted soil samples either with Cd^{2+} or Pb^{2+} at various concentration values were put in a solution together with different combination of surfactant-ligand mixture. The V/m ratios were 20 and 40 mL g^{-1} and contact time was 24 hours. The supernatant was removed by filtration and analyzed by AAS only for removal of lead samples due to having limited time for analyzing by DPASV.

9.6. Instrumental Analysis

9.6.1. Voltammetric Measurements

9.6.1.1. Working Conditions. Determination and voltammetric parameters for the analysis of cadmium and lead were given in the Table 9.4 and 9.5, respectively.

Table 9.4. Working Parameters for Cd and Pb

Deposition Potential (V)	-1.10
Deposition Time (s)	90
Equilibrium Time (s)	10
Start Potential (V)	-1.10
End Potential (V)	0.0499
Voltage Step (V)	0.005951
Pulse Amplitute (V)	0.05
Pulse Time (s)	0.04
Voltage Step Time (s)	0.1
Sweep Rate (V/s)	0.0595
Stirring Rate (rpm)	2000

Table 9.5. Determination Parameters for Cd and Pb

Cell Volume (mL)	10.6
Sample Volume (mL)	10.0
Addition Purge Time (s)	20
Blank Purge Time (s)	300
Number of additions	2
Number of replications	2

9.6.1.2. Sample Preparations. In order to measure the concentration of sample with the voltammetric instruments, 10 mL sample volume which was diluted with respect to the sample concentration, 0.5 mL of acetate buffer solution, and 0.1 mL of supporting electrolyte, 3 M KCl solution were added to the analyte cell. Dilutions of the sample solutions were done by using deionized water.

Different concentration values of standard solutions were prepared and two times standard additions were done for the voltammetric analysis. Concentration values of standard solution were changed with respect to the sample concentrations.

9.6.2. AAS Measurements

9.6.2.1. Working Conditions

Cadmium Determination: Determination and AAS parameters for the analysis of cadmium were given in the table 9.6.

Table 9.6. Working Parameters for cadmium

Lamp current (mA)	5
Spectral bandpass (nm)	1
Wavelength (nm)	228.8
Air flow (L min^{-1})	15
Acetylene flow (L min^{-1})	1.5
Detection limit (mg L^{-1})	0.0006
Standard solutions (mg L^{-1})	0.2, 0.4, 0.8, and 1.0

Lead Determination:

Determination and AAS parameters for the analysis of lead were given in the table 9.7.

Table 9.7. Working Parameters for lead

Lamp current (mA)	6
Spectral bandpass (nm)	1
Wavelength (nm)	217
Air flow (L min^{-1})	15
Acetylene flow (L min^{-1})	1.5
Detection limit (mg L^{-1})	0.02
Standard solutions (mg L^{-1})	1, 2.5, 5, and 10

10. RESULTS AND DISCUSSION

10.1. Lead (Pb)-Soil Interaction

The experiments were carried out by using lead solutions in different concentration levels (2, 4, 6, 8, 12, 16, and 20 mg L^{-1}) and V/m ratios of 20 and 40 mL g^{-1} for 2, 6, 12, 24, 36, 50, 72, and 96 hours in order to find the equilibrium time for lead-soil interactions.

The quantity of lead not retained by the soil was determined by DPSAV under optimized voltammetric conditions as specified in section 9.6.1.1.

Experimental results of the equilibrium time between the soil and lead was found to be 72 hours for 2, 4, 6, 8, and 12 mg L^{-1} lead concentration levels and 96 hours for 16 and 20 mg L^{-1} lead concentration levels at each V/m ratios equal to 20 and 40 mL g^{-1} . The graphs that show the equilibrium time are given in Figures 10.1, 10.2, and 10.3.

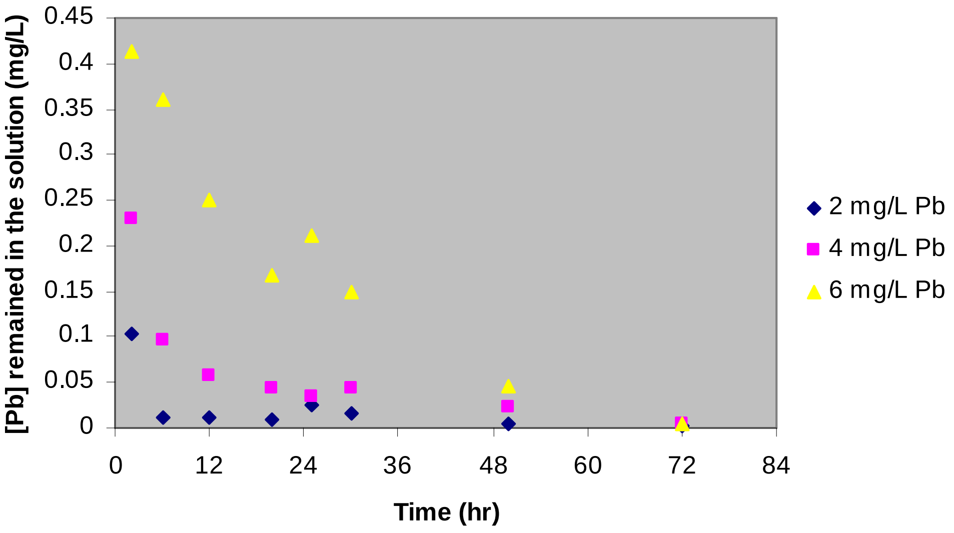


Figure 10.1. Plot of [Pb] remained in solution versus time for 2, 4, and 6 mg L^{-1} Pb interaction with soil (V/m=40 mL g^{-1})

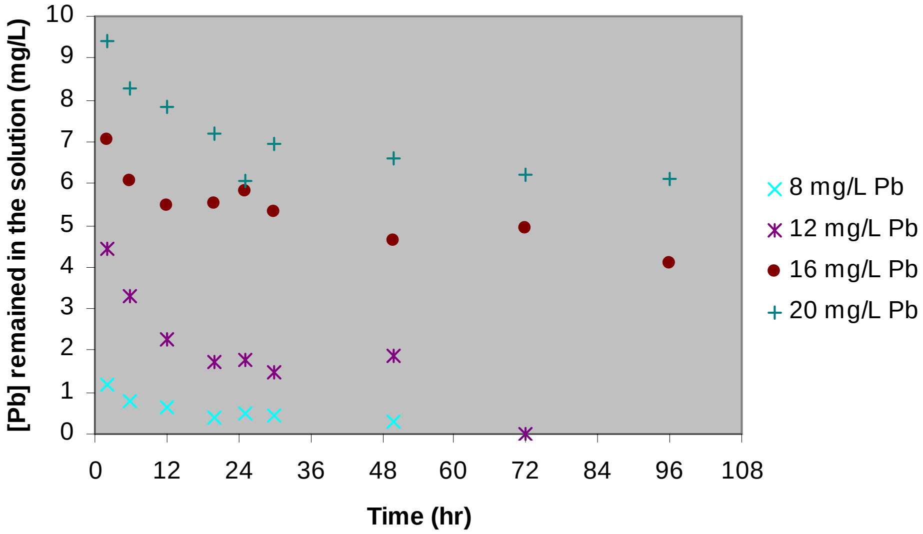


Figure 10.2. Plot of [Pb] remained in the solution versus time for 8, 12, 16, and 20 mg L^{-1} Pb interaction with soil (V/m=40 mL g^{-1})

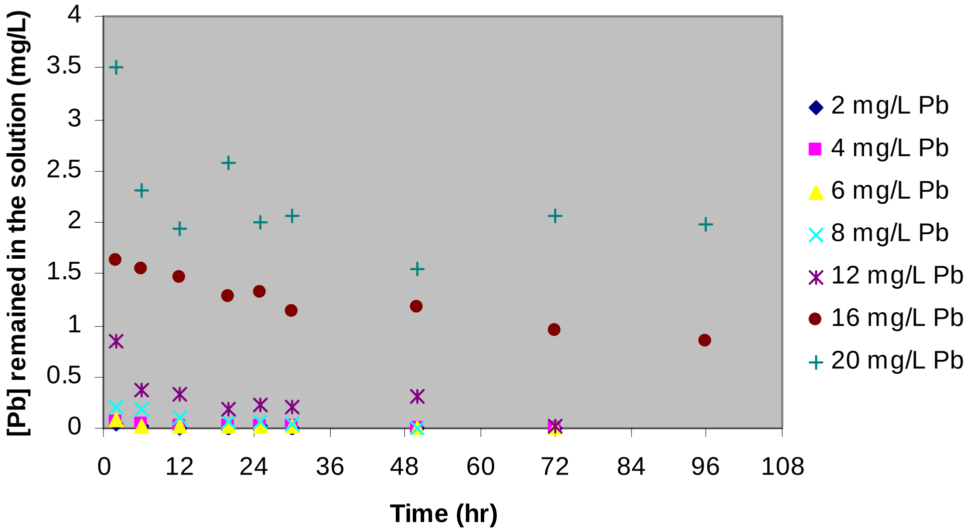


Figure 10.3. Plot of [Pb] remained in the solution versus time for 2, 4, 6, 8, 12, 16, and 20 mg L^{-1} Pb interaction with soil (V/m=20 mL g^{-1})

Table 10.1. The percentage of Pb remained in the test solutions at the equilibrium time for 2, 4, 6, 8, 12, 16, and 20 mg L^{-1} concentrations and different V/m ratios:

V/m (mL/g)	**2 mg L^{-1} Pb**	**4 mg L^{-1} Pb**	**6 mg L^{-1} Pb**	**8 mg L^{-1} Pb**	**12mg L^{-1} Pb**	**16 mg L^{-1} Pb**	**20 mg L^{-1} Pb**
20	0.14%	0.05%	0.03%	0.263%	0.17%	5.27%	9.90%
40	0.15%	0.10%	0.08%	0.513%	0.225%	25.67%	30.65 %

The results of the study have shown that as the V/m increased, the amount of lead was taken up by the soil decreased. Also, lesser amount of lead was adsorbed by he soilwith respect to its increasing concentration in the artificially polluted soil.

10.2. Cadmium (Cd)-Soil Interactions

This part of the study was done previously for 4, 6, and 8 mg L^{-1} concentration levels of Cd^{2+} solutions with V/m ratios of 20, 30, and 40 mL g^{-1}. It was found that the equilibrium between the cadmium and soil was established at 25 hours for each cadmium concentrations at each V/m ratio [38]. An example for the voltommogram of the results of polluting the soil for 25 hours is given in Figure 10.4.

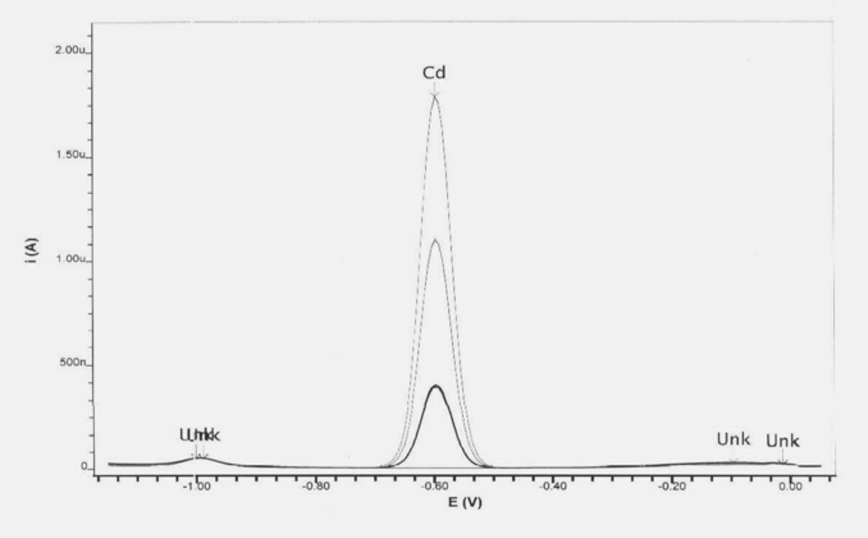


Figure 10.4. Soil polluted with 8 mg L^{-1} Cd for 25 hours at 20 mL g^{-1} ratio

10.3. Effects of Contact Area on the Lead Adsorption

In this part of the study, 100 and 250 mL volume of the erlenmeyer flasks were used for 20 mg L^{-1} Pb^{2+} solutions with V/m of 40 mL g^{-1} to observe a effect of the surface area on the soil adsorption. Measurements were carried out by DPASV and the results of experiments are given in Figure 10.5.

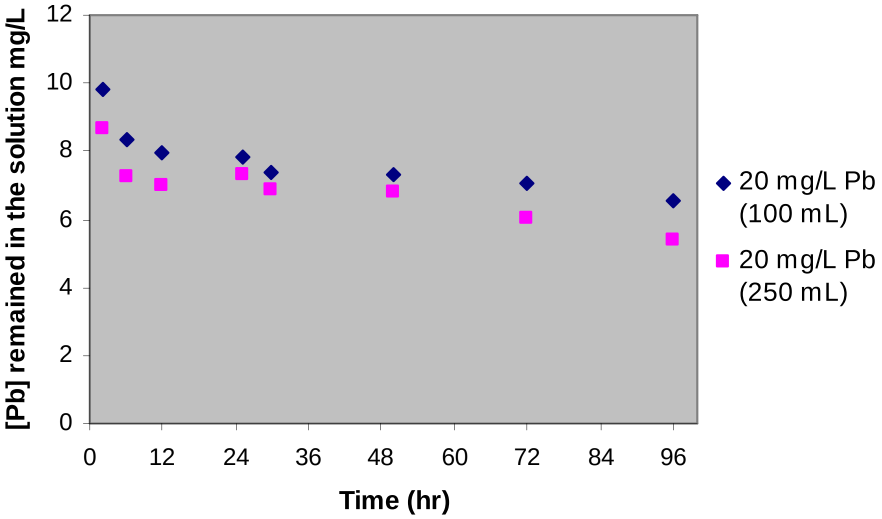


Figure 10.5. Concentration of Pb remained in the test solution versus time for 40 mL g^{-1}

At 72 and 96 hours of previously determined equilibrium times for the soil and lead interaction, the concentrations of lead remained in the solution were 7.08, and 6.37 mg L^{-1} and 6.02, and 5.84 mg L^{-1} for the test sets in 100 mL and 250 mL erlenmeyer flasks, respectively. Thus, it was concluded that the role of the surface area on the adsorption of lead by the soil was not very effective.

10.4. Competitive Sorption of Cadmium and Lead on to Soil

In order to examine the effect of the simultaneous presence of Pb^{2+} and Cd^{2+} on sorption behavior to the soil, the experiments were carried out by cadmium and lead solutions together with 4, 6, and 8 mg L^{-1} equimolar concentration levels to contaminate the soil for 6 and 20 hours where the V/m = 20 mL g^{-1}.

The quantity of cadmium and lead not retained by the soil (i.e. remained in the solution) was determined by DPSAV and results of experiments were given in Figures 10.6-10.11.

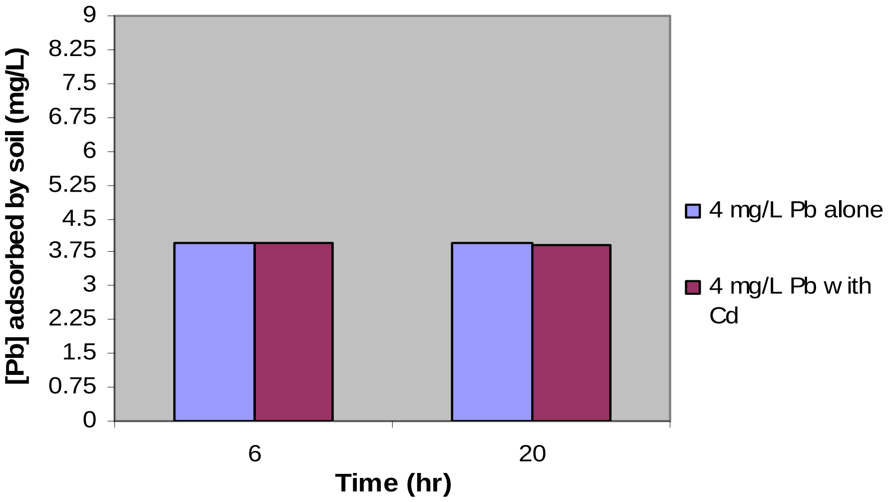


Figure 10.6. Plot of [Pb] adsorbed by the soil from both single (Pb) and binary (Pb+Cd) metal solutions versus time at 4 mg L^{-1}

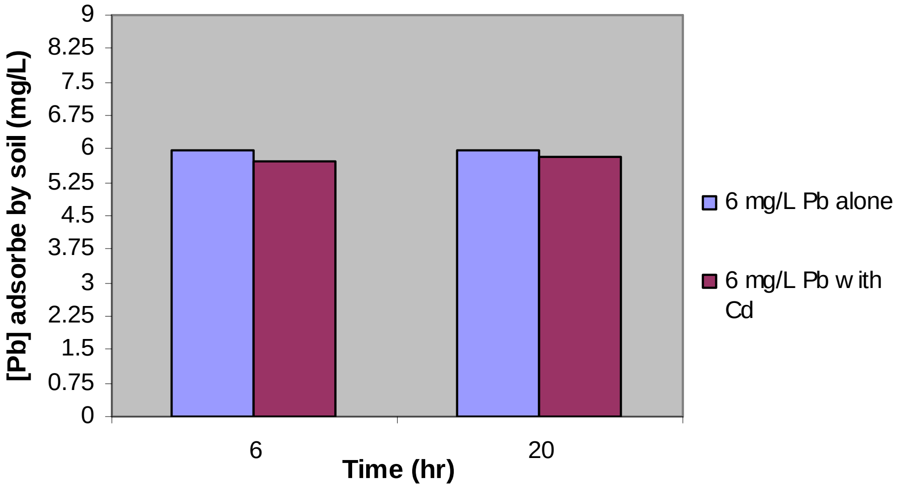


Figure 10.7. Plot of [Pb] adsorbed by the soil from both single (Pb) and binary (Pb+Cd) metal solutions versus time at 6 mg L^{-1}

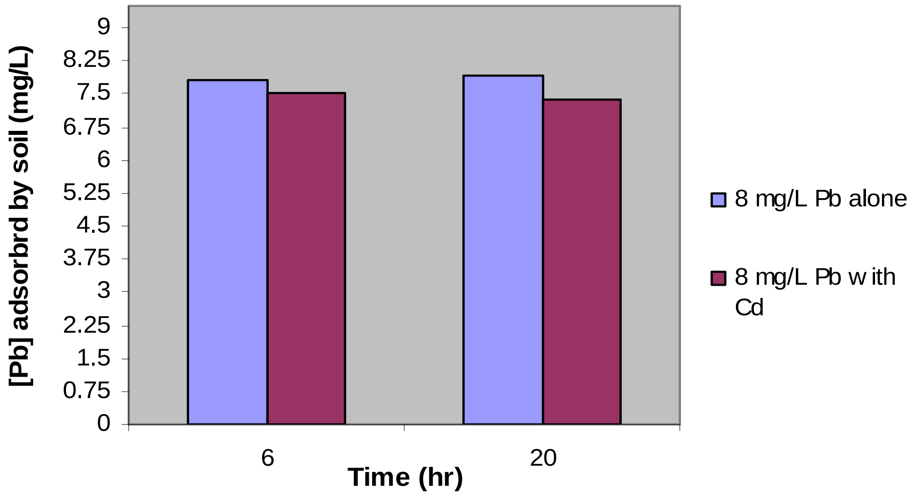


Figure 10.8. Plot of [Pb] adsorbed by the soil from both single (Pb) and binary (Pb+Cd) metal solutions versus time at 8 mg L^{-1}

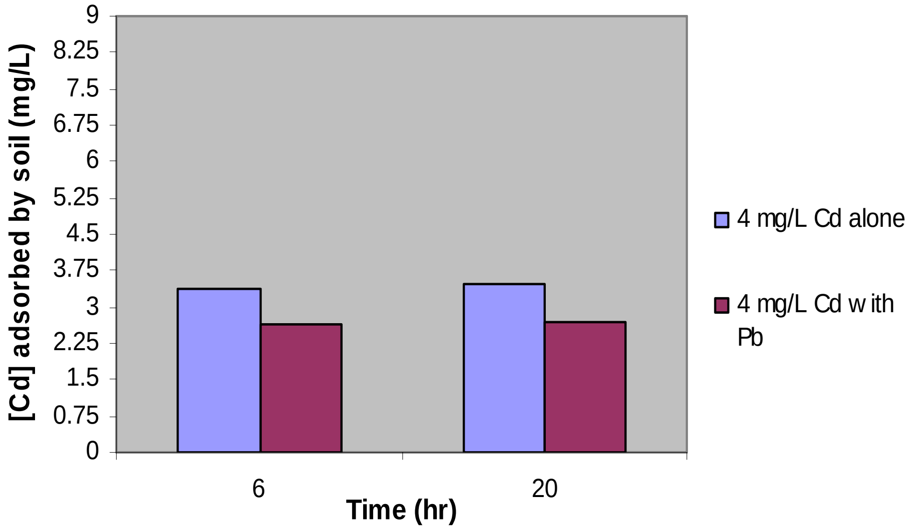


Figure 10.9. Plot of [Cd] adsorbed by the soil from both single (Cd) and binary (Cd+Pb) metal solutions versus time at 4 mg L^{-1}

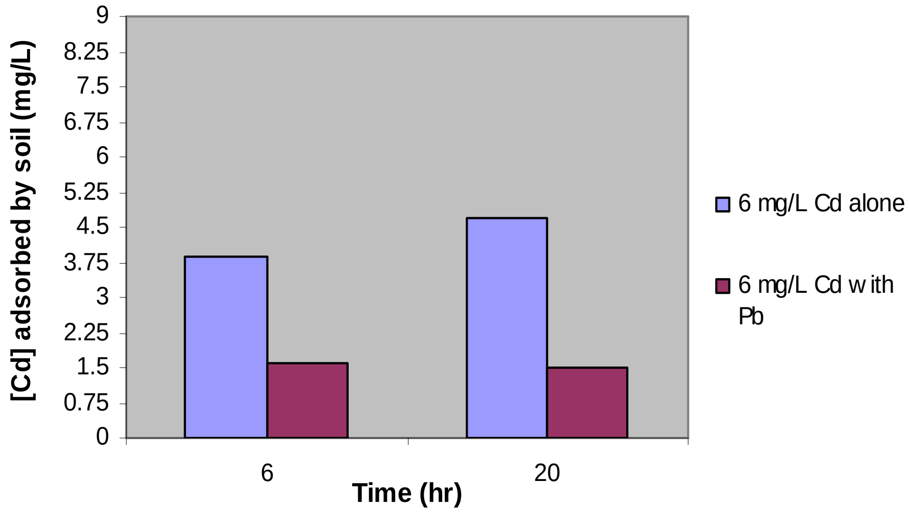


Figure 10.10. Plot of [Cd] adsorbed by the soil from both single (Cd) and binary (Cd+Pb) metal solutions versus time at 6 mg L^{-1}

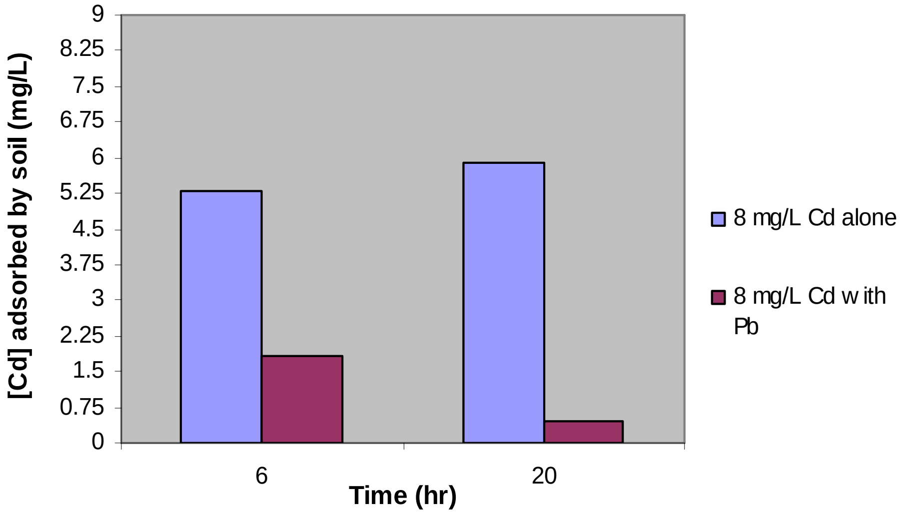


Figure 10.11. Plot of [Cd] adsorbed by the soil from both single (Cd) and binary (Cd+Pb) metal solutions versus time at 8 mg L^{-1}

The experiments showed that the soil exhibited greater sorption capacity for Pb than Cd when the metals were introduced to the soil separately. The introduction of both metals together reduced the tendency for either to be sorbed, although Cd sorption was affected to a greater extend than that of Pb. In the presence of binary mixtures, soil adsorption behavior for Cd was highly reduced by the presence of Pb.

However, at 6 mg L^{-1} level, Pb concentration remained in the solution was 0.025 mg L^{-1} when the soil was polluted with Pb alone and it was 0.15 mg L^{-1} when Pb and Cd were present together in the media.

10.5. Metal Removal with Surfactant

10.5.1. Desorption of Lead with SDS

Soil samples polluted initially with 6, 8, 12, 16, and 20 mg L^{-1} Pb, were remediated by SDS in wide range concentration levels to observe the effect of different concentrations of SDS. The concentration values of SDS were 6 mM (below CMC), 8 mM (at CMC), 12 mM, 20 mM, 50 mM, and 100 mM (all above CMC) to remove Pb from the soil. The quantity of Pb in the remediation solutions were determined by the DPASV. Only at higher concentration levels of SDS such as 20, 50, and 100 mM, analyte solutions were analyzed by AAS due to the adverse foaming effects of SDS on the DPASV measurements.

Experiments were conducted in two parts. First of all, the time effect on remediation studies at different SDS concentrations were studied for soil samples initially polluted with 6 mg L^{-1} to 20 mg L^{-1} of Pb $^{2+}$. Test hours were changed between 24 hours and 96 hours and the concentrations of SDS were kept between 6 mM and 12 mM, the V/m ratio values were 20 and 40 mL g^{-1}. Results were shown in Figures 10.12-10.17.

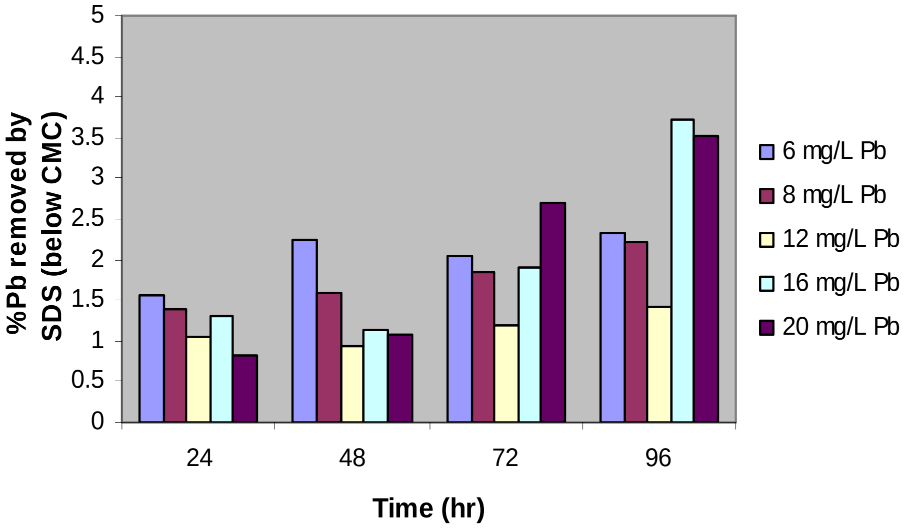


Figure 10.12. Plot of the percentage of Pb removed from the polluted soil by 6 mM (below CMC) SDS versus time for V/m = 20 mL g^{-1}

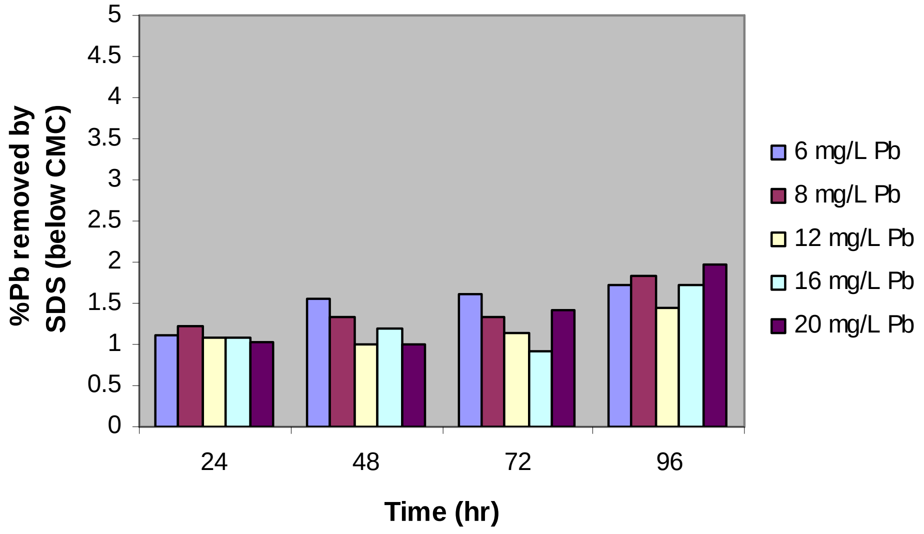


Figure 10.13. Plot of the percentage of Pb removed from the polluted soil by 6 mM (below CMC) SDS versus time for V/m = 40 mL g^{-1}

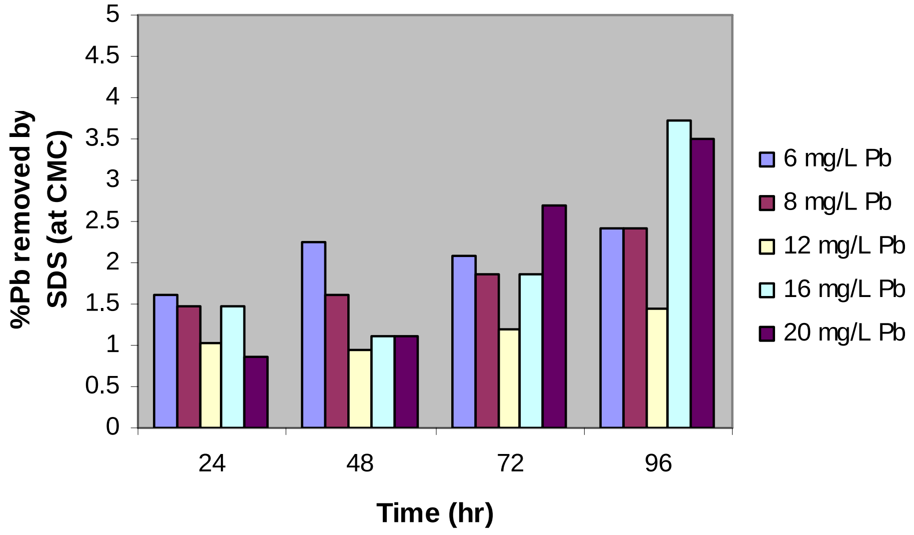


Figure 10.14. Plot of the percentage of Pb removed from the polluted soil by 8 mM (at CMC) SDS versus time for V/m = 20 mL g^{-1}

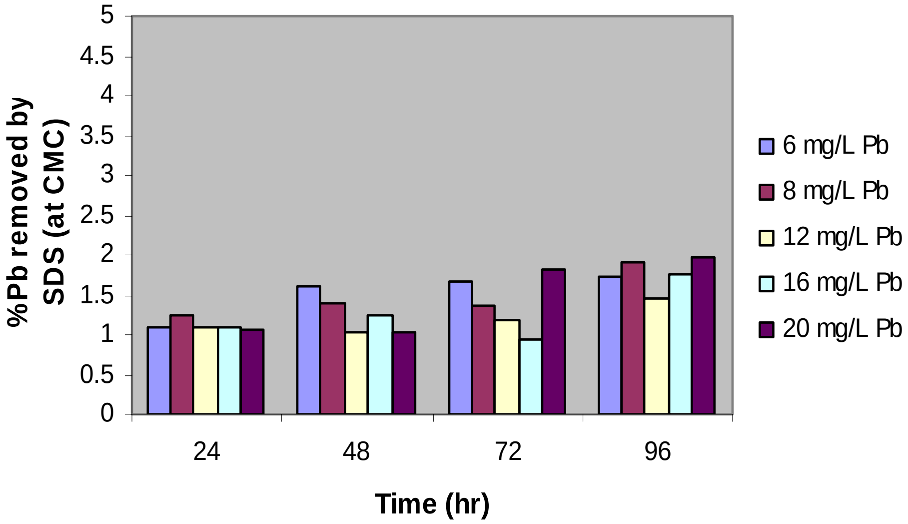


Figure 10.15. Plot of the percentage of Pb removed from the polluted soil by 8 mM (at CMC) SDS versus time for V/m = 40 mL g^{-1}

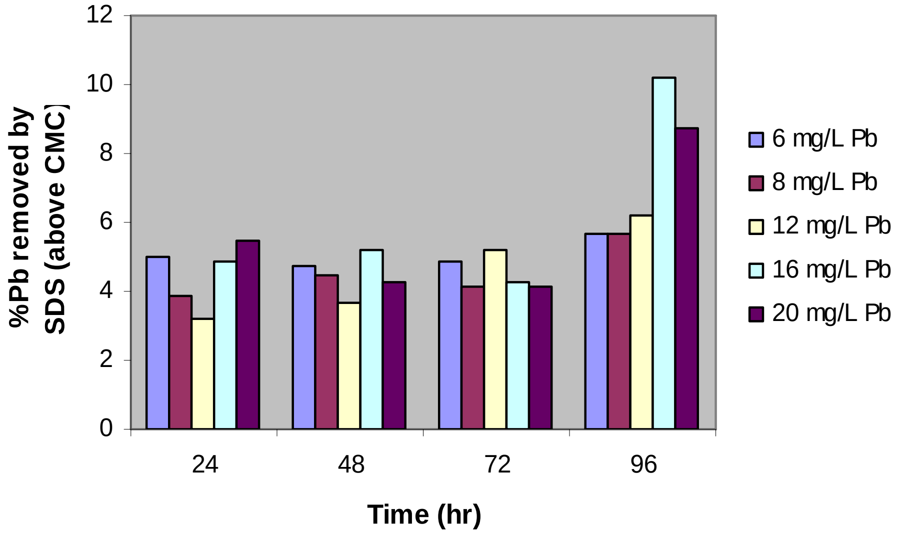


Figure 10.16. Plot of the percentage of Pb removed form the polluted soil by 12 mM (above CMC) SDS versus time for V/m = 20 mL g^{-1}

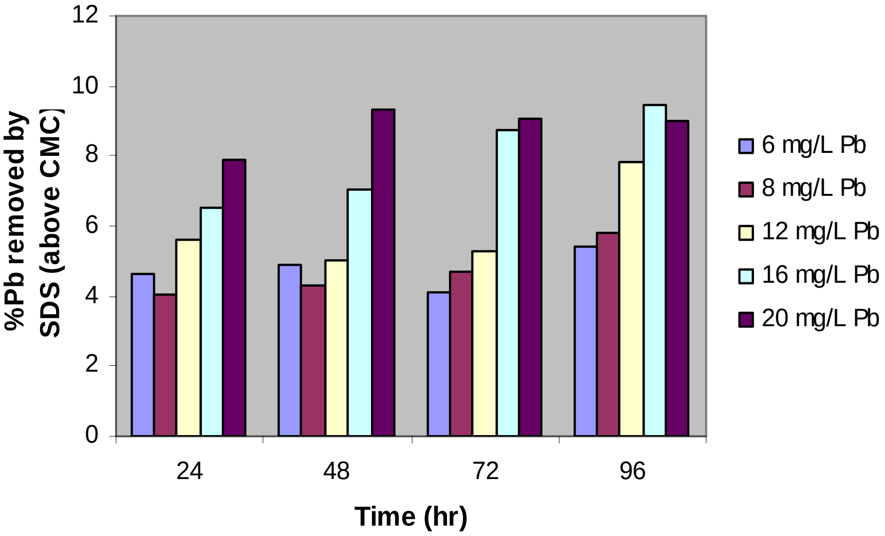


Figure 10.17. Plot of the percentage of Pb removed form the polluted soil by 12 mM (above CMC) SDS versus time for V/m = 40 mL g^{-1}

It was observed that as the contact time of the surfactant SDS with the initially polluted soil was increased the amount of Pb^{2+} removed from the soil was increased. This effect was especially pronounced at higher concentration levels of Pb^{2+} for 20 mL g^{-1}.

However, all other remediation studies were carried out at 24 hours to keep the overall experiment time reasonably short prior to DPASV and AAS measurements.

The Pb-uptake by an aqueous solution containing 6, 8, and 12 mM SDS was at most 5.5 and 8 percent for V/m of the 20 and 40 mL g^{-1} systems, respectively. The results obtained from different concentration levels of SDS (8 mM and 20 mM) in remediation of soil showed that the amounts of metal removal from the soil were only slightly different from the above results. Thus, these experimental results made it necessary to go up to much higher values of SDS, such as 50 and 100 mM in the solution (Figures 10.18 and 10.19)

The second part of the soil remediation experiments were carried out in the following way: initially polluted soil samples with 8, 12, 16, and 20 mg L^{-1} of Pb^{2+} were put into contact with SDS for 24 hours and the remediation solutions were analyzed by DPASV and AAS. Figures 10.18 and 19 were obtained from DPASV results.

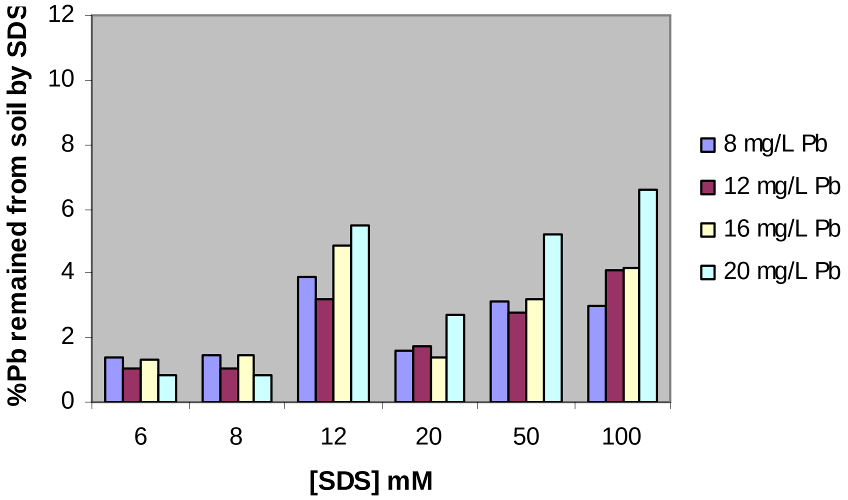


Figure 10.18. Plot of the percentage of Pb removed form the polluted soil by 20, 50, and 100 mM SDS versus [SDS] for V/m = 20 mL g^{-1}

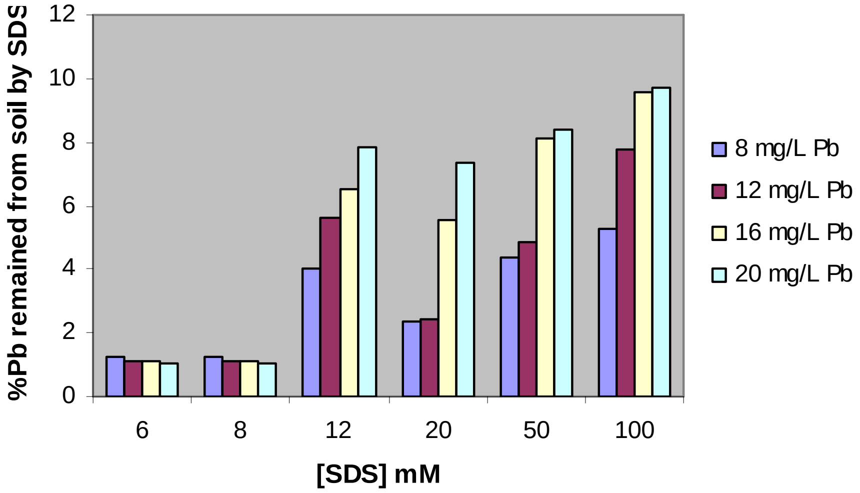


Figure 10.19. Plot of the percentage of Pb removed form the polluted soil by 20, 50, and 100 mM SDS versus [SDS] for V/m = 40 mL g^{-1}

The results of experiments illustrated that even though applying SDS at higher concentrations such as 50 and 100 mM was not efficient in removing lead from the soil. Thus, in order to remove lead from the soil, SDS had to be combined with an effective ligand.

10.5.2. Desorption of Cadmium with SDS

Soils initially polluted with 4, 6, 8 mg L^{-1} Cd^{2+}, were remediated by SDS with 20, 50, and 100 mM concentrations. In the previous study, 6, 8, and 10 mM SDS were applied to remediate the soils [38]. The quantity of Cd^{2+} in the analyte solutions containing 20, 50, and 100 mM SDS were determined by the AAS, because of the adverse foaming effect of SDS on DPASV.

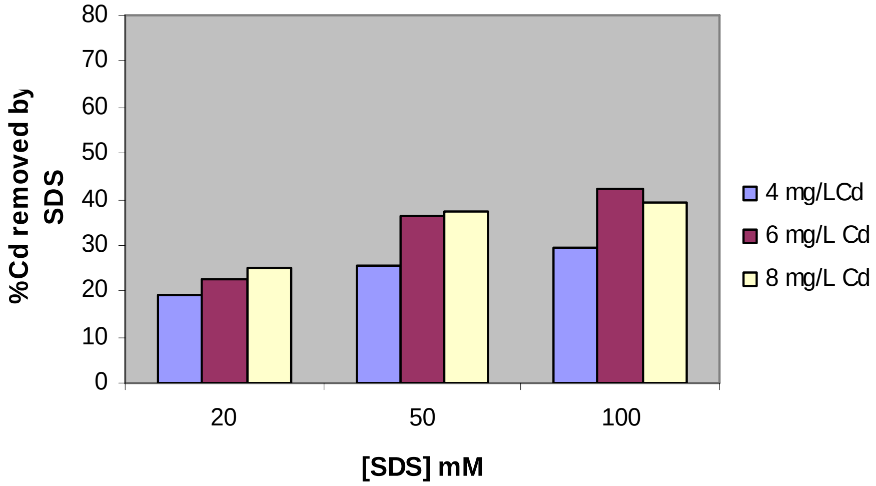


Figure 10.20. Plot of the percentage of Cd removed form the polluted soil by 50 and 100 mM SDS versus [SDS] for V/m = 20 mL g^{-1}

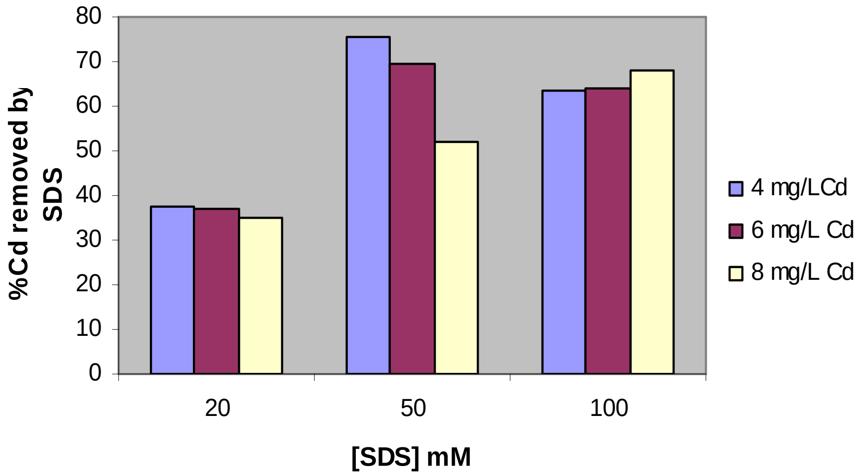


Figure 10.21. Plot of the percentage of Cd removed form the polluted soil by 50 and 100 mM SDS versus [SDS] for V/m = 40 mL g^{-1}

Experimental results of this study showed that high concentration values of SDS are effective in the remediation of soil. Almost 40 percent remediation for V/m of the 20 mL g^{-1} and 70 percent; remediation for V/m = 40 mL g^{-1} was obtained, as illustrated in Figure 10.20 and Figure 10.21.

10.5.3. Desorption of Lead with Triton X-100

Soils initially polluted with 8, 12, 16, and 20 mg L^{-1} Pb^{2+}solutions, were remediated by Triton X-100 with 50, and 100 mM concentration levels. The CMC value of Triton X-100 was reported to be 0.24 mM [4]. The test concentrations of Triton X-100 in this study were kept much higher levels than its CMC, because, the aim was to study and compare the effects of the anionic (SDS) and non-ionic surfactant (Triton X-100) on soil remediation at the same concentration levels. The quantity of Pb^{2+} in the analyte solutions containing 50, and 100 mM Triton X-100 was determined by AAS.

Figure 10.22 indicated that removal efficiency of the Triton X-100 at both 50 and 100 mM levels was almost 10 percent for V/m of 20 mL g^{-1}. But the percent removal of Pb by Triton X-100 was at most 55 percent for V/m of 40 mL g^{-1} as shown in Figure 10.23. These results have shown that, as the V/m ratio for the Triton X-polluted soil system was increased, percentage of lead taken from the polluted soil was also increased. Also, the remediation efficiency of Triton X-100 remained between 35-40 percent for the entire test concentrations.

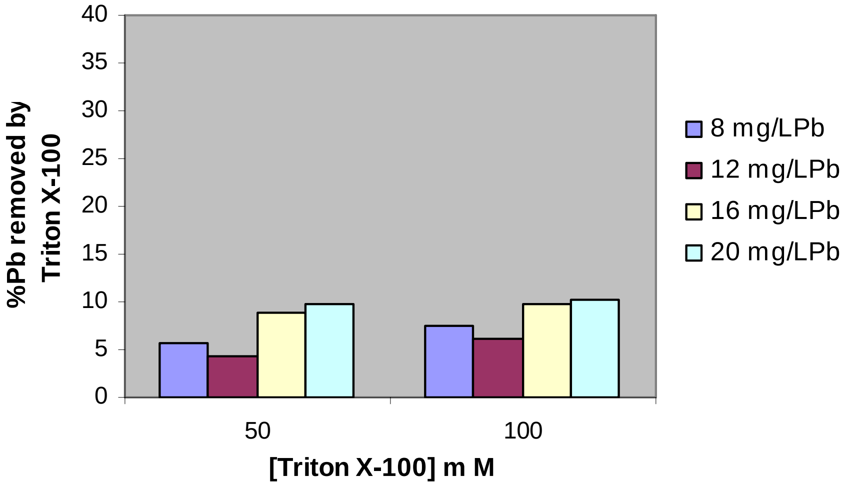


Figure 10.22. Plot of the percentage of Pb remained form the polluted soil by 50 and 100 mM Triton X100 versus [Triton X-100] for V/m = 20 mL g^{-1}

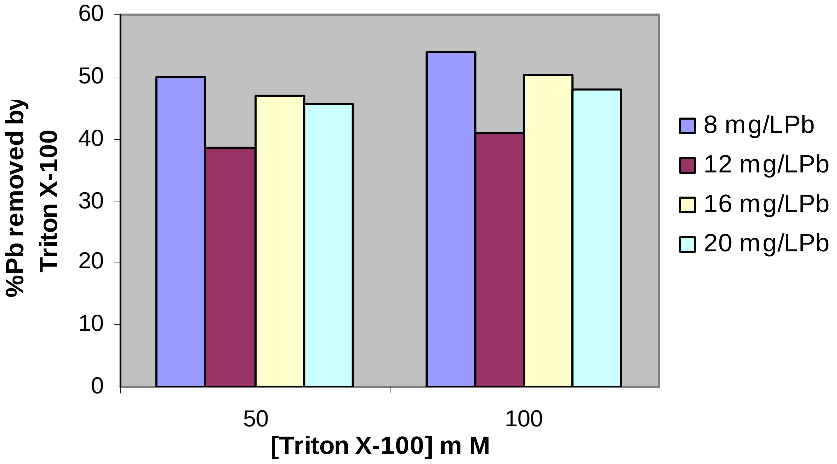


Figure 10.23. Plot of the percentage of Pb removed from the polluted soil by 50 and 100 mM Triton X100 versus [Triton X-100] for V/m = 40 mL g^{-1}

10.5.4. Desorption of Cadmium with Triton X-100

Soils samples polluted with 4, 6, 8 mg L^{-1} Cd^{2+}, were remediated by Triton X-100 with 0.6 mM concentration levels for 25 hours. The quantity of Cd^{2+} in the analyte solutions containing 0.6 mM was analyzed by DPASV.

Table 10.2. Percentage of Cd removed from the polluted soil by 0.6 mM Triton X-100 for 25 hours at V/m = 20 mL g^{-1}

Percentage of Cd removed from soil		
4 mg L^{-1}	6 mg L^{-1}	8 mg L^{-1}
0.41%	0.8%	1.04%

Table 10.3. Percentage of Cd removed from the polluted soil by 0.6 mM Triton X-100 for 25 hours at V/m = 40 mL g^{-1}

Percentage of Cd removed from soil		
4 mg L^{-1}	6 mg L^{-1}	8 mg L^{-1}
0.27%	0.27%	0.37%

In the application of Triton X-100 alone at the concentration of 0.6 mM, the amount of cadmium removed from the soil was not efficient for both V/m of 20 mL g^{-1} and 40 mL g^{-1}. There is no available data for Triton X-100 at 50 and 100 mM concentrations.

10.6. Soil Remediation with Ligand

10.6.1. Desorption of Lead with Iodide

Soils initially polluted with 8, 12, 16, and 20 mg L^{-1} Pb^{2+}, were remediated by iodide alone at 50, 100, 200, an 400 mM concentration levels. The concentration of Pb^{2+} in the analyte solutions was determined by AAS.

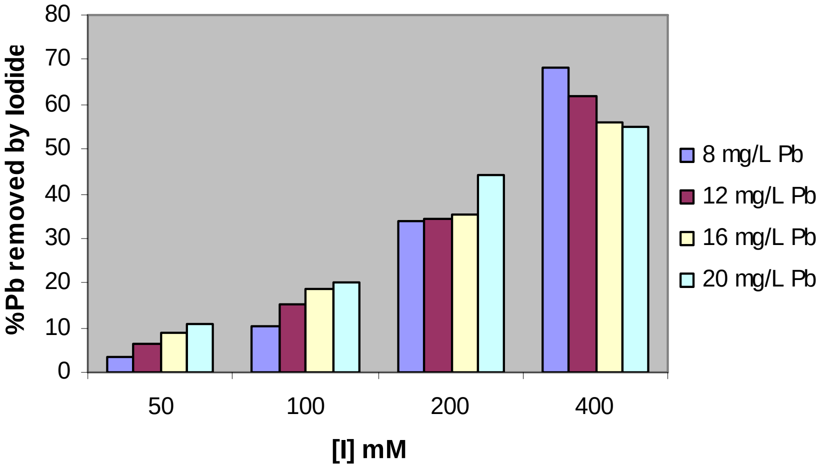


Figure 10.24. Plot of the percentage of Pb removed from the polluted soil by 50, 100, 200, and 400 mM iodide alone versus [Iodide] for V/m = 20 mL g^{-1}

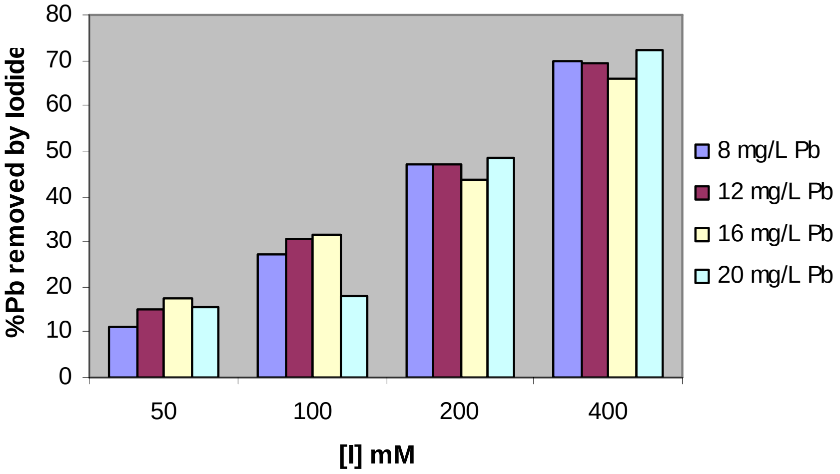


Figure 10.25. Plot of the percentage of Pb removed from the polluted soil by 50, 100, 200, and 400 mM iodide alone versus [iodide] for V/m = 40 mL g^{-1}

The results are given in the Figure 10.24 and 10.25 for removal of lead from the soil by applying different concentrations of iodide as a ligand. The results indicated that the increase in the iodide concentration resulted in increasing in the amount of lead taken from the polluted soil and also the quantity of lead removed from polluted soil increased as the V/m ratio increased for the same concentration of iodide used.

The presence of Pb removal was between 5-10 percent for V/m = 20 mL g^{-1} at 50 mM iodide concentration. Also, the percentage removal of Pb reached to 70 percent at 400 mM iodide for V/m = 40 mL g^{-1} whereas it was between 50-70 percent for V/m = 20 mL g^{-1} for the same ligand concentrations.

Hence, it was concluded that the release of Pb from the soil was depend on the iodide concentration as well as V/m ratio.

10.6.2. Desorption of Cadmium with Iodide

Experiments were carried out in the presence of initially polluted soils with 4, 6, and 8 mg L^{-1} Cd^{2+} and ligand iodide. Iodide concentration levels were the same as given in section 10.6.1. Figure 10.26 and 10.27 show that the cleansing effect of iodide gradually increased with the increasing iodide concentration in the remediation solution. However, for a given iodide concentration in solution, its effect in taking up the metal ion showed a slight decrease as the soil was more heavily contaminated with Cd^{2+}. Hence a soil, polluted with 4 mg L^{-1} Cd^{2+} initially, was more readily cleaned as compared with the soil initially polluted with 8 mg L^{-1}. The amount of Cd^{2+} removed from soil was determined by AAS and DPASV, but Figures 10.26 and 10.27 were obtained from AAS results.

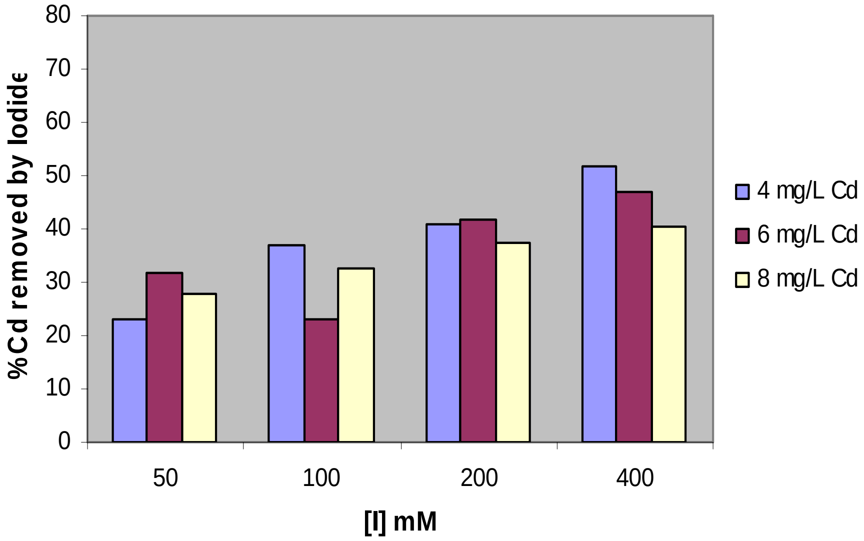


Figure 10.26. Plot of the percentage of Cd removed form the polluted soil by 50, 100, 200, and 400 mM iodide versus [iodide] for V/m = 20 mL g^{-1}

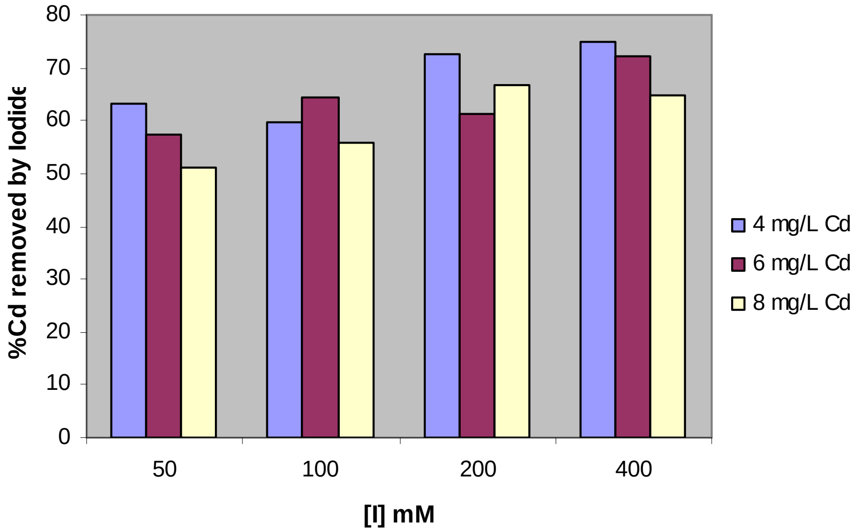


Figure 10.27. Plot of the percentage of Cd removed form the polluted soil by 50, 100, 200, and 400 mM iodide versus [iodide] for V/m = 40 mL g^{-1}

When the results for different V/m values were compared, the percent remediation of the samples with higher V/m values (i.e.40 mL g^{-1}) went up to 75 percent (Fig. 10.27). The samples with lower V/m ratios (i.e.20 mL g^{-1}), for a soil contaminated with 4 mg L^{-1} Cd, the remediation was around 50 percent (Fig. 10.26) and for a soil contaminated with 8 mg L^{-1} Cd, the remediation value was between 30-40 percent (Fig. 10.26 and 10.27). Therefore, the release of Cd from the soil was observed to depend on iodide concentration as well as the V/m ratio.

10.6.3. Desorption of Lead with Citric Acid

Soils initially polluted with 4, 6, and 8 mg L^{-1} Pb^{+2}, were remediated by citric acid alone at 2.5, 5, 10, and 20 mM concentrations. This working range was applied because of the fact that higher concentration levels of citric acid above 20 mM may alter the chemical properties of the soil as well as its pH value. The concentration of Pb^{2+} in the analyte solutions was determined by AAS.

The results of the experiments showed that as the concentration of the citric acid increased from 2.5 to 20 mM, the efficiency of citric acid increased gradually in the remediation of the soil at each metal ion concentration level tested. Also, the role of V/m ratio was important in soil remediation. As an example, for the initially polluted soil at 20 mg L^{-1} level, the percentage of Pb removed by citric acid was between 7 to 22 percent for V/m = 20 mL g^{-1} and it was between 15 to 42 percent for V/m = 40 mL g^{-1} where the citric acid concentration ranged from 2.5 mM to 20 mM. Experiment results were shown in Figures 10.28 and 10.29.

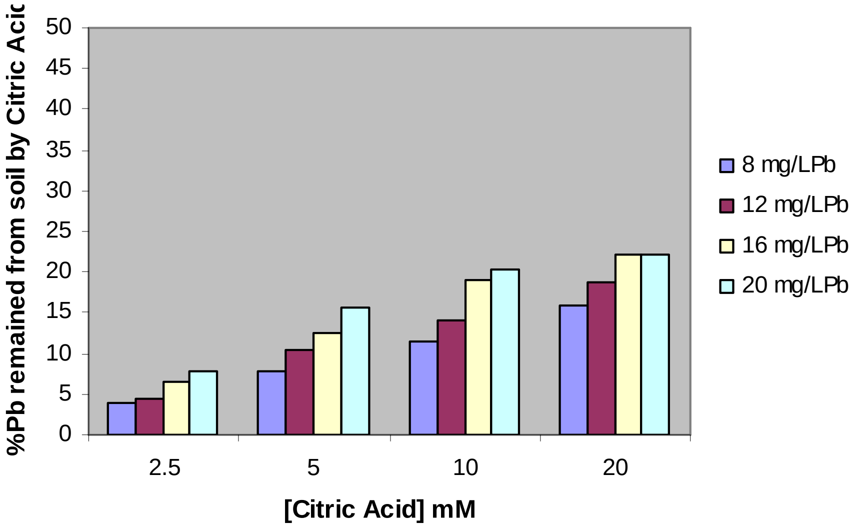


Figure 10.28. Plot of the percentage of Pb removed from the polluted soil by 2.5, 5, 10, and 20 mM citric acid alone versus [citric acid] for V/m = 20 mL g^{-1}

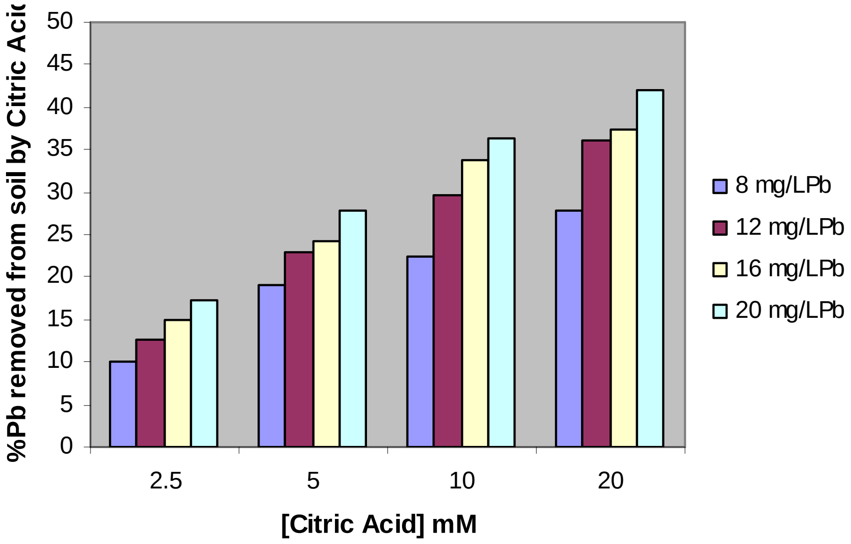


Figure 10.29. Plot of the percentage of Pb removed from the polluted soil by 2.5, 5, 10, and 20 mM citric acid alone versus [citric acid] for V/m = 40 mL g^{-1}

10.6.3. Desorption of Cadmium with Citric Acid

Soils polluted with 4, 6, and 8 mg L^{-1} Cd^{2+}, were remediated by citric acid alone at 0.5, 1, 2.5, 5, and 10 mM concentrations. The quantity of Cd^{2+} in the analyte solutions was determined by DPASV and AAS. Figures 10.30 and 10.31 were obtained from AAS results.

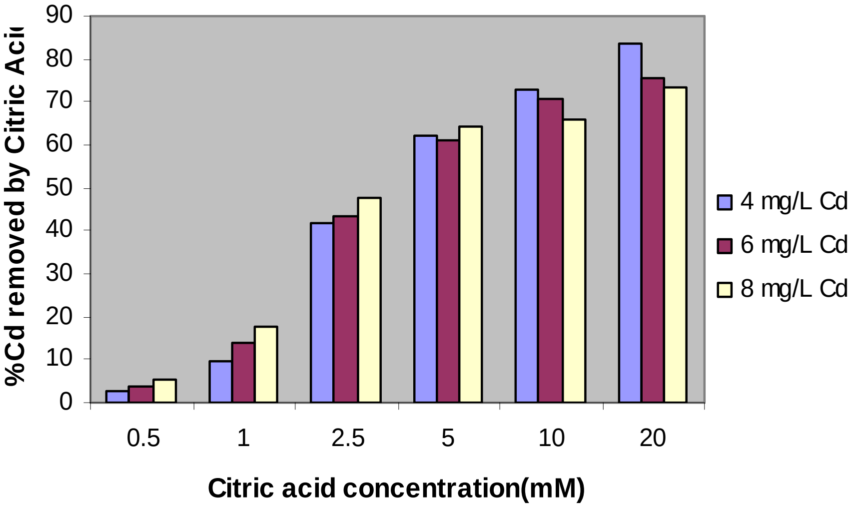


Figure 10.30. Plot of the percentage of Cd removed form the polluted soil by 0.5, 1, 2.5, 5, and 10 mM citric acid versus [citric acid] for V/m = 20 mL g^{-1}

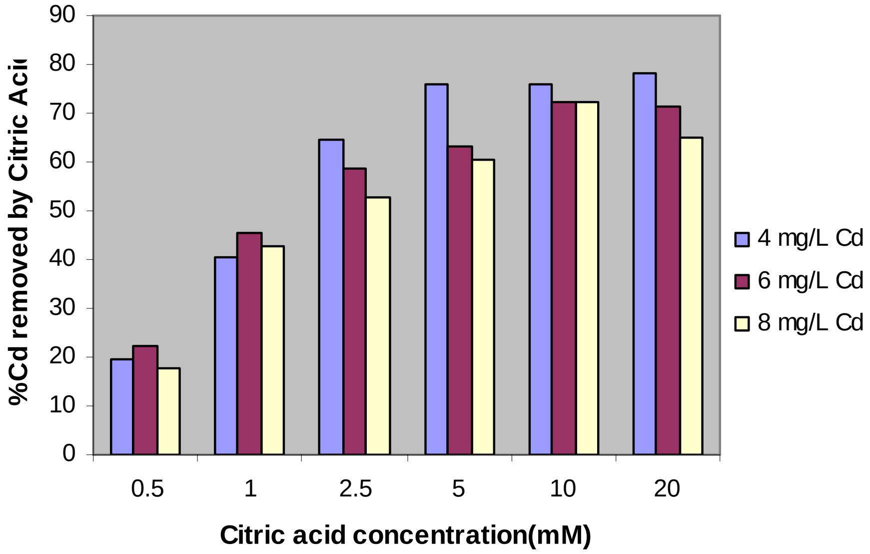


Figure 10.31. Plot of the percentage of Cd removed form the polluted soil by 0.5, 1, 2.5, 5, and 10 mM citric acid versus [citric acid] for V/m = 40 mL g^{-1}

Figures 10.30 and 10.31 indicated that applications of citric acid at concentrations 2.5 mM concentration levels were effective in desorbing cadmium from the soil over 50 percent for V/m of the 20 and 40 mL g^{-1}. There was a slight difference in the results of 10 mM citric acid for 20 and 40 mL g^{-1}. However, the percent removal of cadmium at 0.5 and 1 mM citric acid for V/m of 40 mL g^{-1} was much more efficient than the one for V/m of 20 mL g^{-1}.

The soil remediation by citric acid decreased with the increasing metal ion concentration for V/m ratio 40 mL g^{-1}. Also, the same trend was observed for 10 mM concentration of citric acid at V/m ratio of 20 mL g^{-1}. Overall, the percent removal of Cd reached to 75 percent at 10 mM concentration of citric acid for both V/m ratio values.

10.7. Soil Remediation with Surfactant Micelle-Solubilized Ligand

10.7.1. Desorption of Lead with the Combination of SDS and Iodide

Soil samples artificially polluted with different concentrations of Pb^{2+}, were remediated by SDS and iodide. The concentrations of SDS were 50 and 100 mM, iodide concentrations were 50, 100, 200, and 400 mM. The quantity of Pb^{2+} in the analyte solution was determined by AAS.

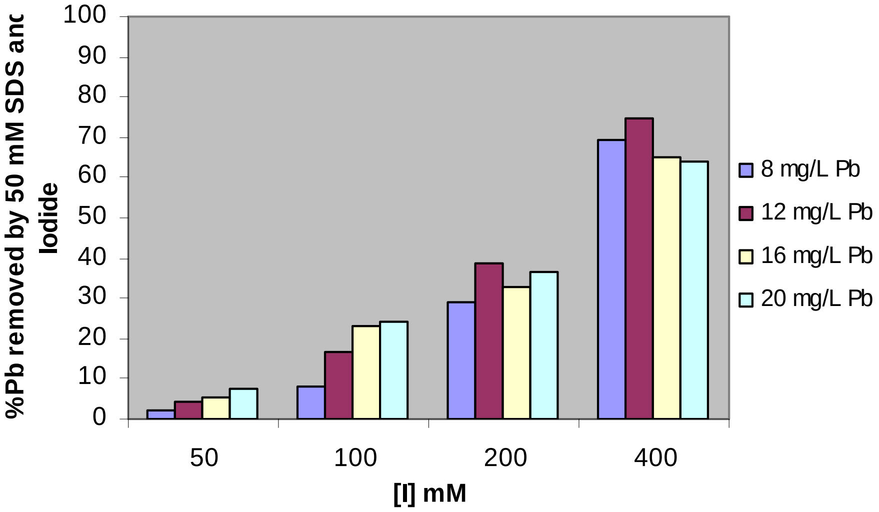


Figure 10.32. Plot of the percentage of Pb removed from the polluted soil by 50 mM SDS and 50, 100, 200, and 400 mM iodide versus [ioide] for V/m = 20 mL g^{-1}

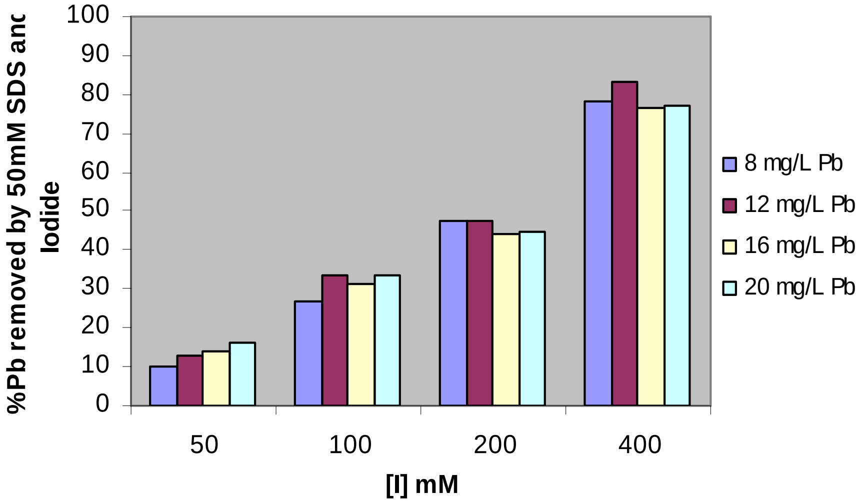


Figure 10.33. Plot of the percentage of Pb removed from the polluted soil by 50 mM SDS and 50, 100, 200, and 400 mM iodide versus [ioide] for V/m = 40 mL g^{-1}

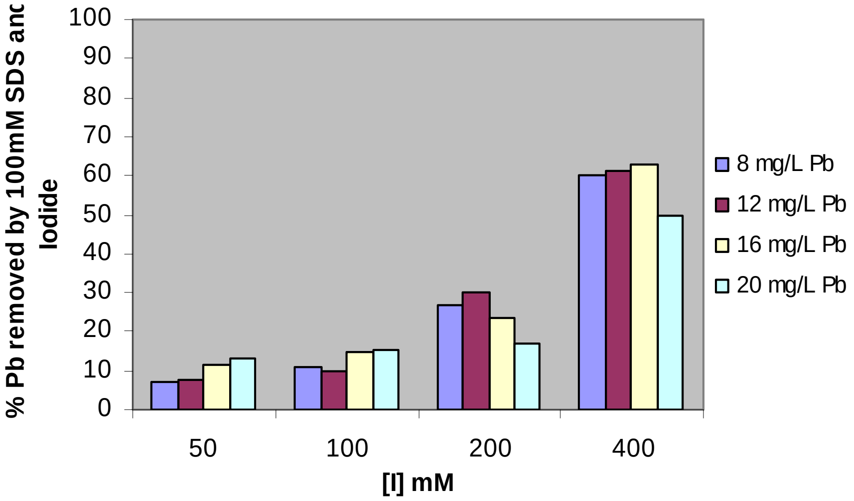


Figure 10.34. Plot of the percentage of Pb removed from the polluted soil by 100 mM SDS and 50, 100, 200, and 400 mM iodide versus [ioide] for V/m = 20mL g^{-1}

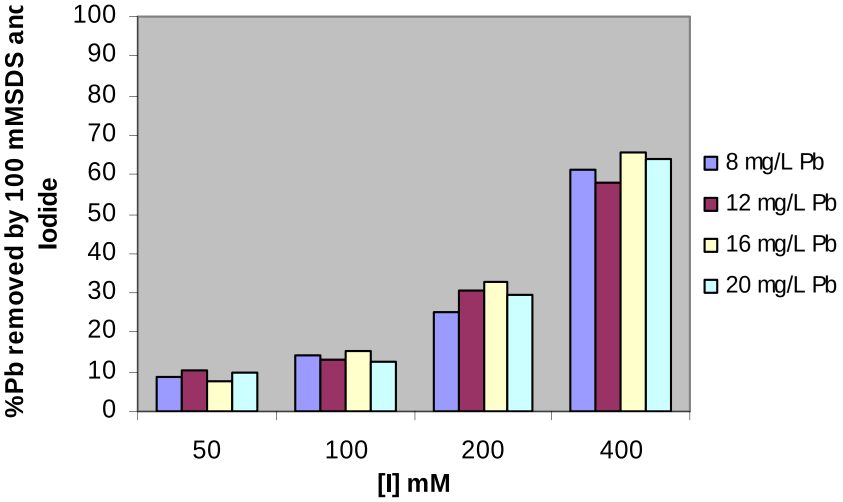


Figure 10.35. Plot of the percentage of Pb removed from the polluted soil by 100 mM SDS and 50, 100, 200, and 400 mM iodide versus [ioide] for V/m = 40 mL g^{-1}

The lead desorbing capability of the surfactant-ligand solution was illustrated in Figures 10.32-10.35. Results of the experiments showed that the percentage removal of Pb increased with increasing ligand-iodide concentration at the given SDS level for each metal ion concentration tested. For V/m = 40 mL g^{-1} ratio, the soil remediation efficiency ranged between 10 and 78 percent for 8 mg L^{-1} Pb with increasing iodide concentration at 50 mM SDS. On the other hand, the removal efficiency was between 2 and 70 percent at 20 mL g^{-1} for 8 mg L^{-1} of Pb under the same experimental conditions.

Generally speaking, the role of the V/m ratio on the percentage of Pb removal was not very effective when the experimental values were compared for the same ligand concentration at each metal test levels.

10.7.2. Desorption of Cadmium with the Combination of SDS and Iodide

Soil samples polluted with 4, 6, and 8 mg L^{-1} Cd^{2+}, were remediated by SDS and iodide together. Concentrations of SDS were 50 and 100 mM, iodide concentrations were 50, 100, 200, and 400 mM. The quantity of Cd^{2+} in the analyte solutions was determined by DPASV and AAS. Figures 10.36-10.39 were obtained from AAS results.

Although increasing either the SDS concentration or the iodide concentration in the remediation solution resulted in enhanced remediation of the soil, the effects did not go above 75 percent, even under the best conditions. SDS concentrations were kept at 50 mM and 100 mM, while the iodide concentrations were varied between 50 to 400 mM for each case.

The results of a lower SDS concentration, i.e. 50 mM for V/m = 20 mL g^{-1}, were given in Figire 10.36. The Cd uptake by the remediation soil increased from approximately 60 percent to 90 percent as the iodide concentration was increased from 50 to 400 mM. However, for a given iodide concentration, the results remained almost unchanged for the soils initially contaminated with different Cd concentrations. Experiments indicated that 50 mM SDS alone had a remediation power of 25-40 percent and iodide alone had a power of 25-50 percent. The combination of the two clearly showed an enhanced remediation effect.

As shown in Figure 10.37, when the same experiments were repeated this time with V/m of 40 mL g^{-1}, again the Cd^{2+} release increased as the iodide concentration increased for soil samples initially contaminated with 4 mg L^{-1} of the metal ion. For the other soil samples contaminated with higher concentrations of Cd^{2+}, remediation was in the range of 65 to 80 percent. This again was higher than the remediation observed for SDS or iodide alone.

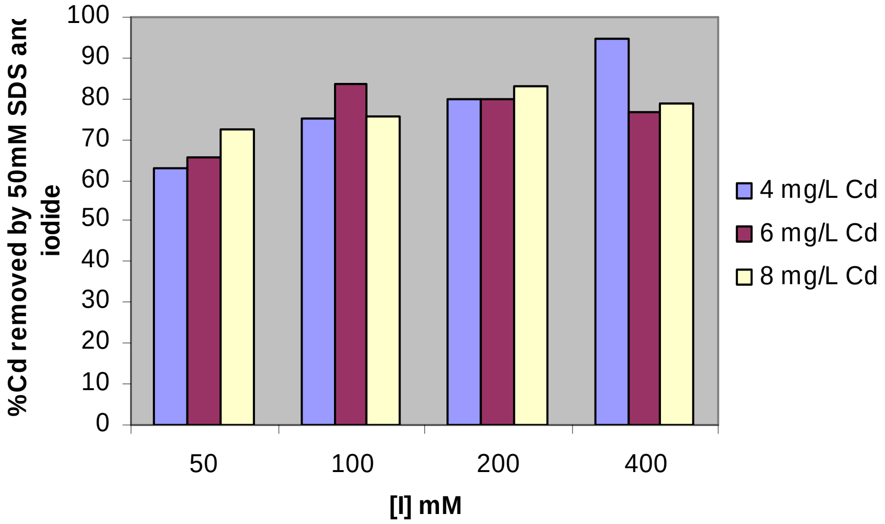


Figure 10.36. Plot of the percentage of Cd removed form the polluted soil by 50 mM SDS and 50, 100, 200, and 400 mM iodide versus [iodide] for V/m = 20 mL g^{-1}

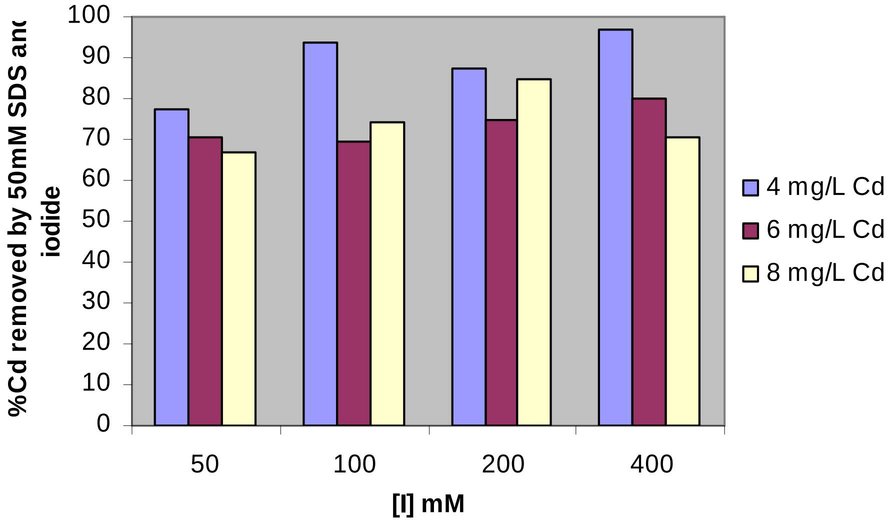


Figure 10.37. Plot of the percentage of Cd removed form the polluted soil by 50 mM SDS and 50, 100, 200, and 400 mM iodide versus [iodide] for V/m = 40 mL g^{-1}

The results for a system with V/m of 20 mL g^{-1} and 40 mL g^{-1} together with SDS concentration of 100 mM are given in Figures 10.38 and 10.39. For a given iodide concentration, soil initially contaminated with 4 mg L^{-1} Cd^{2+} was cleaned up almost by 60 percent. On the other hand, a soil polluted with 6 mg L^{-1} and 8 mg L^{-1} Cd^{2+} could only be cleaned by 40-50 percent and 30-38 percent, respectively.

It was concluded that higher V/m ratio of the remediation solution did have a greater effect in metal ion release from the soil. A similar behavior was observed for soils contaminated with 6 mg L^{-1} of Cd. That was the remediation of 50-55 percent with SDS only and 35-50 percent with iodide only went up to 50-75 percent when the two were together.

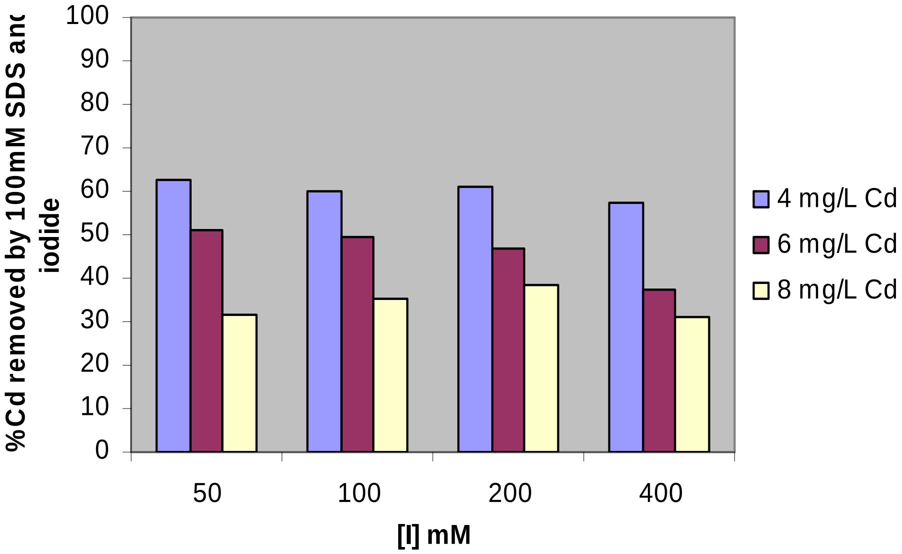


Figure 10.38. Plot of the percentage of Cd removed form the polluted soil by 100 mM SDS and 50, 100, 200, and 400 mM iodide versus [iodide] for V/m = 20 mL g^{-1}

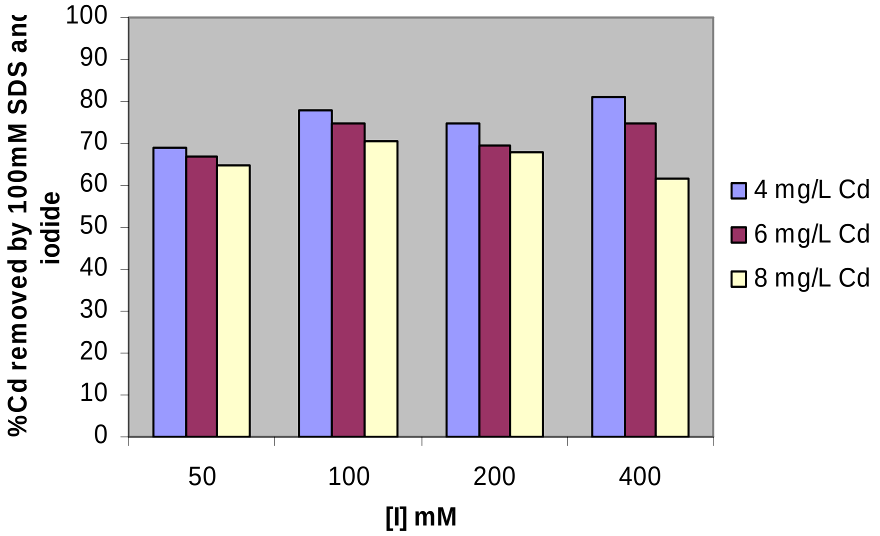


Figure 10.39. Plot of the percentage of Cd removed form the polluted soil by 100 mM SDS and 50, 100, 200, and 400 mM iodide versus [iodide] for V/m = 40 mL g^{-1}

10.7.3. Desorption of Lead with the Combination of SDS and Citric Acid

In this part of the study, the combinations of SDS and citric acid were used in the remediation of polluted soil. The concentrations of SDS were 50 and 100 mM, citric acid concentration values were 5, 10, and 20 mM. The quantity of Pb^{2+} in the analyte solutions was determined by AAS.

The cleansing effects of SDS-citric acid combination were almost 40 percent for V/m of 20 mL g^{-1} and 47 percent for V/m of 40 mL g^{-1} (Figures 10.40 and 41). The results have illustrated that the amount of desorbed lead was higher with V/m of 40 mL g^{-1} than with V/m of 20 mL g^{-1}.

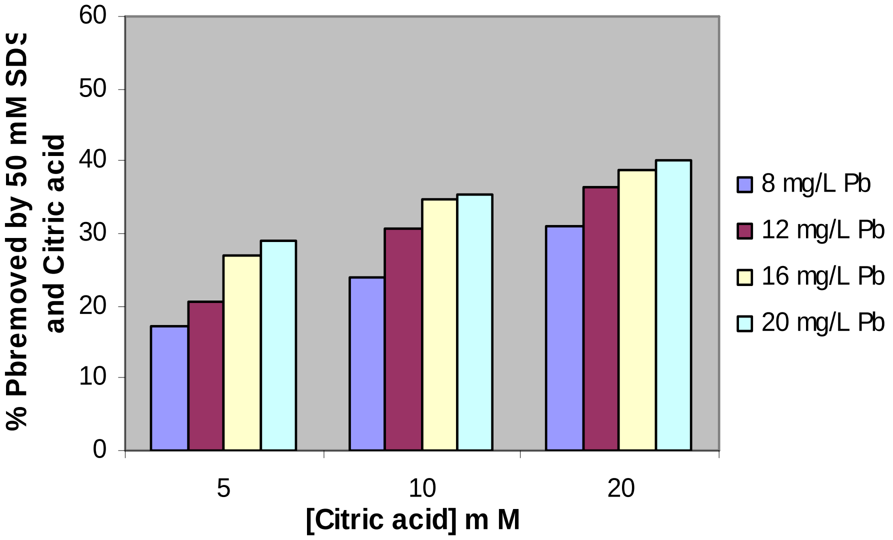


Figure 10.40. Plot of the percentage of Pb removed from the polluted soil by 50 mM SDS and 5, 10, and 20 mM citric acid versus [Citric Acid] for V/m = 20 mL g^{-1}

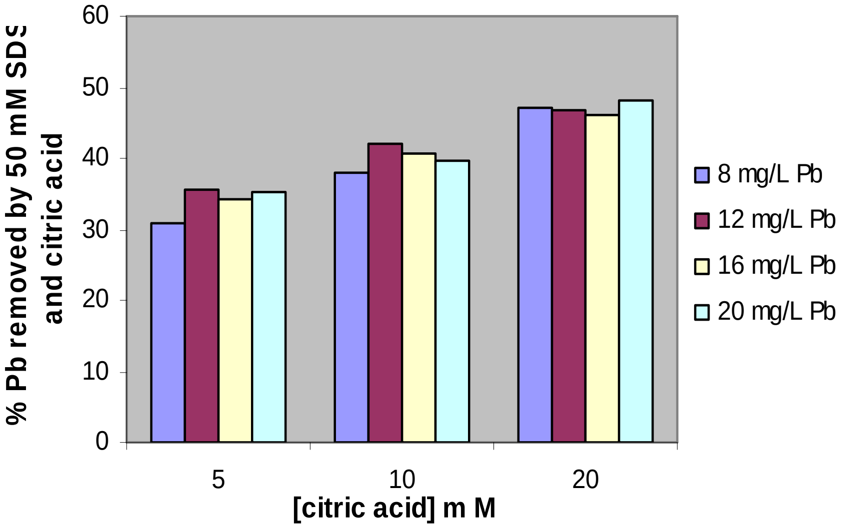


Figure 10.41. Plot of the percentage of Pb removed from the polluted soil by 50 mM SDS and 5, 10, and 20 mM citric acid versus [Citric Acid] for V/m = 40 mL g^{-1}

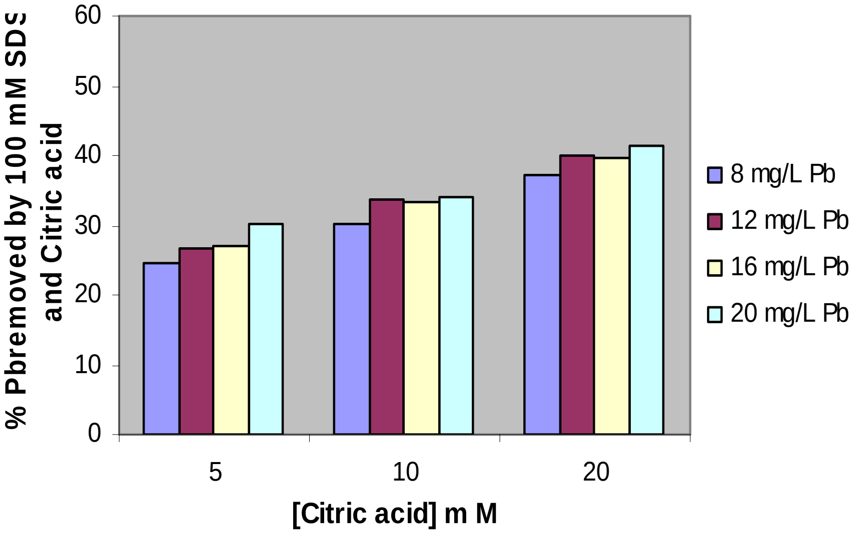


Figure 10.42. Plot of the percentage of Pb removed from the polluted soil by 100 mM SDS and 5, 10, and 20 mM citric acid versus [Citric Acid] for V/m = 20 mL g^{-1}

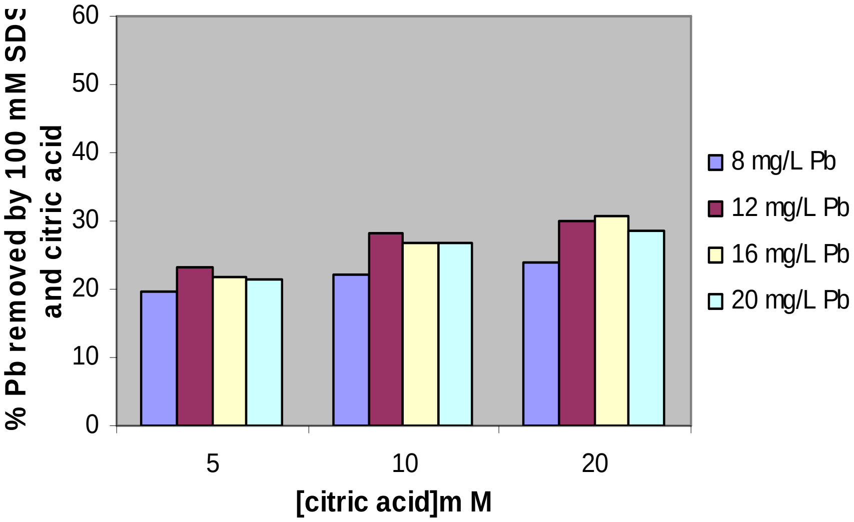


Figure 10.43. Plot of the percentage of Pb removed from the polluted soil by 100 mM SDS and 5, 10, and 20 mM citric acid versus [Citric Acid] for V/m = 40 mL g^{-1}

Also, the results have shown that as the concentration of the citric acid was increased, removing lead from the polluted soil was also increased for each SDS concentration (50 and 100 mM) and each V/m ratio. This statement was confirmed by each lead concentrations used in the experiments (Figures 10.42 and 10.43).

10.7.4. Desorption of Cadmium with the Combination of SDS and Citric Acid

Soils samples initially polluted with 4, 6, and 8 mg $L^{-1}Cd^{2+}$, were remediated by SDS and citric acid together. SDS concentrations were 50 and 100 mM and citric acid concentrations were 0.5, 1, 2.5, 5, and 10 mM. The concentration of Cd^{2+} in the analyte solutions was determined by DPASV and AAS. Figures 10.44-10.47 were obtained from AAS results.

As shown in Figures 10.44-10.47, results indicated that the differences in the desorption of cadmium obtained at different concentrations of citric acid for each SDS concentration level and for each V/m ratio were not as pronounced as they were in the case of SDS-iodide combinations.

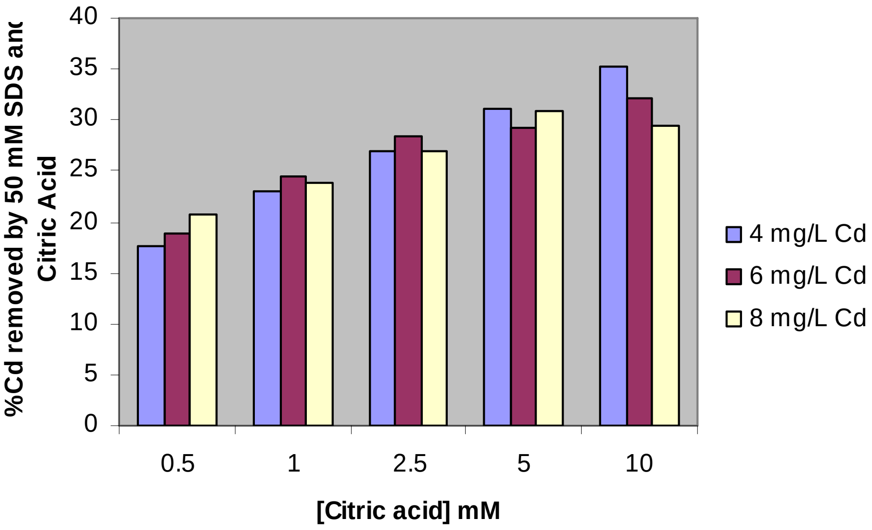


Figure 10.44. Plot of the percentage of Cd removed form the polluted soil by 50 mM SDS and 0.5, 1, 2.5, 5, and 10 mM citric acid versus [citric acid] for V/m = 20 mL g^{-1}

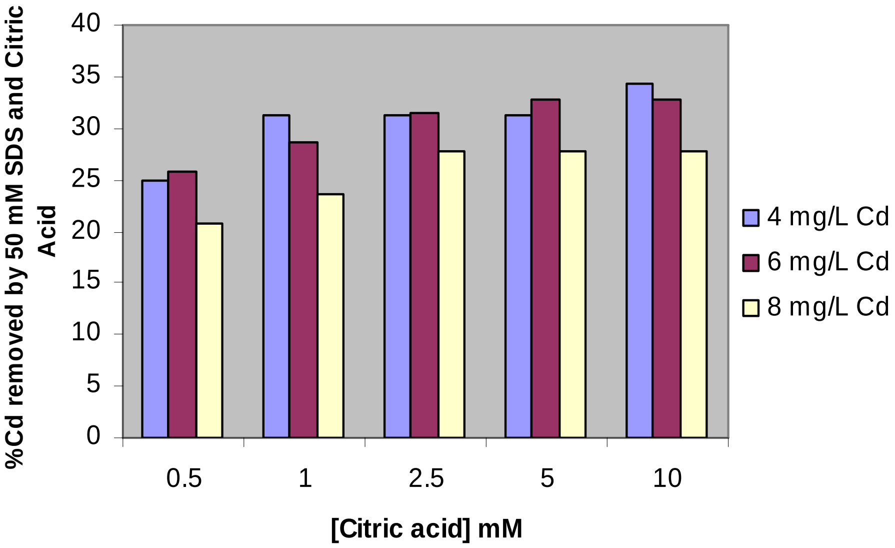


Figure 10.45. Plot of the percentage of Cd removed form the polluted soil by 50 mM SDS and 0.5, 1, 2.5, 5, and 10 mM citric acid versus [citric acid] for V/m = 40 mL g^{-1}

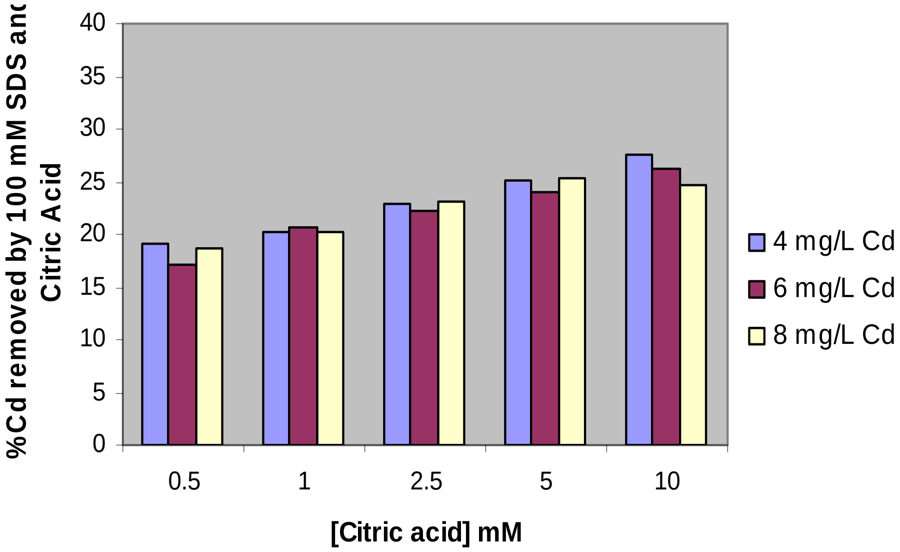


Figure 10.46. Plot of the percentage of Cd removed form the polluted soil by 100 mM SDS and 0.5, 1, 2.5, 5, and 10 mM citric acid versus [citric acid] for V/m = 20 mL g^{-1}

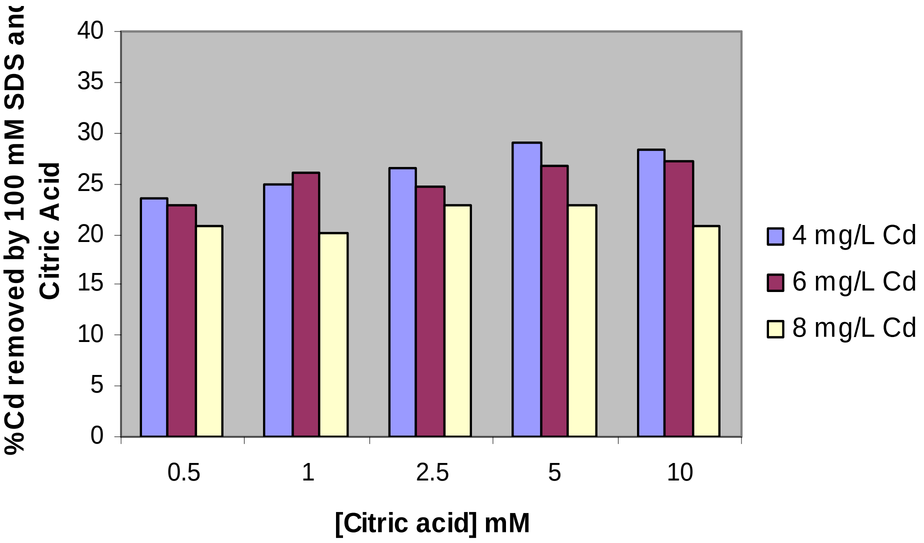


Figure 10.47. Plot of the percentage of Cd removed form the polluted soil by 100 mM SDS and 0.5, 1, 2.5, 5, and 10 mM citric acid versus [citric acid] for V/m = 40 mL g^{-1}

10.7.5. Desorption of Lead with the Combination of Triton X-100 and Iodide

Soils initially polluted with 8, 12, 16, and 20 mg $L^{-1}Pb^{2+}$, were remediated by Triton X-100 and iodide. The concentrations of Triton X-100 were 50 and 100 mM and iodide concentrations were 50, 100, 200, and 400 mM. The concentration of Pb^{2+} in the analyte solutions was determined by AAS.

The experimental results indicated that as the concentration of the iodide increased, the lead removed from the polluted soil also increased for each Triton X-100 concentration level (50 and 100 mM) and each V/m ratio. The Pb removed by Triton X-100 alone were almost 10 percent for V/m = 20 mL g^{-1} and 50 percent for V/m = 40 mL g^{-1}. In the case of iodide application alone in the remediations of soil, the highest desorption of lead was obtained which was about 70 percent for each V/m ratio. Figures 10.48-10.51 illustrated the combined effects of Triton X-100 and iodide for each Triton X-100 concentrations and each V/m ratio. The highest amount of lead taken up obtained was almost 85 percent for 50 mM Triton X-100-400 mM iodide and 90 percent for 100 mM Triton X-100 and 400 mM iodide.

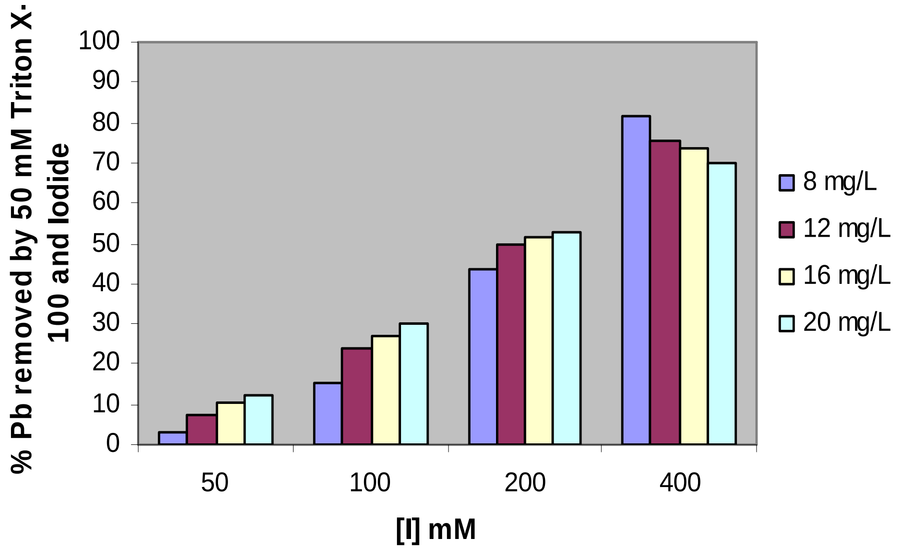


Figure 10.48. Plot of the percentage of Pb removed from the polluted soil by 50 mM Triton X-100 and 50, 100, 200, and 400 mM iodide versus [ioide] for V/m = 20 mL g^{-1}

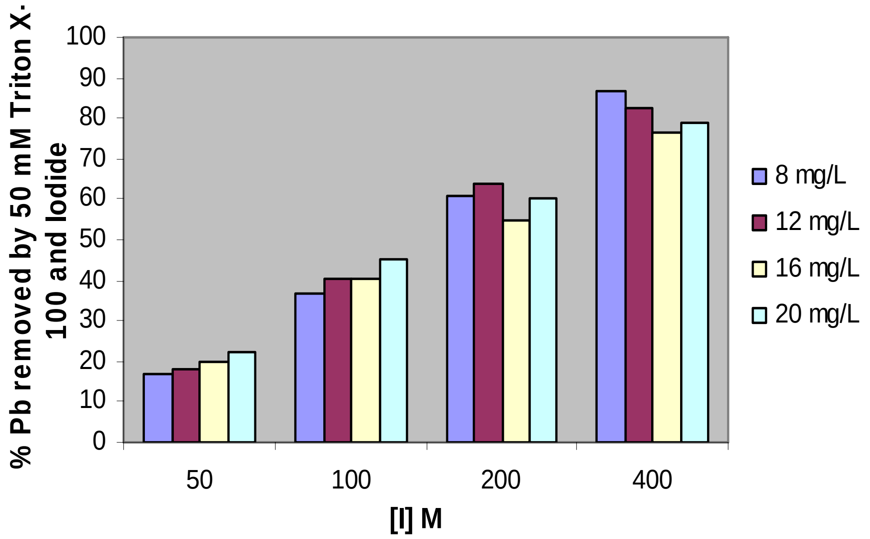


Figure 10.49. Plot of the percentage of Pb removed from the polluted soil by 50 mM Triton X-100 and 50, 100, 200, and 400 mM iodide versus [ioide] for V/m = 40 mL g^{-1}

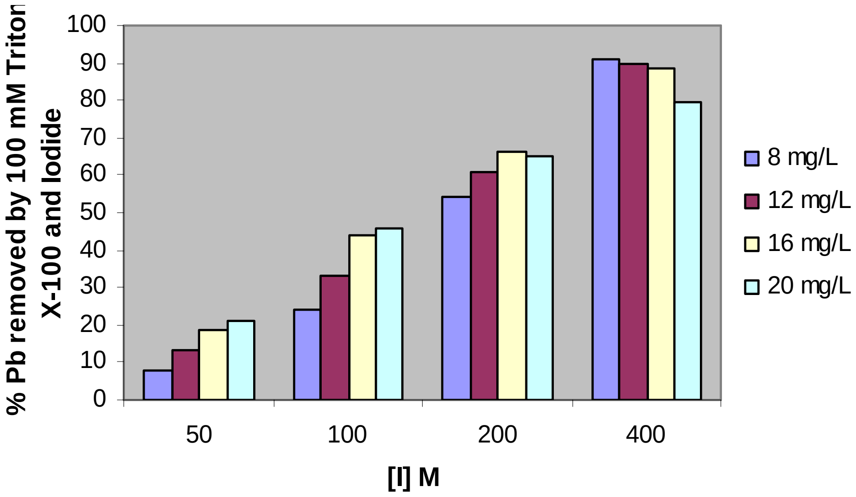


Figure 10.50. Plot of the percentage of Pb removed from the polluted soil by 100 mM Triton X-100 and 50, 100, 200, and 400 mM iodide versus [ioide] for V/m = 20 mL g^{-1}

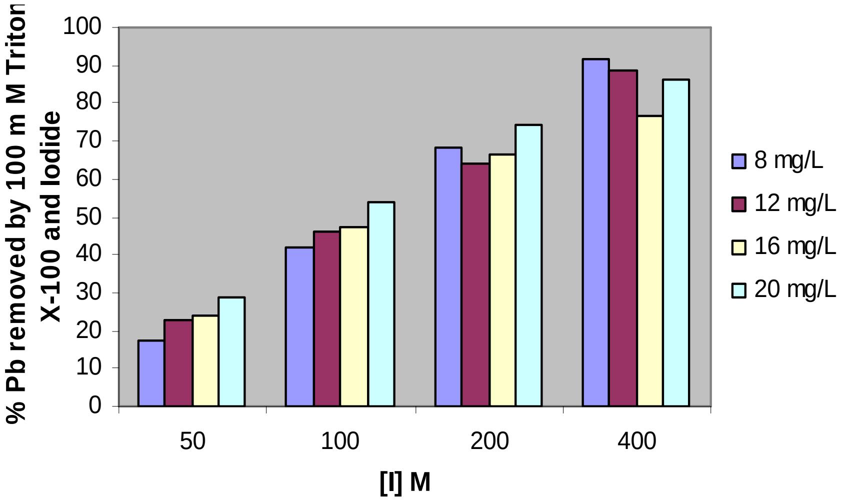


Figure 10.51. Plot of the percentage of Pb removed from the polluted soil by 100 mM Triton X-100 and 50, 100, 200, and 400 mM iodide versus [ioide] for V/m = 40 mL g^{-1}

10.7.6. Desorption of Cadmium with the Combination of Triton X-100 and Iodide

Soils initially polluted with 4, 6, and 8 mg $L^{-1}Cd^{2+}$, were remediated by Triton X-100 and iodide together. Concentrations of Triton X-100 were 50 and 100 mM and iodide concentrations were 50, 100, 200, and 400 mM. The amount of Cd^{2+} in the analyte solutions was determined by DPASV and AAS. Figures 10.52-10.55 were obtained from AAS results.

As shown in Figures 10.52-10.55, a slight increase of removing Cd was observed with the increase in iodide concentrations for each Triton X-100 concentration and each V/m ratio. The combination of Triton X- iodide could remove up to 90 percent of cadmium from the soil which was highly efficient for remediation of soil.

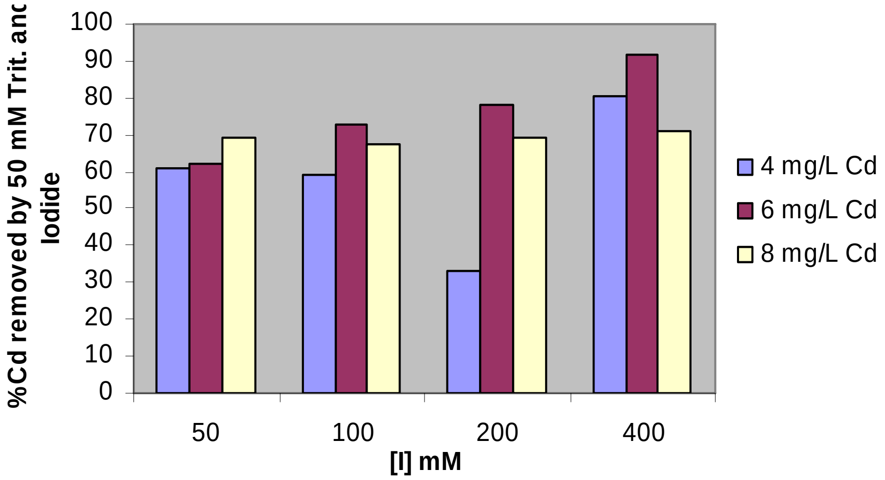


Figure 10.52. Plot of the percentage of Cd removed from the polluted soil by 50 mM Triton X-100 and 50, 100, 200, and 400 mM iodide versus [iodide] for V/m = 20 mL g^{-1}

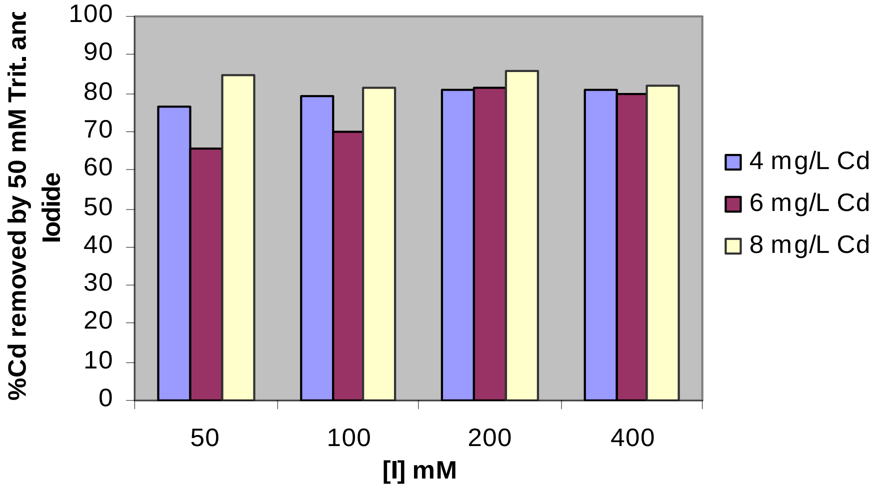


Figure 10.53. Plot of the percentage of Cd removed form the polluted soil by 50 mM Triton X-100 and 50, 100, 200, and 400 mM iodide versus [iodide] for V/m = 40 mL g^{-1}

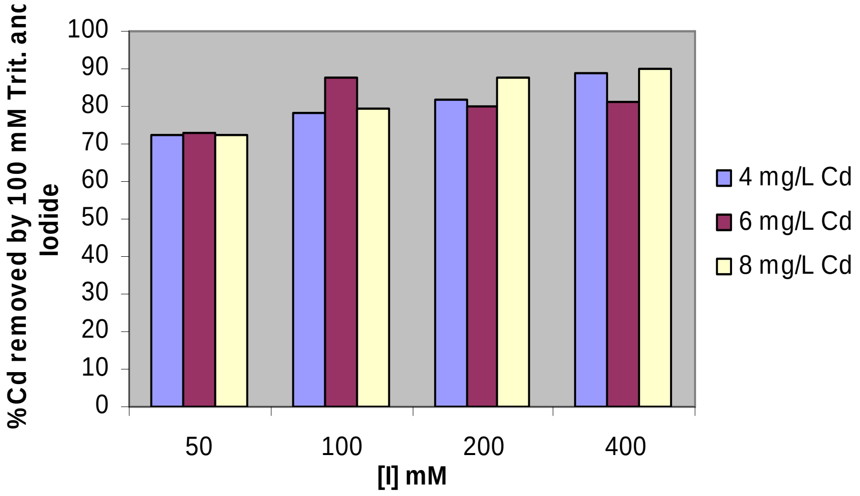


Figure 10.54. Plot of the percentage of Cd removed form the polluted soil by 100 mM Triton X-100 and 50, 100, 200, and 400 mM iodide versus [iodide] for V/m = 20 mL g^{-1}

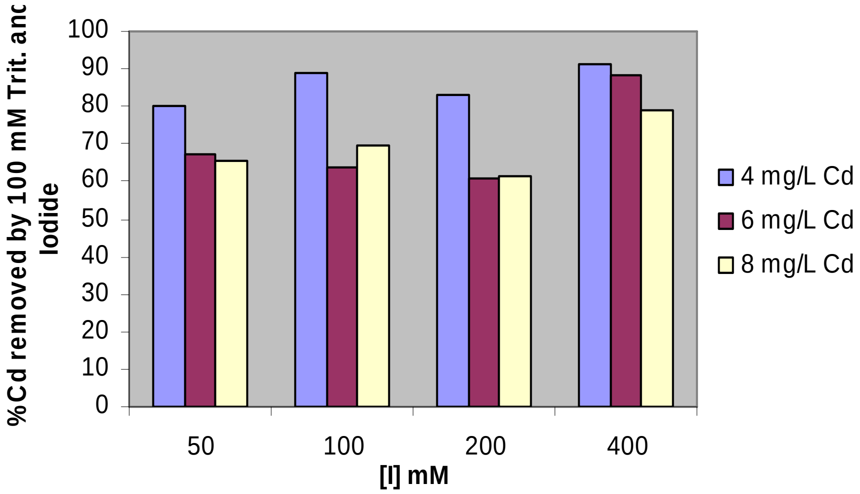


Figure 10.55. Plot of the percentage of Cd removed form the polluted soil by 100 mM Triton X-100 and 50, 100, 200, and 400 mM iodide versus [iodide] for V/m = 40 mL g^{-1}

10.7.7. Desorption of Lead with the Combination of Triton X-100 and Citric Acid

Soils samples artificially polluted with 8, 12, 16, and 20 mg $L^{-1}Pb^{2+}$, were remediated by Triton X-100 and citric acid together. The concentrations of Triton X-100 were 50 and 100 mM, citric acid concentrations were 2.5, 5, 10, and 20 mM. The concentration of Pb^{2+} in the analyte solutions was determined by AAS.

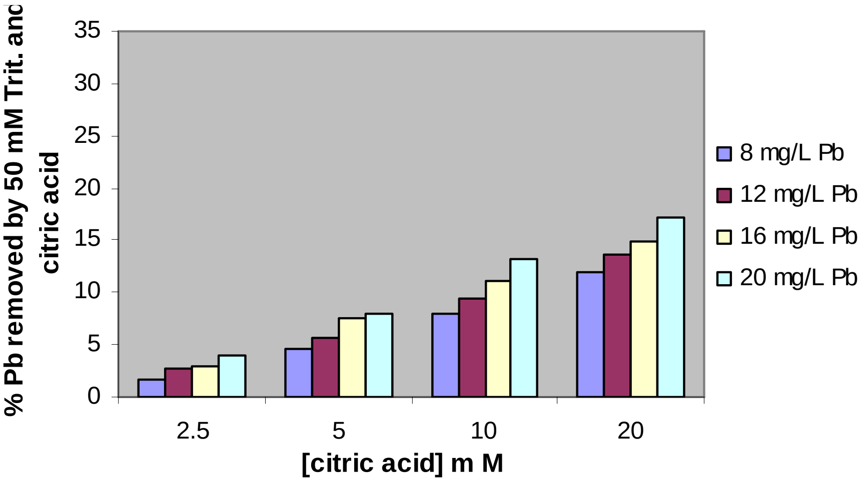


Figure 10.56. Plot of the percentage of Pb removed from the polluted soil by 50 mM Triton X-100 and 2.5, 5, 10, and 20 mM citric acid versus [citric acid] for V/m = 20 mL g^{-1}

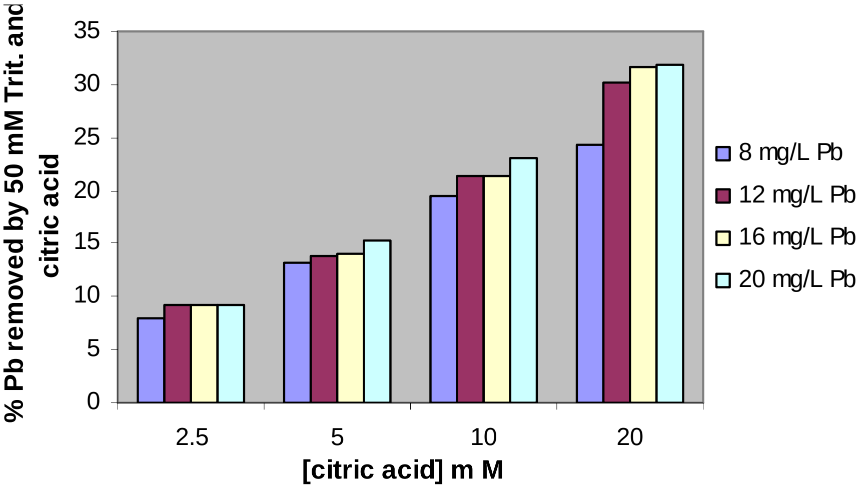


Figure 10.57. Plot of the percentage of Pb removed from the polluted soil by 50 mM Triton X-100 and 2.5, 5, 10, and 20 mM citric acid versus [citric acid] for V/m = 40 mL g^{-1}

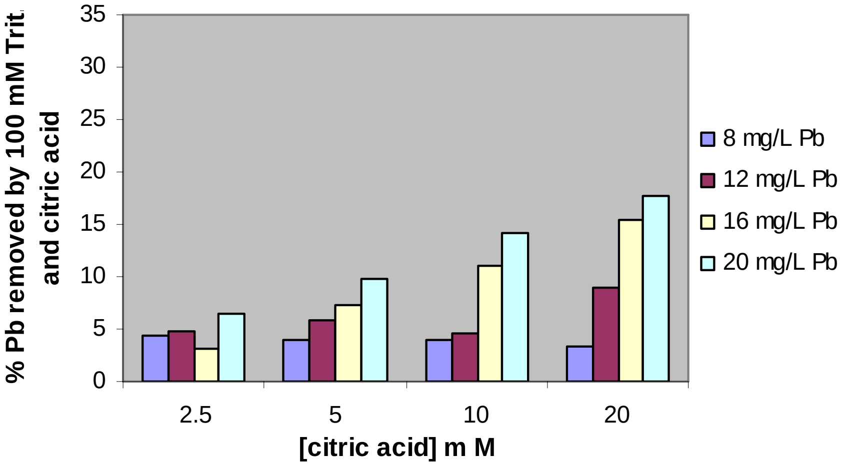


Figure 10.58. Plot of the percentage of Pb removed from the polluted soil by 100 mM Triton X-100 and 2.5, 5, 10, and 20 mM citric acid versus [citric acid] for V/m = 20 mL g^{-1}

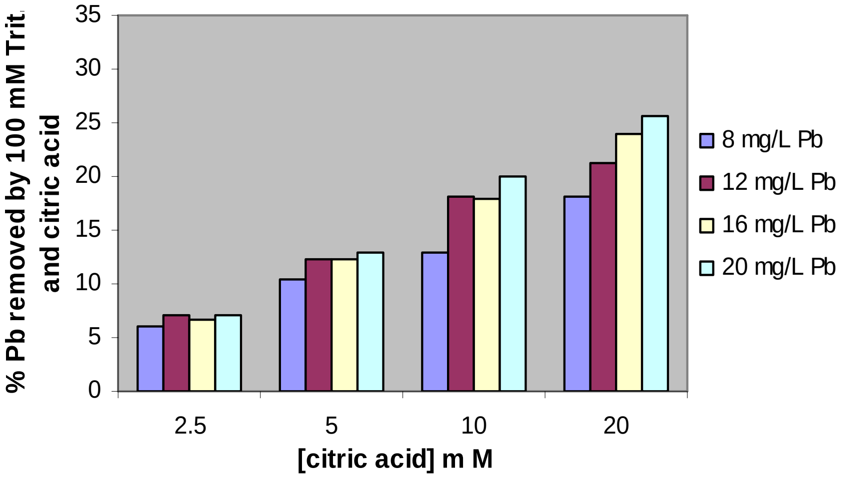


Figure 10.59. Plot of the percentage of Pb removed from the polluted soil by 100 mM Triton X-100 and 2.5, 5, 10, and 20 mM citric acid versus [citric acid] for V/m = 40 mL g^{-1}

Experimental results are given in Figures 10.56-10.59. It was determined that as the concentration of the citric acid was increased from 2.5 to 20 mM for each V/m ratio, the amount of lead removed from the soil was also increased for each Triton X-100 concentration level. At 50 mM of Triton X-100 and for each citric acid concentration level, the amount of Pb^{2+} removed from the soil for V/m=40 mL g^{-1} was about twice as much to that of V/m = 20 mL g^{-1}.

However, the same trend was not observed for the experimental sets, especially for the soil samples polluted with high concentration levels of heavy metal ions, i.e., 16 and 20 mL g^{-1} at 100 mM of Triton X-100.

10.7.8. Desorption of Cadmium with the Combination of Triton X-100 and Citric Acid

Soils polluted with 4, 6, and 8 mg $L^{-1}$$Cd^{2+}$,were remediated by Triton X-100 and citric acid together. Concentrations of Triton X-100 were 50 and 100 mM, citric acid concentrations were 2.5, 5, 10, and 20 mM. The amount of Cd^{2+} in the analyte solutions was determined by DPASV and AAS. Figures 10.60-10.63 were obtained from AAS results.

The experimental results have indicated that as the concentration of the citric acid increased, the cadmium removed from the polluted soil also increased for each citric acid concentration and each V/m ratio. Soil polluted with 4 mg L^{-1} Cd^{2+}, the cadmium removal percentage values were increased from 20 percent to 80 percent and from 10 percent to 80 percent with respect to the increased citric acid concentrations with 50 mM Triton X-100 for 40 mL g^{-1} and 20 mL g^{-1}, respectively. Soils polluted with 8 mg L^{-1} Cd^{2+}, the cadmium percentage values were increased from 20 percent to 60 percent with respect to the increased citric acid concentrations with 50 mM Triton X-100 for 40 mL g^{-1} and 20 mL g^{-1}, respectively. Exactly the same cadmium desorbed percentage value was obtained for the set at the highest test concentration level of citric acid, i.e. 10 mM but at V/m ratio of 20 mL g^{-1}.

The highest cadmium removal, i.e. about 100 percent was observed for the polluted soil at 8 mg L^{-1} Cd^{2+} for 100 mM Triton X-100 with citric acid concentrations of 5 and 10 mM. Overall, the cadmium desorbed percentage values were increased from 10 percent to 100 percent with respect to the increased citric acid concentrations for 40 mL g^{-1} ratio. The results indicated that the interaction effects of Triton X-100 with citric acid in soil remediation initially polluted with Cd^{2+} were additive.

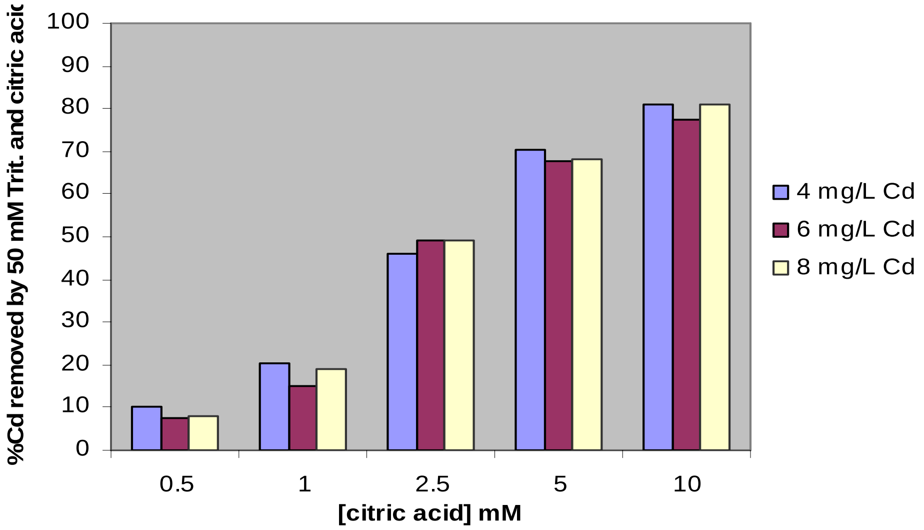


Figure 10.60. Plot of the percentage of Cd removed form the polluted soil by 50 mM Triton X-100 and 0.5, 1, 2.5, 5, and 10 mM citric acid versus [citric acid] for $V/m = 20\ mL\ g^{-1}$

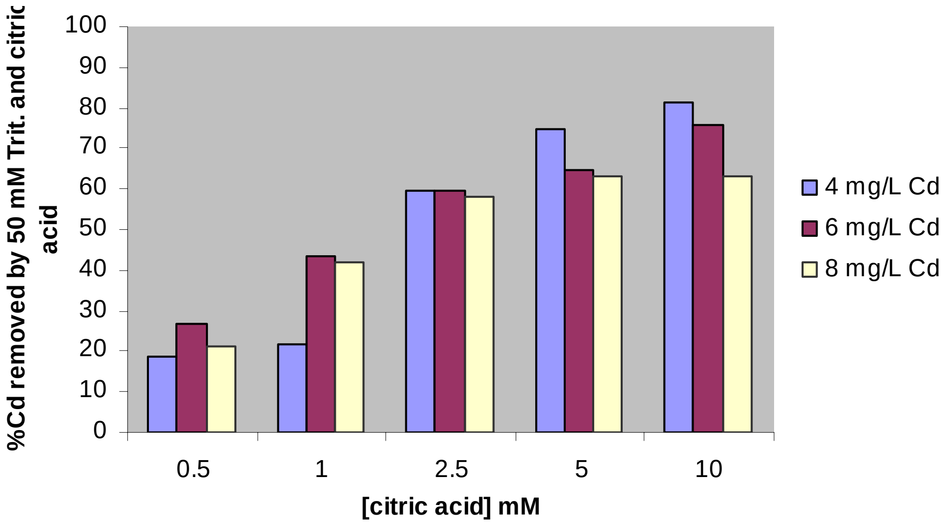


Figure 10.61. Plot of the percentage of Cd removed form the polluted soil by 50 mM Triton X-100 and 0.5, 1, 2.5, 5, and 10 mM citric acid versus [citric acid] for $V/m = 40\ mL\ g^{-1}$

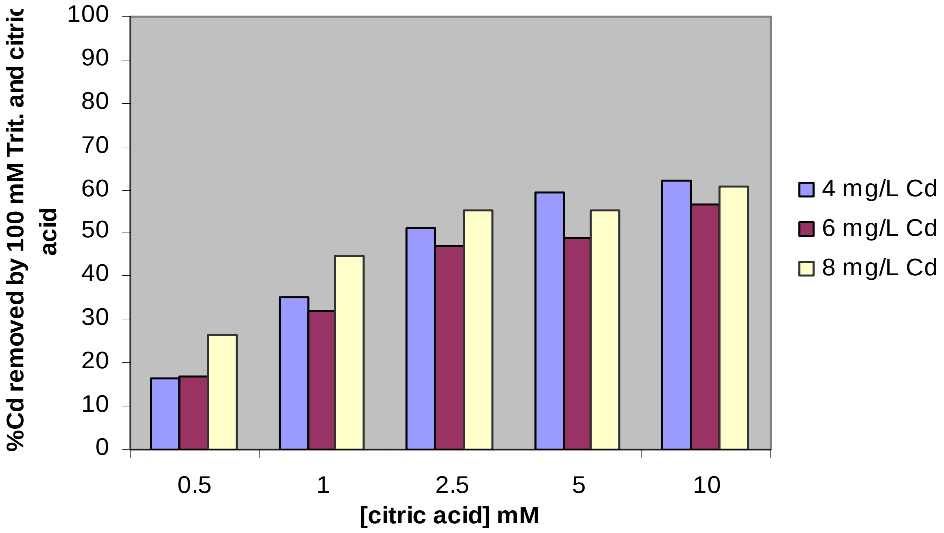


Figure 10.62. Plot of the percentage of Cd removed form the polluted soil by 100 mM Triton X-100 and 0.5, 1, 2.5, 5, and 10 mM citric acid versus [citric acid] for V/m = 20 mL g^{-1}

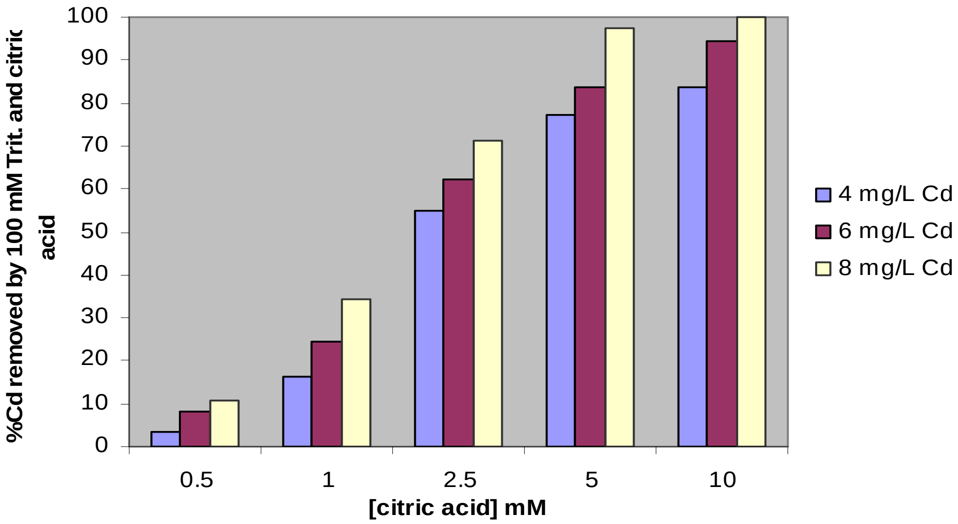


Figure 10.63. Plot of the percentage of Cd removed form the polluted soil by 100 mM Triton X-100 and 0.5, 1, 2.5, 5, and 10 mM citric acid versus [citric acid] for V/m = 40 mL g^{-1}

10.8. Comparison of Experimental Results of DPASV with AAS

Both voltammetric and AAS analyses were used for cadmium sets of experiment and the results were compared. The results from AAS measurements were used to confirm the voltammetric results of the experiments. Although, always the lower results were obtained using AAS in soil remediation studies than the voltammetry results, good correlation factors were obtained. Correlation factors (R^2) of 0.98 1, 0.9724. and 0.9822 were obtained for 4 mg L^{-1}, 6 mg L^{-1} and 8 mg L^{-1} of Cd, respectively in sets where iodide concentration changed between 50 mM and 400 mM and the concentration of SDS was kept at 50 mM. Only one set of data is given in Figure 10.64 as an example to the comparison studies for AAS and voltammetric measurements.

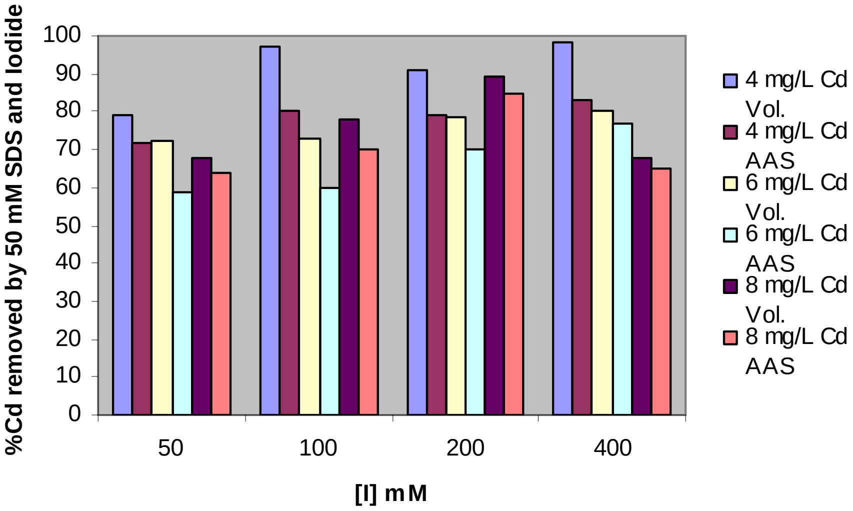


Figure 10.64. Comparison of AAS and Voltammetry results for a set of V/m = 40 mL g^{-1}, [SDS] = 50 mM, [I] = 50-100 mM

11. CONCLUSIONS

In the present work the evaluation of metal desorption from artificially contaminated soil as a function of washing solutions which were SDS, Triton X-100 as surfactants and iodide, citric acid as the chelating agents, and the comparisons of removal percentages were summarized in the Tables 10.7-10.10:

Table 10.4. Maximum desorption values of Pb and Cd

		50 mM SDS	100 mM SDS	Iodide	50 mM SDS +Iodie	100 mM SDS+Iodide
Pb	20 mL/g	5%	6.50%	65%	75%	62%
	40 mL/g	8%	9.50%	70%	82%	65%
Cd	20 mL/g	37%	42%	50%	90%	58%
	40 mL/g	70%	68%	70%	95%	81%

Table 10.5. Maximum desorption values of Pb and Cd

		Citrate	50mM SDS and Citrate	100mM SDS and Citrate
Pb	20 mL/g	22%	40%	42%
	40 mL/g	40%	47%	32%
Cd	20 mL/g	70%	35%	27%
	40 mL/g	75%	34%	28%

Table 10.6. Maximum desorption values of Pb and Cd

		Triton X	400 mM iodide	50mM Triton X and iodie	100mM Triton X and iodide
Pb	20 mL/g	10%	65%	80%	90%
	40 mL/g	55%	70%	87%	92%
Cd	20 mL/g	not determined	50%	90%	90%
	40 mL/g	not determined	70%	80%	90%

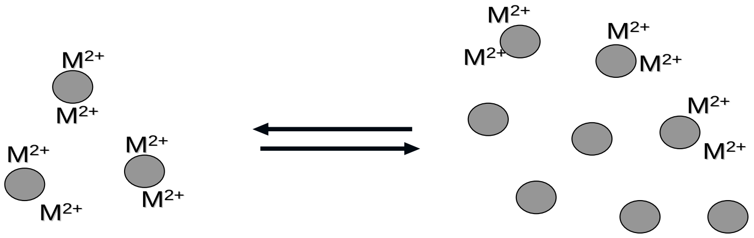
Table 10.7. Maximum desorption values of Pb and Cd

		Citrate	50mM Triton and Citrate	100mM Triton and Citrate
Pb	20 mL/g	22%	17%	17%
	40 mL/g	40%	32%	20%
Cd	20 mL/g	70%	80%	62%
	40 mL/g	75%	80%	100%

1. Anionic surfactant SDS alone was an ineffective remediation reagent in desorbing Pb from the contaminated soil. Ligand iodide was highly effective in the remediation. However, the best effects were observed for the SDS+iodide combinations where the remediation effects are enhanced in a combined amount, too.

2. SDS alone was much more effective in desorption of Cd when compared with the desorption of Pb. However, the percentage of Cd removal was decreased for V/m= 40 mL g^{-1} with further increase in the SDS concentration.

We expect M^{2+} to adsorb onto the negatively charged micellar surface, probably exchanging the surface counter ions (i.e. Na^{+}) with M^{2+}. However, these seem to be a limit to which the micellar surface could take up the M^{2+} ions. From the Figure 10.21, it seemed that an increase from 50 to 100 mM in SDS concentration result in an obvious decrease in the M^{2+} uptake when the metal concentration in the soil was low. This might be explained by high concentration of micelles not being able to exchange all their Na^{+} counterions with the M^{2+} ions. In other words, local M^{2+} concentration around the micellar surface might be decreasing as micelle concentration in the solution is increasing.



low [micele], relatively
high M^{2+} uptake

higher [micelle],
lower M^{2+} uptake

Since Triton X-100 is non-ionic, this interaction between M^{2+} and the negatively charged micelle surface was no longer observed. The different behavior of Cd^{2+} and Pb^{2+} on SDS micellar surface might be due to the differences in their hydration spheres, i.e. Pb^{2+} had a smaller hydrated sphere.

3. Citrate was a less effective ligand in soil remediation as compared with iodide at both V/m ratios. Citrate has three carboxyl groups and one OH group, which enabled its adsorption to soil oxide surfaces. Thus, the adsorbed citrate might serve as a complexing agent at the surface and increased the metal adsorption [7]. Citric acid is a polyprotic acid and its dissociation is highly dependent on pH with

$Ka_1 = 7.94 \times 10^{-4}$ ($C_6H_8O_7 \rightleftharpoons H^+ + C_6H_7O_7^-$),

$Ka_2 = 1.58 \times 10^{-5}$ ($C_6H_7O_7^- \rightleftharpoons H^+ + C_6H_6O_2^{2-}$) and

$Ka_3 = 3.98 \times 10^{-7}$ ($C_6H_6O_2^{2-} \rightleftharpoons H^+ + C_6H_5O_7^{3-}$).

Citrate-Pb complexes with the corresponding stability constant values were given as followings:

$Pb^{2+} + C_6H_6O_7{}^{3-} \rightleftharpoons Pb(C_6H_6O_7)^-$ $\beta = 1.26 \times 10^4$

$Pb^{2+} + 2\ C_6H_5O_7{}^{3-} \rightleftharpoons Pb(C_6H_5O_7)_2{}^{4-}$ $\beta = 1.26 \times 10^6$

$Pb^{2+} + C_6H_7O_7{}^{-} \rightleftharpoons Pb(C_6H_7O_7)_2{}^{+}$ $\beta = 3.16 \times 10^1$

$Pb^{2+} + C_6H_7O_7{}^{2-} \rightleftharpoons Pb(C_6H_6O_7)_2{}^{0}$ $\beta = 1..0 \times 10^3$

On the other hand, Pb combined with iodide and formed PbI_4^- with formation constant (K_f) of $3.16x10^4$. The stability constant of Cd-citrate complex is $6.3x10^3$ and its complex with iodide is CdI_4^- with K_f of $1.3x10^6$ [34, 39].

Citrate is generally a weaker ligand in the removal of Pb^{2+} compared iodide. This might be explained by the fact that I^-, being a π-donor ligand, forms relatively strong ML complexes, whereas citrate, being a π- acceptor ligand, is enable to do it the same extend.

Citric acid solubilize heavy metal ions through complex formation at low pH values. As a result the distribution of the chemical forms of heavy metal ions in soil may change. According to the complex formation constant values, citrate can remove Pb and Cd effectively from the soil which was observed for Cd but not obtained for Pb in this study. Pb was relatively immobile as compared to Cd, possibly because of its smaller hydrated ionic radius, and therefore its greater attraction for soil adsorption sites. Also, citrate may undergo rapid microbial degradation in soil; hence its corresponding concentration declines. Thus, the biodegradation process of citrate most possibly eliminates the citrate-enhanced Pb mobility. However, the effects of SDS+citrate were additive for Pb, but to a much lower extent than the SDS+iodide cases.

4. Nonionic surfactant Triton X-100, on its own, was slightly better than SDS alone, but still was ineffective in soil remediation. Up to 90% soil remediation was observed, for both Pb and Cd cases, when Triton X-100 was used with ligand iodide.

5. The results indicate that citrate is the less effective ligand for the desorption of Pb, even if it was combined with Triton X-100. On the other hand Triton X-100+citrate combinations gave the best remediation results in the desorption of Cd.

6. DPASV is a very sensitive analytical tool for the determination of trace quantities of substances. In this study, the results from AAS measurements were used to confirm the voltammetric results of the experiments.

REFERENCES

1. Leep, N. W., *Effect of heavy metal pollution on plants*, Vol. 2, Applied Science Publishers Ltd, 1981.

2. Mulligan, C. N., R. N., Yong, B. F., Gibbs, "Remediation technologies for metal-contaminated soils and groundwater: an evaluation", *Engineering Geology,* Vol. 60, pp. 193-207, 2001.

3. Abumaizar, R. J., E. H., Smith, "Heavy metal contaminants removal by soil washing", *Journal of Hazardous Materials,* Vol 70, pp. 71-86, 1999.

4. Reddy, K. R., S., Chinthamreddy, “Comparison of Extractants for Removing Heavy Metals from Contaminated Clayey Soils", *Soil and Sediment Contamination* Vol. 9, pp. 449 -462, 2000.

5. Polettini, A., R., Pomi, E., Rolle, "The effect of operating variables on chelant-assisted remediation of contaminated dredged sediment", *Chemosphere* Vol. 66, pp. 866 -877, 2007.

6. Shin, M., S. F., Barrington, W. D., Marshall, L., Wang, "Complexation of a ligand with a surfactant micelle for soil heavy metal desorption", *Soil and Sediment Contamination*, Vol. 14, pp. 357- 372, 2005.

7. Schwab, A. P., Y., He, M. K., Banks, "The influence of organic ligands on the retention of lead in soil", *Chemosphere*, Vol. 61, pp. 856- 866, 2005.

8. Rodríguez-Cruz, M. S., M. J., Sanchez-Martin, M., Sanchez-Camazano, "A comparative study of adsorption of an anionic and a non-ionic surfactant by soils based on physicochemical and mineralogical properties of soils", *Chemosphere*, Vol. 61, pp. 56-64, 2005.

9. Bear, F. E., *Chemistry of the soil*, Reinhold Publishing Corporation, Vol. 2, 1958.

10. Donahue, R. L., *Soils; An Introduction to Soils and Plant Growth*, Vol. 2, pp. 23-25, Prentice-Hall, 1965.

11. University of Arizona, http://cals.arizona.edu/pubs/garden/mg/soils/images/p6large.gif

12. Van Loon, G. W., J., Duffy, Stephen, *Environmental Chemistry*: A Global Perspective, 2000.

13. Texas A&M University Home Page, http://organiclifestyles.tamu.edu/soilbasics/soilchemical.html

14. Soils and Nutrient Management, http://www.umassvegetable.org/soil_crop_pest_mgt/soil_ nutrient_mgt/soil_basics_ II.html

15. http://www.grounds-mag.com/news/grounds_maintenance_soil_chemical_properties/

16. http://www.lenntech.com/heavy-metals.htm

17. McBridge, M. B., *Environmental chemistry of soils*, NY: Oxford University Press, 1994.

18. Rajaie, M., N., Karimian, M., Maftoun, J., Yasrebi, M.T., Assad, "Chemical forms of Cadmium in two calcerous soil textural classes as affected by application of cadmium-enriched compost and incubation time", *Geoderma*, 136 (3), p.533-541, 2006.

19. Knepper, T.P., D., Barcelo, P., De Voogt, *Wilson & Wilson's Comprehensive Analytical Chemistry*, Vol. 40, pp. 3-10, Netherlads, 2003.

20. Rosen, M. J., *Surfactants and Interfacial Phenomena*, Wiley, New York, 1989.

21. Mulligan, C. N., R. N., Yong, B. F., Gibbs, "Surfactant-Enhanced Remediation of Contaminated Soil: a Review," *Engineering Geology*, Vol. 60, pp. 371-380, 2001.

22. 1999-2002 *Key Centre for Polymer Colloids,* http://www.kcpc.usyd.edu.au/

23. Watanabe, K., S., Imai, Y. H., Mori, "Surfactant effects on hydrate formation in an unstirred gas/liquid system: An experimental study using HFC-32 and sodium dodecyl sulfate", *Japan Chemical Engineering Science,* Vol. 60, pp. 4846-4857, 2005.

24. http://www.sigmaaldrich.com/sigma/product%20information%20sheet/t8532pis.pdf

25. http://www2.mst.dk/common/Udgivramme/Frame.asp?pg=http://www2.mst.dk/udgiv/Publications/2001/87-7944-596-9/html/kap05_eng.htm

26. Myers, D., *Surfaces, Interfaces, and Colloids*, pp. 194-210, Wiley-VCH, Canada, 1999.

27. Bradl, H. B., "Adsorption of heavy metal ions on soils and soils constituents"*, Journal of Colloid and Interface Science*, Vol. 277, pp. 1-18, 2004.

28. Weber, W. J., F. A., Digiano, *Process Dynamics in Environmental System*, pp. 353-356, John Wiley &Sons, Canada, 1996.

29. Gomes, P. C., M. P. F., Fontes, A. G., da Silva, E. S., Mendonça, and A. R., Netto, "Selectivity Sequence and Competitive Adsorption of Heavy Metals by Brazilian Soils", *Soil Science Society of America Journal*, Vol. 65, pp. 1115-1121, 2001.

30. Dube, A., R., Zbytniewski, T., Kowalkowski, E., Cukrowska, B., Buszewski, "Adsorption and Migration of Heavy Metals in Soil"*, Polish Journal of Environmental Studies*, Vol. 10, pp. 1-10, 2001.

31. Atay, N. Z., O., Yenigün, M., Asutay, "Sorption of anionic surfactants SDS, AOT and cationic surfactant Hyamine 1622 on Natural Soils", *Water, Air, and Soil Pollution*, Vol. 136, pp. 55-67, 2002.

32. http://Citrate - Wikipedia, the free encyclopedia.htm

33. Kounaves, S. P., *Handbook of Instrumental Techniques for Analytical Chemistry*, Prentice Hall; Har/Cdr edition, (June 4, 1997)

34. Skoog, A. D., D. M, West, F. J., Holler, S. R., Crouch, *Fundamentals of Analytical Chemistry*, ISE, United States of America, 2004.

35. Wang, J., *Analytical Electrochemistry*, pp. 107-109, Wiley-VCH, Canada, 2000.

36. Wang, J., *Stripping Anilysis*, pp. 3-5, VCH, Florida, 1985.

37. http://elchem.kaist.ac.kr/vt/chem-ed/spec/atomic/aa.htm

38. Çağdaş, F. M., "Surfactant Interaction with Soils Contaminated by Heavy Metals", M.S. Thesis, Boğaziçi University, 2006.

39. http://Waste site reclamation with recovery of radionuclides and metals - US Patent 5292456.htm