

STUDY OF SURFACTANT INTERACTION WITH SOILS CONTAMINATED BY
HEAVY METALS USING VOLTAMMETRY

by

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ABSTRACT

STUDY OF SURFACTANT INTERACTION WITH SOILS CONTAMINATED BY HEAVY METALS USING VOLTAMMETRY

The objectives of this study were to develop a method to assess the heavy metal-surfactant-soil interaction and to clean the contaminated soils by a surfactant-ligand system.

Soil was taken from Trakya, Tekirdağ region. The soil samples were artificially polluted by cadmium with different concentrations and V/m ratios (where V stands for the solution volume added on the soil and m for the weight of soil taken) for 25 hours which was determined as the equilibrium time of the interaction between cadmium ions and soil. The artificially polluted soil by cadmium at various concentration levels were brought into contact with anionic surfactant, SDS (Sodium dodecyl sulfate) for 25 hours on a shaker at a temperature of $25 \pm 2^{\circ}\text{C}$. The concentrations of SDS were set at critical micelle concentration (CMC), below and above CMC level. The amount of remaining cadmium was determined by Differential Pulse Anodic Stripping Voltammetry (DPASV) with the optimized method parameters of -1.10 V of deposition potential, 90 s of deposition time, and 2000 rpm of a stirring rate. Hanging Mercury Dropping Electrode (HMDE) was used as the working electrode. It was concluded that with the increasing SDS concentration, the amount of desorbed cadmium from the soil increased.

Preliminary experiments were done to optimize the heavy metal-ligand-surfactant system. Ethylenediaminetetraacetic acid (EDTA) and metal interaction was studied under acidic, neutral and basic conditions but no reproducible results were obtained with DPASV. Therefore, another ligand ethylene diamine (EN) was used in combination with a phosphate buffer. Cd-EN peaks were reproducible but Cd-EN-SDS aqueous mixture resulted in an emulsion formation. DPASV experiments showed that the Cd-EN complex was not taken into SDS micelle. EN was a good ligand for cadmium complexation reactions. However, the optimized method parameters for DPASV was inadequate to verify the role of SDS for remediation approaches in the presence of EN.

ÖZET

AĞIR METALLERLE KİRLETİLMİŞ TOPRAKLARLA YÜZEY AKTİF MADDELERİN ETKİLEŞİMİNİN VOLTAMMETRİ İLE İNCELENMESİ

Bu çalışmanın amaçları, ağır metal-yüzey aktif madde-toprak etkileşimini tayin eden ve kirletilmiş toprağı yüzey aktif madde- ligand sistemi ile temizleyebilecek bir yöntem geliştirmektir.

Toprak, Trakya bölgesinin Tekirdağ yöresinden alınmıştır. Toprak, değişik derişimlerde ve değişik V/m oranlarında kadmiyum ile 25 saat süre ile kirletilmiştir (V toprağın üzerine konulan solüsyon hacmini, m kullanılan toprağın ağırlığını ifade eder). 25 saat, önceden yapılan deneylerle kadmiyum ile toprağın dengeye gelmesi için gerekli zaman olarak belirlenmiştir. Değişik kadmiyum konsantrasyonları ile yapay olarak kirletilen toprak anyonik yüzey aktif madde, SDS (Sodyum dodesil sülfat) ile mekanik çalkalayıcıda $25 \pm 2^{\circ}\text{C}$ sıcaklıkta 25 saat süre ile etkileşime sokulmuştur. SDS konsantrasyonları kritik misel konsantrasyonunda (CMC), altında ve üstünde alınmıştır. Desorbe olan kadmiyum miktarı Diferansiyel Puls Anodik Sıyırma (DPASV) yöntemi ile belirlenmiştir. Bu yöntemin parametreleri, yapılan optimizasyon sonucunda -1.15 V birikme potansiyeli, 90 saniye birikme zamanı ve 2000 rpm dönme hızı olarak belirlenmiştir. Asılı Damlayan Civa Elektodu çalışma elektrodu olarak kullanılmıştır. Toprakta desorbe olan kadmiyum miktarının SDS konsantrasyonu ile arttığı belirlenmiştir.

Ağır metal-ligand-yüzey aktif madde sistemini optimize etmek için ön çalışmalar yapılmıştır. EDTA ve metal asidik, nötral ve bazik ortamlarda DPASV ile incelenmiştir ve tekrarlanabilir sonuç elde edilememiştir. Bu yüzden farklı bir ligand olarak EN fosfat tampon çözeltisi ile kullanılmıştır. Cd-EN tekrarlanabilir sonuçlar vermiştir fakat Cd-EN-SDS suda karışımı emülsiyon oluşturmuştur. DPASV deneyleri, Cd-EN komplekslerinin SDS miselleri tarafından alınmadığını göstermektedir. EN, kadmiyum kompleksleşme reaksiyonları için iyi bir ligand olduğu halde, DPASV için optimize edilmiş yöntem parametreleri SDS'in EN varlığında temizleme girişimlerini doğrulamak için yetersiz kalmıştır.

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LIST OF SYMBOLS/ABBREVIATIONS

C	Concentration of the component in the fluid phase
C_A	Analyte concentration
C_e	Concentration of adsorbate in solution at equilibrium
C_s	Amount of adsorbate adsorbed per unit mass of soil
$(C_s)_{\max}$	Concentration required for monolayer coverage
$E_{1/2}$	Half-wave Potential
i_d	Diffusion Current
i_l	Limiting Current
k_a	Rate constant for adsorption
k_d	Rate constant for desorption
K_F	Adsorption Capacity
K_L	Adsorption equilibrium constant
n	Adsorption Intensity
q	Amount of the component adsorbed on the surface
T	Temperature
θ	Fraction of occupied sites
V/m	Volume/mass ratio
AAS	Atomic Absorption Spectrophotometer
AE	Auxiliary Electrode
ASV	Anodic Stripping Voltammetry
BET	Brunauer-Emmett-Teller
CEC	Cation Exchange Capacity
CMC	Critical Micelle Concentration
CSV	Cathodic Stripping Voltammetry
DME	Dropping Mercury Electrode
DPASV	Differential Pulse Anodic Stripping Voltammetry
DPV	Differential Pulse Voltammetry
EDTA	Ethylenediaminetetraacetic acid
EN	Ethylene diamine

HMDE	Hanging Mercury Dropping Electrode
MMME	Multi Mode Mercury Electrode
OMC	Organic Matter Content
RDE	Rotating Disc Electrode
RE	Reference Electrode
SCE	Saturated Calomel Electrode
SDS	Sodium Dodecyl Sulfate
SLES	Sodium Lauryl Ether Sulfate
SMDE	Static Mercury Dropping Electrode
SSE	Solid State Electrode
WE	Working Electrode

1. INTRODUCTION

Contamination of soils with heavy metals occurs as a result of agricultural emissions (fertilisers, pesticides, insecticides) or industrial activities (including battery breaking and recycling, oil refining, paint manufacturing, metal moulding and plating, smelting), or as a consequence of past environmental disposal practices [1].

Heavy metal ions are the most toxic inorganic pollutants in soil. Some of them are toxic even if their concentrations are very low and their toxicity increases with accumulation in water and soil. Adsorption is a major process responsible for their accumulation [2]. The most important parameters controlling heavy metal adsorption and their distribution between soil and water are soil type, metal speciation, metal concentration, soil pH and contact time [3].

Up to early 1990s, the most common remedial practice for the restoration of sites contaminated with heavy metals has been the excavation and transport of polluted soil. This practice does not offer a permanent solution; the environmental problem is simply transferred from high risk areas, i.e. densely populated sites, to areas which are probably better isolated and controlled. Therefore, a few innovative technologies have been developed and applied on a commercial scale for the remediation of metal loaded soils. Remediation options include either the removal of metals from soils or their fixation in an insoluble form. Removal of contaminants is the most permanent solution to the environmental problem. Metals can be removed by physical and chemical methods (i.e. particle size or gravity separation, flotation etc.) or chemical methods involving the application of appropriate leaching solutions to the contaminated soil [4].

The mechanisms of metal retention on soils are classified in two categories: (a) adsorption of ions on the surface of soil components, i.e. clays, organic matter, etc. and (b) precipitation of discrete metal compounds, i.e. oxides, carbonates, sulphides etc. The removal of metals by leaching techniques involves the reversion of these mechanisms. Ions retained by simple electrostatic forces can be released by mixing the soil with a solution of

high ionic strength. It is widely recognized that it is impossible to find one single reactant which could mobilise effectively all the previously mentioned forms of metal contaminants, without destroying the soil matrix. Among the available extractive agents, the ethylenediaminetetraacetic acid (EDTA) is one of the most promising: the ability of this chelating agent to bind the metal ions in extremely stable complexes can be utilised not only for the desorption of adsorbed ions, but also for the dissolution of insoluble metal compounds [5].

Researches were continued to find out different methods to clean up the contaminated soil with heavy metals. Some researches used other chemicals like acids (HCl and HNO₃) in digestion procedures and chemicals like NaNO₃, NH₄NO₃, and CaCl₂ as metal extracting agents to see their effects on different heavy metals [6]. In recent researches involving surfactants on soils, surfactants have been used in the presence of different both solvents and ligands. Surfactant/solvent systems were used to remove the hydrophobic pollutants from the soil and surfactant/ligand systems were used to remove the heavy metals from contaminated soils [7,8]

The removal of heavy metals from soils by using surfactant/ligand systems has a different mechanism than the other methods. In this, the metal ion forms a complex with the ligand with low hydrophilicity. Because of this low hydrophilicity, the complex can be captured and stabilized by the surfactant micelle. Shin, M. *et al* have developed a method to decontaminate cadmium from soil by using surfactant/ligand system, in which non-ionic surfactants and iodide ion ligand (I⁻) were used. It was determined that non-ionic surfactant in the absence of iodide ion desorbed less than one per cent of cadmium. Therefore, it was concluded that ligand took the metal and surfactant stabilized the metal-ligand complex by taking into the micelles [9].

In this study, the artificially contaminated soil was tried to be cleaned from heavy metals with two methods. In the first method, cleaning process was carried out by surfactant alone with different concentrations around the critical micelle concentration (CMC). As the surfactant, sodium dodecyl sulfate (SDS) was used. The aim of this method was to collect the cadmium ions in the micelles formed by SDS. In the second method, a different surfactant/ligand system was formed which included again SDS as a surfactant

and EDTA as a ligand. When the EDTA standard solutions with cadmium were analysed, it was determined that sample solution containing EDTA could not be analysed with Differential Pulse Anodic Stripping Voltammetry (DPASV) in any acidic, neutral and basic media adjusted by using acetate, phosphate and carbonate buffers, respectively.

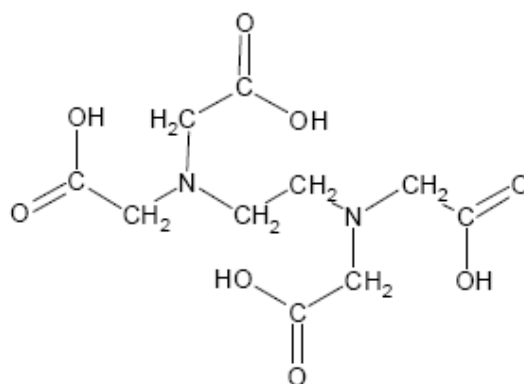


Figure 1.1. Chemical structure of EDTA

Another ligand, ethylene diamine (EN), was found that allows to analyse the amount of complex formed metal in neutral media adjusted by using phosphate buffer.

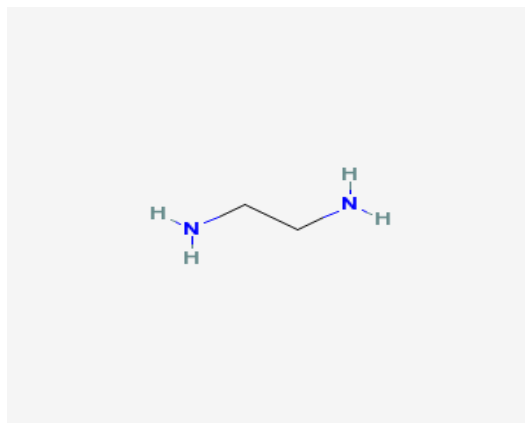


Figure 1.2. Chemical structure of EN

Although a ligand that could be analysed with DPASV was found, EN did not work in the presence of SDS efficiently. As a result, a surfactant-ligand system that gave reproducible results with DPASV could not be found. Therefore, the analysis of the desorbed cadmium amount from soil could not be determined.

2. SOIL

2.1. Definition of Soil

Soil is an essential multipurpose resource for man. It provides the nutrient bearing-environment for plant life and is of essential importance for degradation and transfer of biomass [2]. Soil is a reactive heterogeneous medium containing numerous different microenvironments in which many physical, chemical, and biological processes occur that affect the availability and toxicity of accumulated pollutants in space and time, depending on factors like soil type, climate, and vegetation. Therefore, cause and effect relationships are often complex, and harmful effects may go unrecognized until a change in use takes place.

There is constant exchange of matter between soil and water as well as with the atmosphere. Soil, being a solid phase, may act as a final sink in which many persistent pollutants accumulate in an irreversible manner. In contrast to air and water, soil is only to a small extent amenable to natural or man-made processes for restoring its quality once pollution has occurred. Because of this, prevention of pollution by protection is the only rational approach to preservation of soil quality. Although natural background concentrations for heavy metals show a great variation, agreement on permissible levels is essential for effective management and development of realistic controls [10].

Soils are developed from two classes of materials: (1) decomposed plant substances (organic material) and (2) rocks and minerals (mineral material). To a limited extent, soils develop in a mixture of both organic and mineral matter [11].

The organic material in soils derives from plants and animals living in, on and above the soil. Organic soil matter amass at the soil surface to form a distinct organic layer. The roots, leaves and stems of plants form the largest part of the organic material of the soil. In addition to the remains of higher plants, the bodies of small organisms produce a lot of organic matter [12].

Minerals are natural inorganic compounds. They have physical and chemical properties. They are grouped as primary and secondary minerals. Primary minerals are formed due to disintegration of rocks. They are caused by physical and chemical weathering. Many of these primary mineral particles become sand and silt particles. Primary minerals release their elements to the soil solution. Secondary minerals result from the decomposition of primary minerals. It is also produced by the precipitation of the decomposition products of minerals. Secondary minerals originate when a few atoms precipitate from solution to form very small crystals. Because of the small particle size of secondary minerals, they dominate the clay fraction of soils [13].

2.2. Soil Properties

2.2.1. Physical Properties

2.2.1.1. Particle Size. Particle size is a primary physical property. Soil is arbitrarily defined as the material with particle size less than 2.0 mm. In fact many soil analysis protocols begin with a sieving (2.0 mm) step to separate soil from non-soil. Within the material defined as soil, there are three primary size categories-in order of decreasing particle size, sand, silt, and clay.

Sand is light, easily worked, has good drainage (but poor water retention) properties and is readily aerated. Chemically, the most important components of sand are usually primary minerals such as quartz and feldspars; these are relatively inert and poor sources of nutrients. The clay-sized fraction is at the small particle size end range. Soils rich in clay are heavy, difficult to work with, and have poor drainage and aeration properties. Clay-sized materials may be composed of some combination of the clay minerals themselves, organic matter, and of finely divided primary minerals and hydrous iron and aluminium oxides. All of these fine materials have large surface areas and take part in ion exchange and/or adsorption processes. Therefore, the clay-sized particles are able to interact with and retain nutrients, and may be productive plant growth media [14].

2.2.1.2. Texture. Soil texture is a collective term that defines a real soil by the proportion of different particle size components. Texture nomenclature is based on triangular phase diagrams such as the one shown in the Figure 2.1.

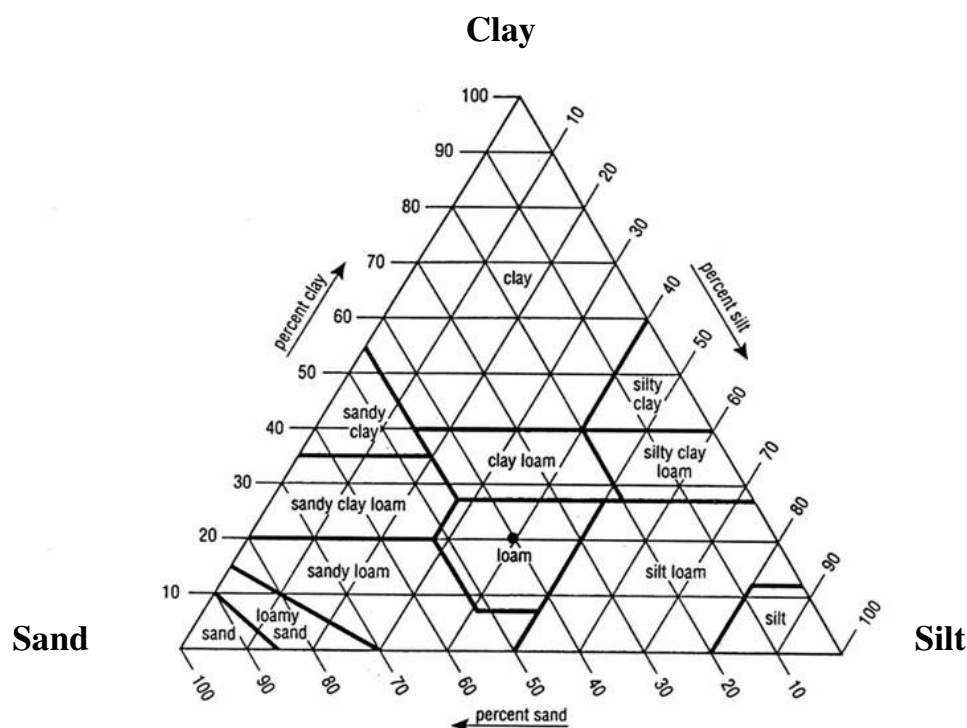


Figure 2.1. Soil texture triangle [6]

Soils that are desirable from an agricultural perspective often fall in the middle region of the diagram. Such soils have the beneficial physical properties of lighter soils and tend to be quite easy to work, but also have moderate moisture-retaining ability, and chemical reactivity due to the contribution of the clay-sized materials[14].

2.2.1.3. Density. The density of soil reflects that of the minerals or organic components that make up its composition. Density of individual particles, called particle density, is considerably less than 1 g mL^{-1} for organic matter, and greater than 5 g mL^{-1} for some metal oxides or 7 g mL^{-1} for less-common minerals such as metal sulfides. Many widely distributed soil minerals, including quartz and clay minerals, have densities that fall inside the approximate range from 2.5 to 2.8 g mL^{-1} .

In the case of mineral soils situated within a depth of 1 m or so from the surface, the bulk density is often between 1.2 and 1.8 g mL⁻¹ for materials containing a good proportion of sand. For soils with higher clay content, the density falls in a slightly lower range from 1.0 to 1.6 g mL⁻¹ [14].

2.2.1.4. Structure. Structure is a term used to describe the way in which individual particles are aggregated together to form larger units. Organic matter acts as a cementing agent and plays a key role in developing soil structure. Other chemical entities and the nature of the parent material are also determining factors. Structure is a field characteristic and is usually destroyed when a soil sample is collected and brought to a laboratory for analysis [14].

2.2.1.5 Permeability. Permeability, is also called hydraulic conductivity, is a measure of the ability of soil to conduct water. For example, when it rains heavily, a permeable soil transports the water rapidly downwards. Many soils have downward permeabilities in the range 1 to 5 cm hr⁻¹, rates smaller than 0,5 cm hr⁻¹ are very low, while rates greater than 15 cm hr⁻¹ are high [14].

2.2.2. Chemical Properties

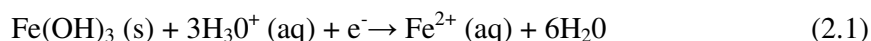
2.2.2.1. Cation-Exchange-Capacity (CEC). The solid phase particles of the soil often carry a negative surface charge. The overall electroneutrality of the system is then maintained by the presence of an excess of cations. This excess of cations cannot be separated from the surface. However, it is possible to exchange these cations against others while maintaining the electroneutrality of the system by replacing cations.

The total amount of cations held exchangably by a unit mass of soil is termed the CEC of soil and expressed in cmol/kg of soil [15].

2.2.2.2. Soil pH. Soil pH depends on the nature and history of the soil. Soils rich in carbonate minerals tend to be somewhat alkaline. On the other hand, those containing large

amounts of humic material are often, but not always, acidic. The acidity arises from microbial decomposition of the organic matter producing organic acids as a metabolic product, as well as from carbon dioxide released during respiration. Soils containing adsorbed iron and aluminium are also acidic as a consequence of the hydrolysis of the iron (III) and aluminium (III) cations. Prolonged leaching of the principal exchangeable metal cations, and their replacement by hydronium ion, also contributes to increased acidity.

Soil pH is affected by changes in the redox status. If a soil containing hydrous iron oxide is submerged, the iron (III) oxide is reduced as represented by the following half reaction.



Because hydronium ions are consumed in the reduction, there is an accompanying rise in pH. Flooded soils therefore tend to exhibit higher pH values than their upland counterparts [14].

2.2.2.3. Organic Matter Content (OMC). Organic matter is found in varying amounts in mineral soils and is almost always most concentrated near the surface. A wide spectrum of material makes up the soil organic matter, which ranges from undecomposed animal tissue to humus. It increases considerably both the water-holding capacity of mineral soils and the cation exchange capacity.

A detailed categorization of the humified organic matter occurring separately on the surface or mixed with mineral material has not been achieved. Therefore, in routine test categorizing soils, total amounts of carbon are determined.

The total amount of organic matter in soils varies from 1 per cent to 90 per cent.

2.2.2.4. Maximum Water Capacity. The capacity of the soil to absorb moisture varies considerably. Soils with a well developed structures of coarse texture allow free entry of moisture, whereas dispersed clays are virtually impermeable. Variations in the capacity of the soil to absorb moisture are particularly important in areas of high rainfall where low

infiltration rates cause water to collect at the surface creating a serious erosion hazard. No further additions can take place if the soil is already saturated [15].

2.3. Soil Pollution

Soil pollution can be defined as the malfunctioning of soil as an environmental component due to the contamination with certain compounds, which are particularly the result of human activities.

One of the problems with soil pollution lies inside the definition of soil pollution. With the term “contaminant” there comes an unclear situation in specifying the limits of permissible and non-permissible human interference with soil. In addition, it is required to broaden this knowledge to the situations involving the presence of contaminants in order to see whether the contaminants interfere, and if so, the contaminant level should be determined where the interference takes place.

There are five different interaction mechanisms between soil and its contaminant. The first one is the positive adsorption as induced by electrostatic attraction between charged compounds and oppositely charged soil constituents. Secondly, electrostatic repulsion takes place when the electric charge of compound and soil constituent is of the same sign. This usually takes place with the certain anions and the predominantly negative charge on e. g. clay minerals. Another interaction mechanism is the chemisorption. This mechanism can hardly be distinguished from electrostatic positive adsorption except for the value of the adsorption energy. This value is considerably higher in chemisorption. Precipitation and dissolution are also considered as the interaction mechanisms and they may play a predominant role in governing the mobility of certain compounds like heavy metals and phosphorus. The final interaction mechanisms are the decomposition and turnover reactions. Many compounds, when present in soil, are subjected to reactions such as photochemical degradation, microbial degradation, or a combination of these.

The above interaction mechanisms may either occur separately or in combination with each other, either successively, simultaneously or even alternating [16].

Soil pollution can be classified as physical and chemical pollution. Physical pollution is mainly erosion. Chemical pollution of soil is the result presence of excess nitrogen, phosphorus, heavy metals and trace elements (As, Cd, Co, Cr, Hg, Mo, Ni, Pb, Se, V, Zn), organic pesticides, and others like oil, gas, sanitary landfills. A pollutant is any chemical of natural or anthropogenic origin, which accumulates in the soil medium. It changes the natural soil equilibrium as a result of human activity. A modern society, however, cannot be developed without the use of natural and synthetic compounds which may be added to various ecosystems. Utilizing land as a waste management alternative causes many environmental problems to rise. Soil builds a medium to support the growth of plants. Many compounds, which are present in particular soils may become inhibitive beyond certain limits. Some of the soils are able to handle the introduction of pollutants, such as salts and heavy metals, better than others [17].

3. HEAVY METALS

3.1. General Information

"Heavy metals" are chemical elements with a specific gravity that is at least 5 times the specific gravity of water. The specific gravity of water is 1 at 4°C. Simply stated, specific gravity is a measure of density of a given amount of a solid substance when it is compared to an equal amount of water. Some well-known toxic metallic elements with a specific gravity that is 5 or more times that of water are arsenic, 5.7; cadmium, 8.65; iron, 7.9; lead, 11.34; and mercury, 13.546.

3.1.1. Beneficial Heavy Metals

In small quantities, certain heavy metals are nutritionally essential for a healthy life. Some of these are referred as trace elements (e.g., iron, copper, manganese, and zinc). These elements, or some form of them, are commonly found naturally in foodstuffs, in fruits and vegetables, and in commercially available multivitamin products. Heavy metals are also common in industrial applications such as in the manufacture of pesticides, batteries, alloys, electroplated metal parts, textile dyes, steel, and so forth. Many of these products are in our homes and actually add to our quality of life when properly used.

3.1.2. Toxic Heavy Metals

Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues. Heavy metals may enter the human body through food, water, air, or absorption through the skin when they come in contact with humans in agriculture and in manufacturing, pharmaceutical, industrial, or residential settings. Industrial exposure accounts for a common route of exposure for adults. Ingestion is the most common route of exposure in children. Less common routes of exposure are during a radiological procedure, from inappropriate dosing or monitoring during intravenous (parenteral) nutrition, from a broken thermometer, or from a suicide or homicide attempt [18].

3.2. Commonly Encountered Toxic Heavy Metals

3.2.1. Arsenic

Arsenic is the most common cause of acute heavy metal poisoning in adults and is the most toxic one among the other heavy metals. Arsenic is released into the environment by the smelting process of copper, zinc, and lead, as well as by the manufacturing of chemicals and glasses. Arsine gas is a common byproduct produced by the manufacturing of pesticides that contain arsenic. Arsenic may also be found in water supplies worldwide, leading to exposure of shellfish, cod, and haddock. Other sources are paints, rat poisoning, fungicides, and wood preservatives. Target organs are the blood, kidneys, and central nervous, digestive, and skin systems.

3.2.2. Lead

Lead is the second most toxic heavy metal. It is a very soft metal and was used in pipes, drains, and soldering materials for many years. Millions of homes built before 1940 still contain lead (e.g., in painted surfaces), leading to chronic exposure from weathering, flaking, chalking, and dust. Every year, industry produces about 2.5 million tons of lead throughout the world. Most of this lead is used for batteries. The remainder is used for cable coverings, plumbing, ammunition, and fuel additives. Other uses are as paint pigments and in PVC plastics, x-ray shielding, crystal glass production, pencils, and pesticides. Target organs are the bones, brain, blood, kidneys, and thyroid gland.

3.2.3. Mercury

Mercury is generated naturally in the environment from the degassing of the earth's crust, from volcanic emissions. It exists in three forms: elemental mercury and organic and inorganic mercury. Mining operations, chloralkali plants, and paper industries are significant producers of mercury. Atmospheric mercury is dispersed across the globe by winds and returns to the earth in rainfall, accumulating in aquatic food chains and fish in lakes. Mercury compounds were added to paint as a fungicide until 1990. These compounds are now banned; however, old paint supplies and surfaces painted with these

old supplies still exist. Mercury continues to be used in thermometers, thermostats, and dental amalgam. (Many researchers suspect dental amalgam as being a possible source of mercury toxicity.) Medicines, such as mercurochrome and merthiolate, are still available. Algaecides and childhood vaccines are also potential sources. Inhalation is the most frequent cause of exposure to mercury. The organic form is readily absorbed in the gastrointestinal tract (90-100 per cent); lesser but still significant amounts of inorganic mercury are absorbed in the gastrointestinal tract (7-15 per cent). Target organs are the brain and kidneys.

3.2.4. Cadmium

Cadmium is a byproduct of the mining and smelting of lead and zinc. It is used in nickel-cadmium batteries, PVC plastics, and paint pigments. It can be found in soils because insecticides, fungicides, sludge, and commercial fertilizers that use cadmium are used in agriculture. Cadmium may be found in reservoirs containing shellfish. Cigarettes also contain cadmium. Lesser-known sources of exposure are dental alloys, electroplating, motor oil, and exhaust. Inhalation accounts for 15-50 per cent of absorption through the respiratory system; 2-7 per cent of ingested cadmium is absorbed in the gastrointestinal system. Target organs are the liver, placenta, kidneys, lungs, brain, and bones.

3.2.5. Iron

Discussion of iron toxicity in this protocol is limited to ingested or environmental exposure. Ingestion accounts for most of the toxic effects of iron because iron is absorbed rapidly in the gastrointestinal tract. The corrosive nature of iron seems to further increase the absorption. Most overdoses appear to be the result of children mistaking red-coated ferrous sulfate tablets or adult multivitamin preparations for candy. Other sources of iron are drinking water, iron pipes, and cookware. Target organs are the liver, cardiovascular system, and kidneys [18].

3.3. Entry of Heavy Metals into Soil

3.3.1. Entry from Air

Although the normal atmosphere (air) is contaminated with dust particles, the contamination of soils with heavy metals by this mechanism is relatively unimportant. In many instances, the major part of the heavy metal emission in industrial and urban areas remains in a zone of 3 km around the center of emission. The 3-7 km zone around these cities is an area of lesser enrichment. In addition to the above distribution pattern for emission, there is an enrichment zone, particularly for Pb, Cd, and other pollutants, of up to 50 m in width on either side of highways. Our present knowledge would indicate that these are the two main aerial mechanisms for heavy metal enrichment of soils.

3.3.2. Entry from Wastes

Land disposal of wastes must be made without damage to the ecological balance of the land or the total environment-land, water, air. If land is to be repository of wastes-industrial, urban (including sewage sludge and garbage), agricultural- then precautions are required to avoid its pollution by contaminants in the waste, while utilizing the noncontaminants (nutrients, organic matter, etc.) to maintain and enhance the soil productivity. In order to develop the knowledge necessary to obtain the maximum benefit from these wastes and to minimize their harmful effects on the terrestrial ecosystem, it is necessary to have information on the physical, chemical, and microbiological properties of the wastes as well as on the various soil properties and their relationship to waste disposal or utilization.

Specific problems relating to land disposal of wastes include occurrence of pathogens, smell during application, risks to ground water, eutrophication due to leaching of nutrients, and contamination of the soil due to pesticides and heavy metals. When the levels of heavy metals in an “urban” and “industrial” sludge are compared, it is seen that the amount of heavy metal found in the industrial sludge is much greater than that in the urban sludge. This difference in the levels of heavy metals demonstrates the need for

control of application of this material to soil if quality and productivity are to be maintained.

3.3.3. Entry from Direct Application

The application of heavy metals in fertilizers, lime, pesticides, and manures is considered generally of little significance in relation to existing background levels in the soil.

3.3.4. Entry from Water

Irrigation water may be a source of heavy metals in situations where water (industrial and sewage effluents, etc.) is held in impoundment for this purpose or enters into river systems subsequently used for irrigation [10].

3.4. General Information About Cadmium

The heavy metal that was used in this work was Cadmium. Therefore, cadmium should be considered under more details.

3.4.1. Geological Information

Cadmium ores are rare. Cadmium occurs associated with zinc ores such as sphalerite (zinc sulphide, ZnS). Greenockite (CdS) is the only mineral of any consequence which contains cadmium. Most cadmium is produced as a by-product from the extraction of zinc, copper, and lead ores [19].

3.4.2. Cadmium Uses

Cadmium is used to a small extent as coatings (often achieved by electroplating) to protect metals such as iron. Its use is restricted because of environmental concerns. The metal is a component of some specialist alloys including solders and alloys with low

coefficients of friction and good fatigue resistance. Cadmium is a component of Ni-Cd batteries. Cadmium is used in some control rods and shields within nuclear reactors.

Cadmium is used in black and white television phosphors and in blue and green phosphors for colour TV tubes. Some semiconductors contain cadmium. The sulphide (CdS) is used as a yellow pigment. Some compounds are used as stabilizers for PVC [19]

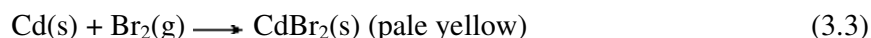
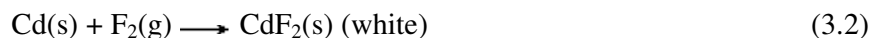
3.4.3. Reactions of Cadmium

3.4.3.1. Reaction of Cadmium with Air. Cadmium metal burns in air to form cadmium(II) oxide. This material is coloured variously, depending upon how it was made.

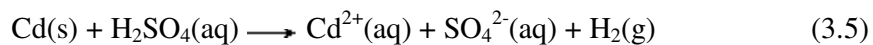


3.4.3.2. Reaction of Cadmium with Water. Cadmium metal does not react with water.

3.4.3.3. Reaction of Cadmium with Halogens. Cadmium difluoride, CdF_2 , cadmium dibromide, CdBr_2 , and cadmium diiodide, CdI_2 , are formed in the reactions of cadmium metal and fluorine, F_2 , bromine, Br_2 , or iodine, I_2 .



3.4.3.4. Reaction of Cadmium with Acids. Cadmium metal dissolves slowly in dilute sulphuric acid (H_2SO_4) to form solutions containing the aquated Cd(II) ion together with hydrogen gas, H_2 . In practice, the Cd(II) is present as the complex ion $[\text{Cd}(\text{OH}_2)_6]^{2+}$.



The reacts of cadmium with oxidizing acids such as nitric acid, HNO_3 , are complex and depend upon precise conditions.

3.4.3.5. Reaction of Cadmium with Bases. Cadmium metal does not dissolve in aqueous alkalis such as potassium hydroxide, KOH [19].

3.4.4. Compounds of Cadmium

In compounds of cadmium (where known), the most common oxidation number of cadmium is 2. The cadmium compounds include hydrides (CdH_2), fluorides (CdF_2), chlorides (CdCl_2), bromides (CdBr_2), iodides (CdI_2), oxides (CdO), sulfides (CdS), selenides (CdSe), tellurides (CdTe) and nitrides (Cd_3N_2) [19].

4. SURFACE-ACTIVE-AGENTS (SURFACTANTS)

Surface-active-agents (surfactants), also known as emulsifiers, detergents or wetting agents, lower the surface tension of a liquid, and/or the interfacial tension between two liquids allowing easier spreading. Most of the interest has been centered on the behaviour of surfactant in aqueous system. These are used in wetting, foaming and detergency, etc. Surfactants are usually organic compounds that are amphiphilic, meaning they contain both a hydrophobic group (the “tail”) and a hydrophilic group (the “head”) as it is shown in Figure 4.1. Therefore, they are sparingly soluble both in organic solvents and in polar media such as water.

Surfactants are classified according their ionic (electrical) charge on the head group of the molecule. The head group may carry a negative charge (anionic surfactant) or a positive charge (cationic surfactant). If the surfactant head group bears both a negative and a positive charge, it is called zwitterionic. Surfactants with no charge on the head group are termed as nonionic surfactant [20].

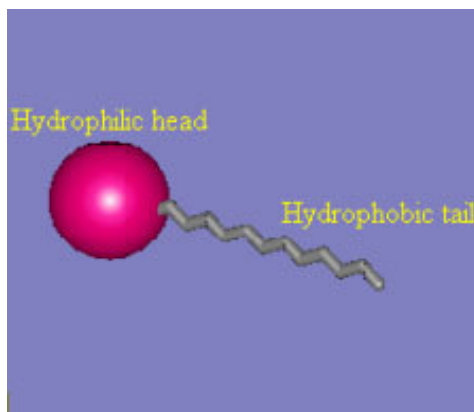


Figure 4.1. Schematic representation of a surfactant molecule

Surfactant molecule can arrange itself at the surface of water such that the polar hydrophilic head group interacts with water and the non-polar hydrophobic tail group interacts with air. Another arrangement of the surfactants molecules can allow each component to interact with its favored environment. Molecules can form aggregates in

which the hydrophobic portions are oriented within the cluster and the hydrophilic portions are exposed to the solvent. Such aggregates are called micelles. When a certain critical surfactant concentration is reached in aqueous solutions, micelle formation takes place as illustrated in Figure 4.2. This point is called the critical micelle concentration (CMC). A sudden change in physical properties indicates the CMC. After CMC, the free surfactant concentration in solution no longer changes. That is, beyond this point the concentration of unassociated molecules stay constant [21].

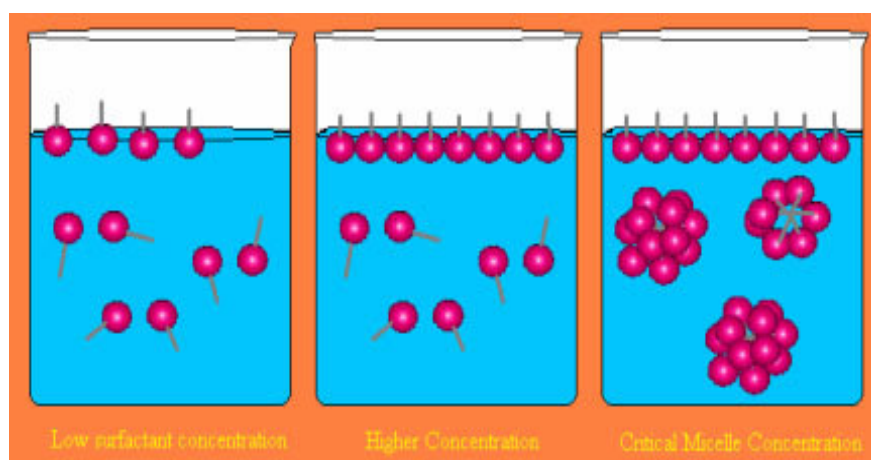


Figure 4.2. The self-assembly mechanism of micelle formation with increasing concentration of surfactant

All surfactants possess the common property of lowering surface tension when added to water in small amounts, as illustrated in Figure 4.3. The characteristic discontinuity in the plots of surface tension against surfactant concentration can be experimentally determined. The corresponding surfactant concentration at this discontinuity corresponds to the CMC.

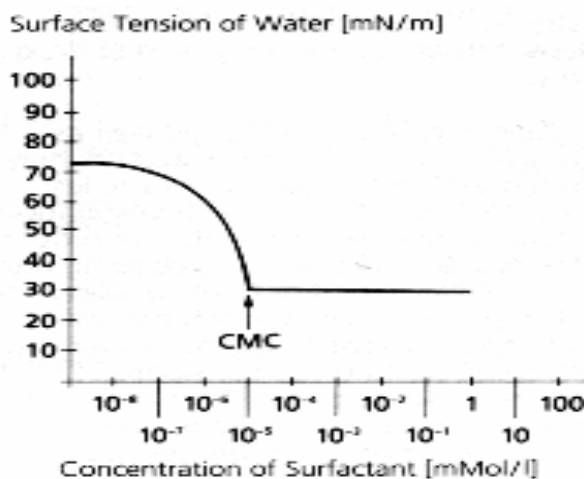


Figure 4.3. Typical decrease of the surface tension of water by surfactants [22]

The surfactants are of widespread importance in the detergent industry, in emulsification, lubrication, catalysis, tertiary oil recovery, and in drug delivery. In analytical chemistry, surfactants have been recognized as being very useful for improving analytical methodology, e.g. in chromatography and luminescence spectroscopy [23]. Since micelles provide an organic microsphere in an aqueous solution, contaminants such as hydrophobic organic compounds can be easily solubilized within their micellar phase. In recent years, surfactant micelle-mediated extraction has been applied to aqueous solutions to remove metal ions such as cadmium, copper, zinc, cobalt and nickel [7].

4.1. Anionic Surfactants

4.1.1 General Information

Anionic surfactant is derived from an aliphatic hydrocarbon and usually a sodium salt, in which detergent and other properties depend in part on the negatively charged anion of the molecule. They are effective in removing particulate (dirt, dust, etc.) and oily soils and used as active ingredients in products like hair shampoos. Anionic surfactants are known to cause skin irritation and other skin illnesses.

Carboxylates, sulfonates, sulfates and phosphates are the polar solubilizing groups found in anionic surfactants. These groups are combined with a 12 carbon chain hydrophobe for the best surfactant properties. To compensate for the loss of solubility, shorter hydrophobes are used for application in high ionic strength media.

Soap is an example for the mostly used commercial carboxylates. The general structure of soap is $\text{RCOO}^- \text{M}^+$. R represents the straight hydrocarbon chain and M^+ stands for a metal or ammonium ion. Soaps show excellent detergency in soft water. In hard water, they react with positively charged water hardness minerals, such as Ca^{2+} and Mg^{2+} , and they form lime soaps as a result of this reaction. In general, anionic surfactants tend to generate higher suds levels than other classes of surfactants [24].

Another anionic surfactant is the sulfonate. The sulfonate group ($-\text{SO}_3\text{M}$) is attached to an alkyl, aryl and alkylaryl hydrophobe. It is stable to oxidation. It also interacts with Ca^{2+} and Mg^{2+} , the hardness minerals of water. This interaction is less than that of the carboxylates.

In addition to carboxylates and sulfonates, sulfates are another group which is important for anionic surfactants. The structure of the sulfate head group is ($-\text{OSO}_3\text{M}$) where M represents a cation. The sulfate group is more hydrophilic than the sulfonate group due to the presence of an additional oxygen in the head group structure. Most widely used sulfates are the alkyl sulfates [24].

Surfactants with the mono and diesters of ortho phosphoric acid and their salts as the head group are also useful. In contrast to sulfonates and sulfates, the resistance of alkyl phosphate esters to acid is poor. Magnesium and calcium salts are insoluble. In the acid form, the esters show limited water solubility and the surface activity.

4.1.2. SDS

Sodium dodecyl sulfate (SDS or NaDS) ($\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$), also known as sodium lauryl sulfate (SLS), is an anionic 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, giving the molecule the amphiphilic properties required of a detergent. The structure is given in Figure 4.4.

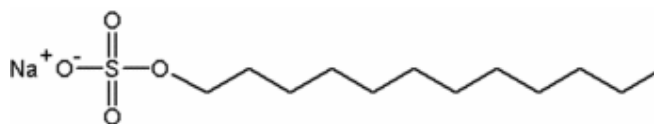


Figure 4.4 Chemical composition of SDS

It is prepared by sulphation of lauryl alcohol ($\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{OH}$) followed by neutralisation 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 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.

The CMC in pure water is 8.2×10^{-3} M, and the aggregation number, which is the number of molecules that are associated together to form a micelle, at this concentration is around 50 [25].

4.2 Cationic Surfactants

4.2.1. General Information

The hydrophilic part of a cationic surfactant is positively charged when dissolved in aqueous media. Two common types of cationic surfactants are long chain amines and quaternary amine salts. The long chain amine types are made from natural fats and oil or

from synthetic amines. They are soluble in strongly acidic medium but become uncharged and insoluble in water at pH greater than 7.

Quaternary amine type cationic surfactants are very important as fabric softeners. They absorb on the surface of fibers with their hydrophobic groups oriented away from the fibers. This reduces the friction between fibers and imparts a soft, fluffy feel to the fabric. This same mechanism accounts for the behavior and use of cationic surfactants as hair conditioners. Quaternary ammonium salts are effective in neutral and alkaline as well as acidic medium.

The cationic surfactants are readily adsorbed on negatively charged surfaces. Most surfaces in contact with water carry a negative charge. Therefore; the cationic surfactants are easily exhausted from solution by adsorption compared to the other types of surfactants.

Cationic surfactants are seldom used in cleaning formulations because they have poor detergency properties when compared with the anionic and nonionic surfactants [26].

4.2.2 Hyamine 1622 (Benzethonium Chloride)

Hyamine 1622 belongs to the quaternary ammonium salts and hydrates. Its chemical structure can be seen in the Figure 4.5.

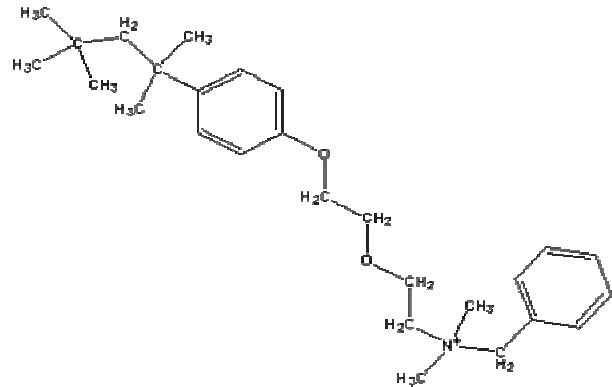


Figure 4.5 Chemical composition of Hyamine 1622

Hyamine 1622 is the condensation product of para-tertiary octylphenol with dichloroethyl ether. The monochloro derivative is converted into a quaternary ammonium compound by a reaction with benzyl dimethylamine chloride. It is used primarily in cosmetics for its antimicrobial and cationic surfactant properties. Hyamine 1622 is also used in sanitization of finished textiles and it is active against bacteria [27].

4.3. Nonionic Surfactants

Nonionic surfactants differ from cationic and anionic surfactants in that the molecules are actually uncharged. The hydrophilic group is made up of some other very water soluble moiety, (a short, water-soluble polymer chain) rather than a charged species. Traditionally, nonionic surfactants contain poly(ethylene oxide) chains as the hydrophilic group. Poly(ethylene oxide) is a water soluble polymer; the polymers used in nonionic surfactants are typically 10 to 100 units long.

One of the classes of nonionic surfactants is the alkyl polyglycosides. In these molecules, the hydrophilic group is sugar - in this case they are just polysaccharides but they can be made from disaccharides, trisaccharides, maltose and various other sugars. Although they are called polyglycosides, they generally only have one or two sugar groups in the chain.

The predominant use of these surfactants is in foods and drinks, pharmaceuticals and skin-care products. It is thought that these surfactants are mild on the skin even at high loadings and long-term exposure [26].

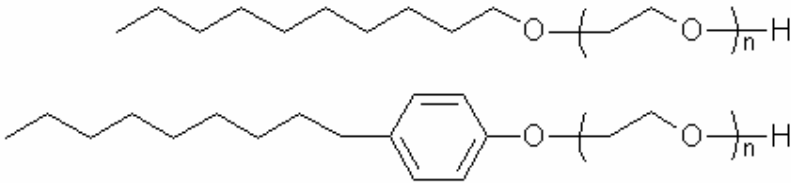


Figure 4.6. Chemical composition of an alcohol ethoxylate and an alkylphenol ethoxylate which are examples for nonionic surfactants.

4.4. Zwitterionic (Amphoteric) Surfactants

A zwitterionic surfactant is a zwitterion that has surface-active properties. A zwitterion is also known as an internal salt, having an anion and a cation in the one molecule chemically joined together. Zwitterionic surfactants are also called amphoteric surfactants. Like cationic surfactants, they also impart a feel of softness to textile materials. They are compatible with all classes of surfactants and are soluble and effective in the presence of high concentrations of electrolytes, acids and alkalies. They exhibit cationic behavior at higher pH values. The isoelectric point depends on the structure of the surfactant [26].

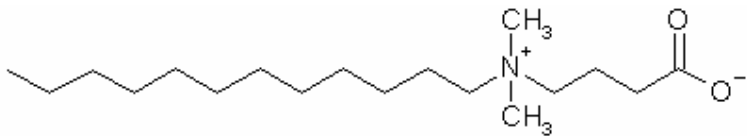


Figure 4.7. Chemical composition of an ammonium carboxylate which is an example for zwitterionic surfactant

4.5. Interaction Between Ionic Surfactants

Anionic and cationic surfactants neutralize each other when they present in the same aqueous solution. The oppositely charged ions form neutral ion pairs. Anionic and cationic surfactants are bonded by coulombic forces and also forces between their hydrophobes. This causes micellisation or precipitation, which occurs when the anionic and cationic surfactants are mixed in a stoichiometric ratio. On the other hand, solubilization occurs if one or the other is added in excess. In spite of this neutralization effect, addition of the opposite type can cause an increase in surface adsorption, hence marked decrease in surface tension and critical micelle concentration is obtained.

The toxicity of many anionic and cationic surfactants is neutralized when both type of surfactant are present together in the media [28].

5. ADSORPTION PHENOMENA

Adsorption is a surface phenomena. It is a process that occurs at an interface between any two phases, such as solid-gas, solid-liquid, liquid-liquid, liquid-gas. The material being concentrated, meaning adsorbed, is the adsorbate and the adsorbing phase is the adsorbent. Adsorption is defined as the excess concentration of pollutants at the soil-solid interface compared with that in the bulk solution regardless of the nature of the interface region or of the interactions between the adsorbate and the solid surface which causes the excess. Adsorption involves the distribution of a substance between two phases. Adsorption isotherms describe the equilibrium conditions at constant temperature. Adsorption deals with utilization of surface forces and the concentration of materials on the surfaces of solid bodies' referred to as adsorbents [29].

The transport and fate of chemicals in soils or sediments and their tendency to migrate in air or water is evaluated from adsorption and desorption data [29]. In this study, adsorption occurs between liquid and solid phases. In a liquid-solid system, solute particles are removed from liquid and concentrated on the solid state. The concentration of the remaining solute is therefore in a dynamic equilibrium with that adsorbed on the solid surface. In this equilibrium, there is a defined distribution of solute between the liquid and solid phases. The distribution ratio may be a function of concentration of the solute, the concentration and nature of competing solutes, the nature of solution, etc.

When an adsorbent is in contact with the surrounding fluid of a certain composition, adsorption takes place and after a sufficiently long time, the adsorbent and the surrounding fluid reach equilibrium. In this state the amount of the component adsorbed on the surface, mainly in the micropore of the adsorbent, can be determined. The relation between amount q (mg/g), and concentration in the fluid phase, C (mg/L), at temperature, T (K), is called the adsorption isotherm at T [30].

$$q = q(C) \text{ at } T \quad (5.1)$$

The relation between concentration and temperature yielding a given amount adsorbed, q , is called the adsorption isotherm for q .

$$C = C(T) \text{ for } q \quad (5.2)$$

When the measured adsorption data are plotted against the concentration value of the adsorbate at equilibrium, the graph obtained is called the adsorption isotherm. By the help of its shape, the adsorption isotherm provides a useful way for determining the adsorption mechanism for a solute-solvent system[30].

Adsorption isotherms can be classified as S, L, H and C curves as shown in the Figure 5.1.

In the S class of isotherms, the initial slope is convex to the concentration axis (S1). It is broken by a point of inflection. This leads to the characteristics of S shape (S2). Further concentration increases may be parallel to those curves of L class [31].

The L-curve isotherm is the most common one. It is identified by its initial region. The initial slope is concave to the concentration axis (L1). As the concentration of the adsorbate increases, the isotherm may reach a plateau (L2). This is followed by a section which is convex to the concentration axis (L3). If the region L3 attains a second plateau, the region is called L4 [31].

The H or high affinity class of isotherm occurs as a result of very strong adsorption at low adsorbate concentration. The consequence is that the isotherms have a positive intercept on the ordinate. Higher concentrations lead to similar changes in the L and S classes.

The final type of isotherm is the C class. The C curve isotherm exhibit an initial slope. This remains independent of concentration of the substance in the solution. This type of isotherm looks like a constant partitioning of a solute between the solvent and the adsorbing surface. It may be due to the proportional increase of the adsorbing surface as the surface excess of an adsorbate increase [30].

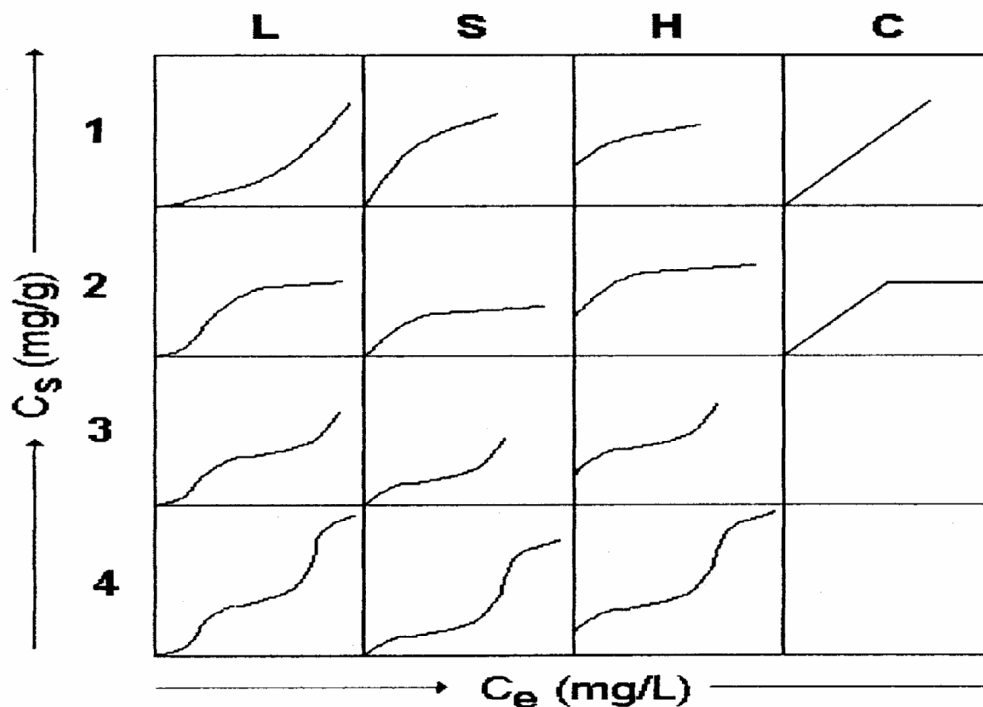


Figure 5.1. Adsorption Curves [32]

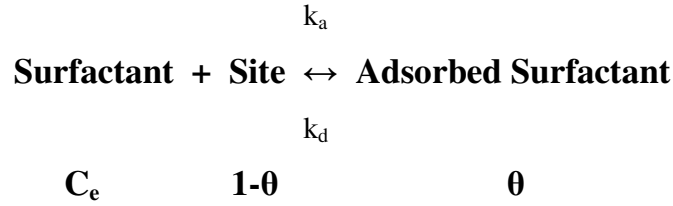
5.1. Adsorption Isotherms

Equations that are often used to describe the experimental isotherm data were developed by Freundlich, Langmuir, and Brunauer-Emmet-Teller (B.E.T). Among these adsorption isotherms, Freundlich and Langmuir isotherms have been used in the evaluation of the experimental data.

Langmuir proposed a theory, which involves the assumption that forces acting in adsorption are similar kind to those involved in chemical combination. Langmuir assumes that elementary spaces or points of residual valiancy exist on the surface of a crystal. The adsorptive forces are concentrated at these points and adsorption consists in the fixing of the adsorbed atoms in the elementary spaces for a certain time. These spaces can hold only one atom or molecule therefore the adsorbed layer can be only one molecule thick. Langmuir also proposed a relation between the concentration in the solution and the

adsorbed quantity on the assumption that equilibrium is established between the rate of adsorption and the rate of desorption [30].

The general formula for Langmuir isotherm at equilibrium is:



Where θ = fraction of occupied sites

k_a = Rate constant for adsorption

k_d = Rate constant for desorption

$$\theta = K_L \times C_e / (1 + K_L \times C_e) \quad (5.3)$$

$$K_L = k_a / k_d \quad (5.4)$$

$$\text{also} \quad \theta = C_s / (C_s)_{\max} \quad (5.5)$$

Hence we can write:

$$\frac{1}{C_s} = \frac{1}{(C_s)_{\max}} + \frac{1}{K_L (C_s)_{\max} C_e} \quad (5.6)$$

C_s is the amount of the adsorbate adsorbed per unit mass of soil (mg/g) and C_e is the concentration of adsorbate remaining in solution at equilibrium (mg/L) and $(C_s)_{\max}$ is the concentration required for monolayer coverage. $K_L = k_a/k_d$ and is called the adsorption equilibrium constant. The plot of $1/C_e$ versus $1/C_s$ gives a straight line with a slope of $1/K_L(C_s)_{\max}$ an intercept of $1/(C_s)_{\max}$.

The Langmuir adsorption model is valid for single layer (monolayer) adsorption whereas BET model represents isotherms reflecting apparent multilayer adsorption. Both equations are limited by the assumption of uniform energies of adsorption surface. Both isotherms are applied for isothermal cases.

The last model for isothermal adsorption is the Freundlich isotherm. It has been widely used for describing pollutant adsorption on the soil solid phase. This equation is a special case for heterogeneous surface energies.

$$C_s = K_F C_e^n \quad (5.7)$$

It has the general form where K_F and n are constants. The Freundlich equation is basically empirical but is often useful as a means of data description. Data are usually fitted to the logarithmic form of the equation.

$$\ln C_s = \ln K_F + n \ln C_e \quad (5.8)$$

The plot of $\ln C_e$ versus $\ln C_s$ gives a straight line with a slope of n and an intercept of $\log K_F$. C_s is the amount of the adsorbate adsorbed per unit mass of soil (mg/g) and C_e is the concentration of adsorbate remaining in the solution at equilibrium (mg/L). K_F is the adsorption capacity and n is the adsorption intensity, it is a measure that reflects the nonlinearity of the adsorption. Higher the n value, higher the bonding energy of the adsorbed solute by soil. n value commonly range between 0.7 and 1.2. At very low concentrations Freundlich equation does not reduce to linear adsorption expression. When adsorption intensity is equal to unity it is called linear adsorption isotherm, when n is smaller than 1 the name given for is nonlinear adsorption isotherm [30].

5.2. Factors Affecting Adsorption

The properties of both the adsorbent and the adsorbate are the main factors that affect the adsorption process. Chemical and physical characteristics of soil determine its adsorption behavior. Surface area, pH, CEC, OMC, and temperature are the main factors

affecting adsorption capacity. Properties of adsorbate like solubility of the contaminant, polarity of the adsorbate and dissociation constant value of the adsorbate determines its adsorption characteristics [33].

5.3. Adsorbent- Adsorbate Interactions

Adsorption occurs via six main intermolecular interactions.

Van der Waals Interactions (physisorption): They are weak interactions, which are common to all molecules. They are a result of formation of short-lived dipoles in atoms or molecules caused by small perturbations of the electronic flux or motion distribution of the electrons in the orbitals. This dipole induces small dipoles in other molecules of opposite charge and these attract each other for a short time [34].

Ligand Exchange and Ion Bonding: Cations or anions can be adsorbed to soil by organic or inorganic components of the soil. This type of adsorption involves electrostatic interactions and exchange reactions. For example, anions bind to the positively charged sites of the clay minerals as a result of electrostatic attraction. But anionic sorption may take place via a ligand exchange reaction. The anions in soil, e.g. silicate, can be replaced by other anions, e.g. hydroxide through exchange reactions. Similarly cations may substitute central cations in clay minerals, central cations compensate the negative charge of clay minerals. The cations of the adsorbate may also bind to the negative surfaces of clay minerals via electrical attraction. In electrostatic attraction the charge of the ion is a determining factor. When two adsorbate compete for the same adsorbent, the one with higher charge is attracted more strongly towards the adsorbent [33].

Hydrophobic Binding: This process is regarded as the partitioning of hydrophobic nonpolar compounds from the aqueous phase into the soil organic matter. The cage of water molecules structured around nonpolar regions of a hydrocarbon molecule is broken. If two nonpolar regions of an adsorbate and an adsorbent approach each other, the space between these molecules decreases and strong adsorption occurs [35].

Hydrogen Bonding: Hydrogen bonding consists of a hydrogen atom covalently bound to a very electronegative atom and another atom of strong electronegativity. This type of interaction depends on the relative strength of the adsorbent-adsorbate, the adsorbent-water interaction and the pH value of the solution [34].

Chemisorption: Chemisorption involves the formation of a bond between the adsorbate molecule and the surface atoms. Because the adsorbate undergoes chemical interaction with the adsorbent the phenomenon is termed Chemical Adsorption. Usually a covalent, sometimes ionic bond is formed and chemically adsorbed molecules are considered not to be free on the surface or within the interface [35].

Charge Transfer: Charge transfer interactions result from the formation of a donor-acceptor complex between an electron-donor molecule and an electron-acceptor molecule, involving the overlap of their respective molecular orbitals and partial exchange of electron density. Alcohols, amines are the lone pair electron donors. Electron acceptor molecules are aromatics with electron cloud acceptors such as weak acids, trinitrobenzenes, etc. In general charge transfer is a likely mechanism for adsorption to humins, especially humic acids [35].

5.4. Surfactant Adsorption

Adsorption of anionic surfactants has been studied extensively with both inorganic and organic adsorbents. Impervious minerals such as sand are generally weak adsorbents. They hold as little as a few micrograms of surfactants per gram, insufficient even to form a monomolecular layer on the mineral surface, very loosely held and easily washed off. Increased surface area provides increased space for adsorption of solute molecules, so silt and clay may adsorb much more per gram of adsorbent, widely variable depending on the physical and chemical structure of the clay. Soils also may vary widely in adsorption properties with their differing content of clay and organic matter. Biological matter such as primary sewage sludge, activated sludge, anaerobic digester sludge and bacteria themselves can likewise adsorb large quantities of surfactants from dilute solutions. An increase in solubilization in water of nonpolar organic chemicals is obtained when

surfactants are present in the water solution. However the solvent power of surfactants is much greater than that of a simple cosolvent. The structure of the surfactant solution above a rather well-defined critical concentration for micelles is that of an ultrafine emulsion. The surfactant molecules are aggregated forming a cluster of 20-200 units or more [28].

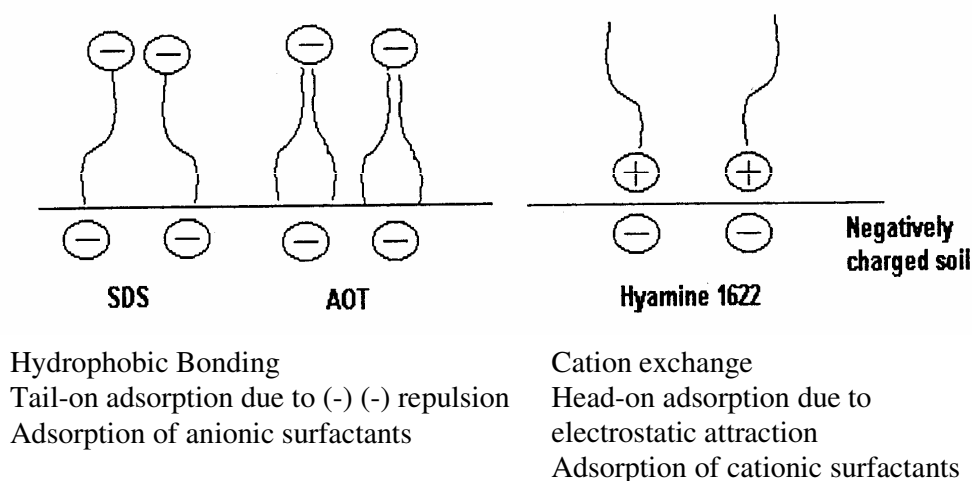


Figure 5.2. Adsorption mechanisms

5.5. Adsorption of Heavy Metals on Soil

Soil is a very complex heterogeneous medium consisting of solid phases (the soil matrix) containing minerals and organic matter and fluid phases (the soil water and the soil air), which interact with each other and ions entering the soil system. The concentration and the mobility of heavy metals that may be originating from the natural phenomena and human activities, such as agricultural issues, or environmental concern activities, such as industrial activities and waste disposal. Adsorption is the major process responsible for the accumulation of heavy metals. The most important interfaces involved in heavy metal adsorption in soils are predominantly inorganic colloids such as clays, metal oxides and hydroxides, metal carbonates and phosphates. In specific literature, heavy metal adsorption is expressed in terms of two basic mechanisms. Specific adsorption is characterized by more selective and less reversible reactions including chemisorbed inner-sphere complexes, and nonspecific adsorption (or ion exchange) involves rather weak and less selective outer-

sphere complexes. In specific adsorption strong and irreversible binding of heavy metal ions with organic matter and minerals occur while in nonspecific adsorption an electrostatic phenomenon in which cations from water are exchanged for cations near the surface. This cation exchange is an outer-sphere complexation with only weak covalent bonding between metals and charged soil surfaces. This action is reversible in nature and occurs rather quickly for diffusion-controlled and of electrostatic nature reactions. Specific adsorption can be described by a surface complexation model. This type of adsorption is based on reactions with OH⁻ groups at the soil surfaces and edges, which at high pH values are negatively charged. The properties of the surface and the nature of the metal constituting the adsorption site influence the tendency for adsorption, which depends on pH and equivalent to metal ion hydrolysis, can be described by the following reaction where M represents metal cation and S represents a surface:



In contrast to adsorption, surface precipitation of metals as oxides, hydroxides, carbonates, sulfides or phosphates onto soils occurs by two reactions; first a surface complex formation and second the precipitation of metal ion at the surface like in the given reaction below:



Adsorption and distribution of adsorbed metals in tree soils of India were studied. In the soils examined, an increase in the amount of heavy metal adsorption with increasing equilibrating concentrations was observed [36]. Another work examining the adsorption of heavy metals on soils determined that the reason for high metal adsorption capacity of soil was because of the presence of smectite clay, carbonates, Al, Fe, Mn (oxides), and high soil pH [2].

6. VOLTAMMETRY

6.1. Fundamentals of Voltammetry

Voltammetry comprises a group of electroanalytical methods in which information about the analyte is derived from the measurement of current as a function of the applied potential to the electrode [37]. The potential of the electrode is the controlled parameter that causes the chemical species to be oxidized or reduced and it can be thought of as an electron pressure which either forces species in solution to gain an electron (reduction) or to lose an electron (oxidation).

The current is simply a measure of electron flow or transfer which takes place when an oxidation or reduction occurs on the electrode surface. The type of current is called Faradaic current and it is proportional to concentration. By convention, cathodic currents are always treated as being positive, whereas anodic currents have a negative sign.

In voltammetry, another type of current is non-faradaic current. Non-faradaic current results from the double layer that forms at the electrode-solution interface. The double layer is caused by the electrostatic attraction or repulsion of cations and anions near the electrode surface to balance its charge. With a non-faradaic current, charge is carried across the electrode solution interface without accompanying oxidation-reduction process. The greater sensitivity of the method is accompanied by an enhancement of the faradaic current and a decrease in the non-faradaic current [38].

Voltammetry measurements are obtained under conditions that encourage polarization of an indicator or working electrode [37]. A plot of current in an electrolytic cell as a function of applied potential should be a straight line with a slope equal to the negative reciprocal of the resistance. Cells that exhibit nonlinear behavior at higher currents are polarized. Generally in order to enhance the polarization, the working electrodes in voltammetry are microelectrodes that have surface areas of a few square millimeters. Polarization can be assumed as overvoltage or overpotential that is formed by

the application of a potential to the working electrode that is greater than the theoretical to give a current of expected value [38].

Voltammetry is widely used by inorganic, physical, and biological chemists for nonanalytical purposes including fundamental studies of oxidation and reduction processes in various media, adsorption processes on surfaces, and electron transfer mechanisms at chemically modified electrode surface.

6.2. Excitation Signals in Voltammetry

In voltammetry, potential is applied to an electrochemical cell containing a microelectrode. This excitation signal forms a characteristic current response depending on the basis of the method. The wave forms of four of the most common excitation signals used in voltammetry are Linear Scan, Differential Pulse, Square Wave, and Triangular and they form the four main types of voltammetry; Linear Scan, Differential Pulse, Square Wave and Cyclic Voltammetry, respectively [37]. A plot of current versus applied potential is called either voltammogram or polarogram. Figure 6.1 shows the different types of excitation signals and the resulting currents in voltammetry and polarography.

6.2.1. Linear-Scan Voltammetry

The earliest and simplest voltammetric methods were of the linear-scan type, in which the potential of the working electrode is increased or decreased at a typical rate of 2 to 5 mV/s (Figure 6.1.a). Linear-scan voltammograms generally take the shape of sigmoidal curve called a voltammetric wave (Figure 6.2). The constant current beyond the steep rise is called the limiting current i_l , because the rate at which the reactant can be brought to the surface of the electrode is restricted by mass-transport process. Limiting currents are generally directly proportional to reactant concentration as given in the equation

$$i_l = kc_A \quad (6.1)$$

where c_A is the analyte concentration and k is a constant.

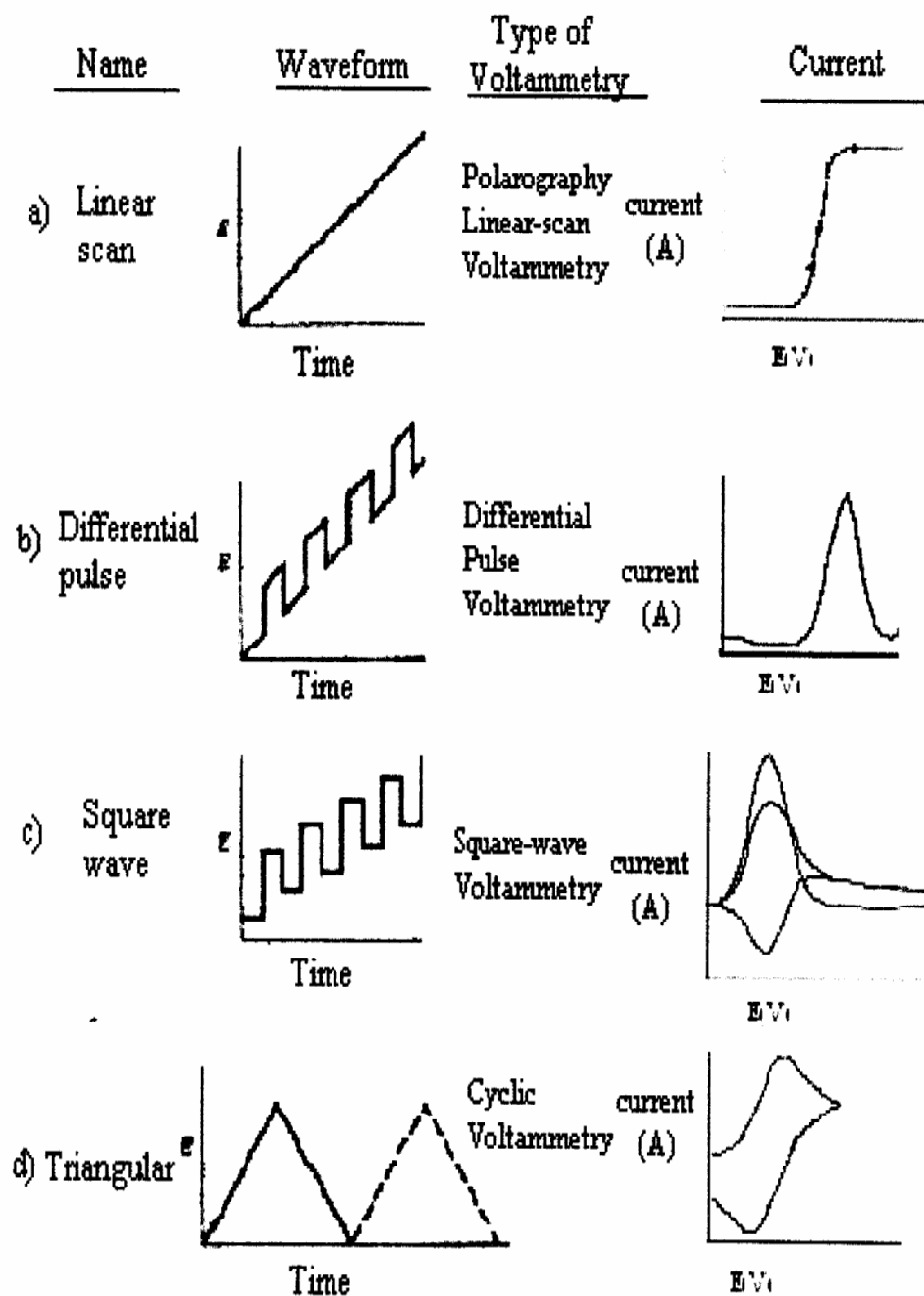


Figure 6.1. Excitation signal types in voltammetry and polarography [37]

The potential at which the current is equal to the half of the limiting current is called the half-wave potential and designated by the symbol $E_{1/2}$. The half-wave potentials are related to the standard electrode potentials of the electroactive species and useful for the identification of the components of a solution qualitatively.

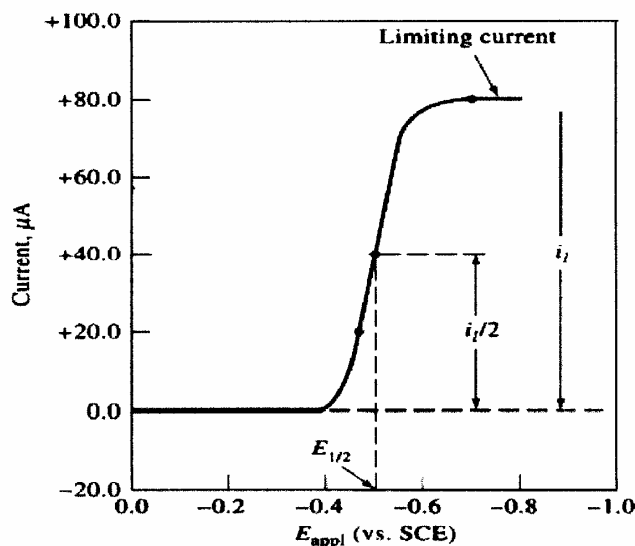


Figure 6.2. Linear-scan voltammogram of the reaction $A + ne^- \leftrightarrow P$ [37]

In order to obtain reproducible limiting currents rapidly, it is necessary either (a) that the solution or the microelectrode be in continuous and reproducible motion or (b) that a dropping mercury electrode be employed. Linear-scan voltammetry is of two types: hydrodynamic voltammetry and polarography.

In hydrodynamic voltammetry, the analyte solution is kept in continuous motion. It can be performed either by stirring the solution vigorously while it is in contact with a fixed microelectrode, or by rotating the microelectrode at a constant high speed in the solution. Another method involves the flowing of the analyte solution through a tube in which the microelectrode is mounted. The last method is widely used in detecting oxidizable or reducible analytes as they exit from a liquid chromatographic column.

In hydrodynamic voltammetry, while the electrolysis takes place, reactant is carried to the surface of the microelectrode by three mechanisms: (a) *migration* under the influence of an electric field, (b) *convection* resulting from stirring or vibration, and (c) *diffusion* due to concentration differences between the liquid film at the electrode surface and the bulk of the solution [37].

In the second type of linear-scan voltammetry, called polarography, Dropping Mercury Electrode (DME) is used as the working electrode and currents are controlled only by diffusion instead of both diffusion and convection.

In polarography, mass transport takes place by only diffusion, and polarograms differ from voltammograms. Limiting currents in voltammetry are named diffusion currents i_d in polarography.

6.2.2. Pulse Voltammetry

Pulse voltammetry techniques are based on the measurement of current as a function of time after applying a potential pulse. The two most common types of pulse techniques are differential pulse voltammetry and square-wave voltammetry.

Differential pulse voltammetry (DPV) is an extremely useful technique for measuring trace levels of organic and inorganic species and it is the most commonly used pulse technique because of its high sensitivity. In differential pulse voltammetry, a direct current potential, which is increased linearly with time, is applied to the voltammetric cell.

DPV provides greater sensitivity comparing to the other types of voltammetric methods. This can be attributed to the two main reasons. The first one is an enhancement of the faradaic current; the second one is the decrease in the nonfaradaic charging current which can be assumed as the background current resulting from electrochemical activity of all other species in the solution except the analyte. Figure 6.3 shows potential and current relations in DPV. This method allows the measurement of the concentrations as low as 10^{-8} M.

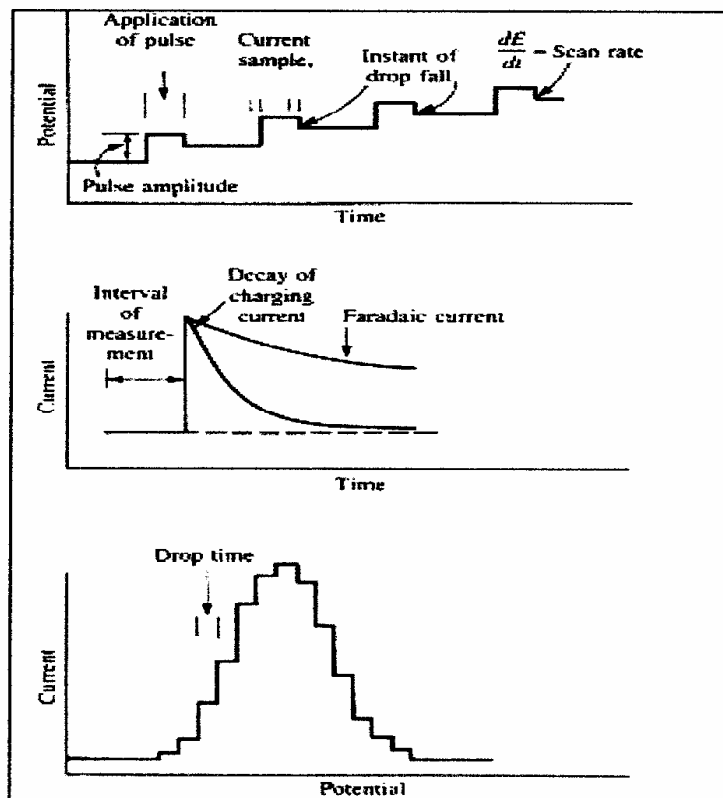


Figure 6.3. Potential and current relations in DPV [37]

6.3. Voltammetric Instruments

Voltammetric components are the voltage source, voltammetric cell and voltammetric data which are shown in the schematic diagram of an apparatus for voltammetric measurements in Figure 6.4.

There are three electrodes in a voltammetric cell. They are immersed in a solution which contains the analyte and an excess amount of a nonreactive electrolyte called supporting electrolyte. Figure 6.5 shows the top and front view of the electrodes in a voltammetric cell.

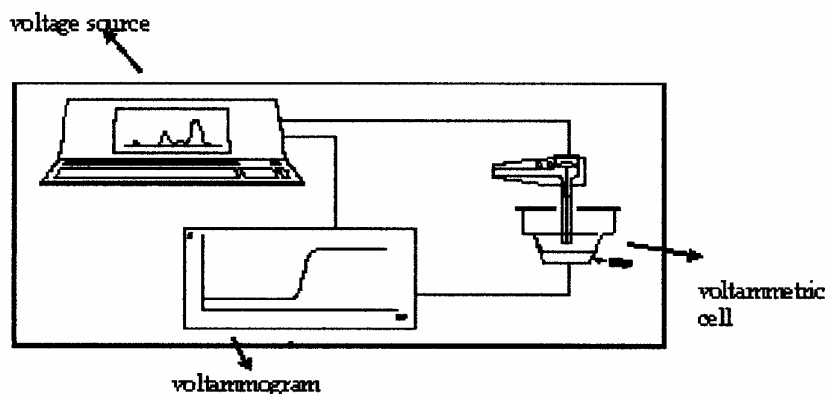


Figure 6.4. General outline of a voltammetric instrument

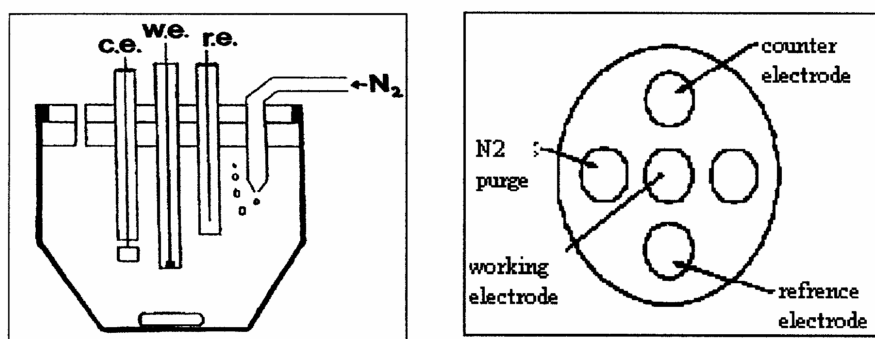


Figure 6.5. Voltammetric cell components

6.3.1. Electrode Types in Voltammetry

Voltammetry is generally carried out by three electrodes which are called Working Electrode (WE), Auxiliary Electrode (AE) and Reference Electrode (RE). A potentiostat controls the potential difference between the working and the reference electrode according to a pre-selected voltage time program supplied by the computer.

6.3.1.1. Working Electrode. Analyte is oxidized or reduced at its surface. The performance of the voltammetric measurement is strongly influenced by the working electrode material.

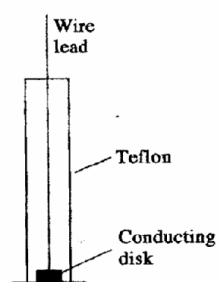
The range of potentials that can be applied to the electrodes depends on the electrode material and the composition of the analyte solution in which the electrode is immersed.

Working electrode dimension is kept small in order to enhance the polarization effect. It should provide high signal-to-noise characteristics, as well as reproducible responses. Therefore, its selection depends primarily on two factors: the redox behavior of the target analyte and the background current that develops over the potential region required for the measurement. Other considerations include electrical conductivity, and surface reproducibility of the electrode material. Its mechanical properties and toxicity are also taken into account. The materials that have been used for building up the working electrodes are mercury, carbon, or noble metals such as platinum or gold.

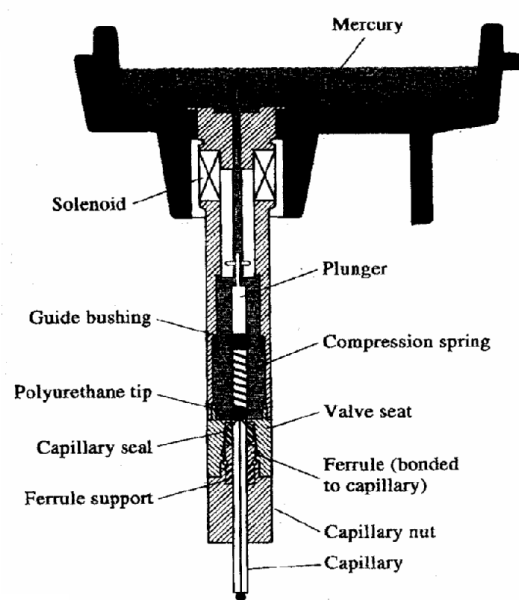
There are two main types of working electrodes in voltammetry which are called Multi Mode Mercury Electrode (MMME) and Solid State Electrode (SSE) also known as Rotating Disc Electrode (RDE) (Figure 6.6.a).

Multi Mode Electrode is found in three different forms called Dropping Mercury Electrode (DME), Static Mercury Dropping Electrode (SMDE) and Hanging Mercury Dropping Electrode (HMDE). Mercury is a very attractive choice for an electrode material because it has a high hydrogen overvoltage that greatly extends the cathodic potential window when compared to solid electrode materials. It possesses highly reproducible, readily renewable, and a smooth surface. Disadvantages of the use of mercury are its limited anodic range due to the oxidation of mercury and its toxicity. At potentials greater than +0.4V, formation of mercury (I) gives a wave that masks the curve of other oxidizable species. Positive potential limitations are caused by the large currents that develop due to oxidation of water, giving oxygen.





(a)



(b)

Figure 6.6. Figures of working electrodes

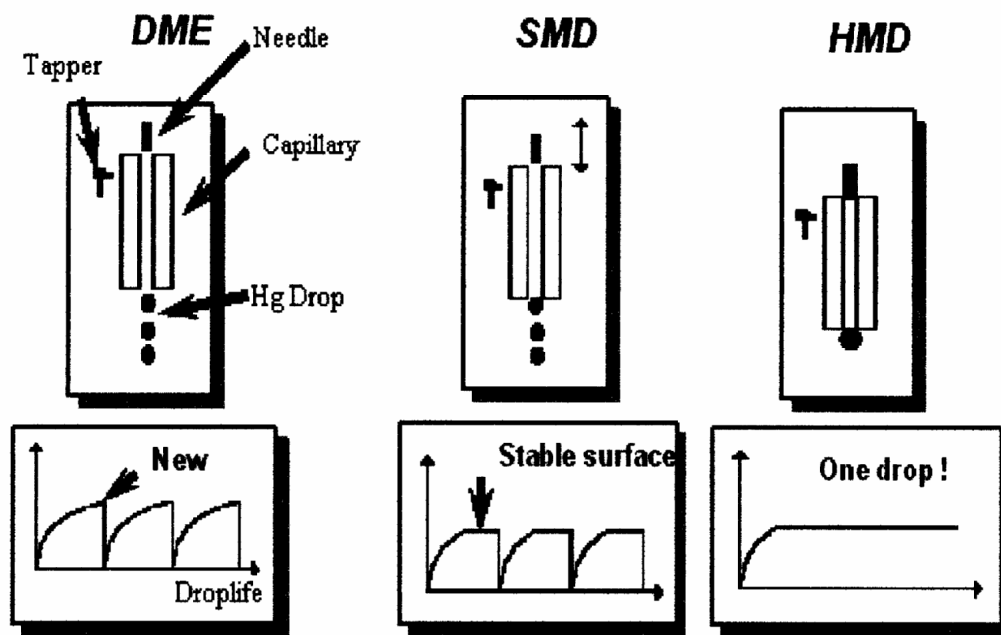


Figure 6.7. Drop profiles of different types of MME

Among the working electrodes, the suitable choice mainly depends on the concentration of the analyte in concern. For analyses at the ppm levels DME is used whereas SMDE is used for low ppm. HMDE and RDE are used for ppb and ppt levels, respectively. The nature of the analyte as well as its reduction and oxidation potentials are also the important parameters affecting the choice of the working electrodes. Figure 6.8 shows the most common working electrodes and their corresponding potential ranges. For organic material analyses usually DME and SMDE are used whereas for the trace metal determination HMDE and SSE are used [39].

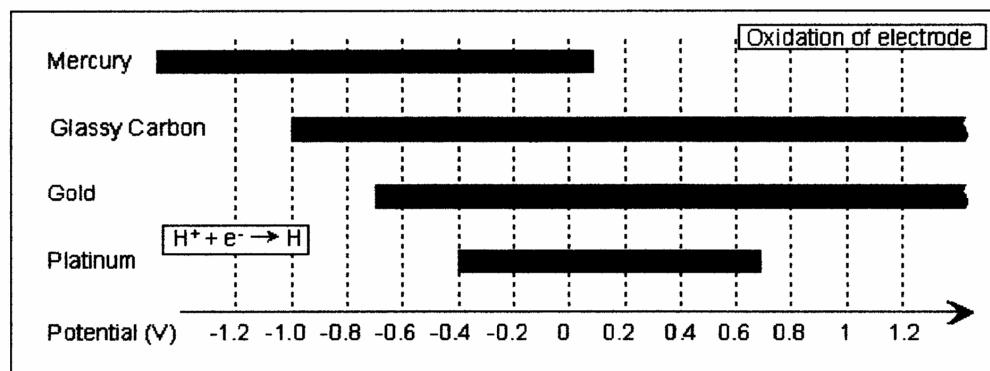
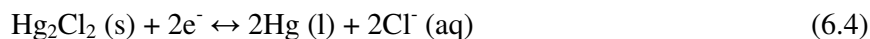


Figure 6.8. Potential ranges of different electrode types

6.3.1.2. Reference Electrode. It provides a precise and a stable potential and it is insensitive to the changes in the composition of the solution under study. The reference electrodes can be of two types; Saturated Calomel Electrode (SCE) $\text{Hg}/\text{Hg}_2\text{Cl}_2$ or $\text{Ag}/\text{AgCl} / \text{KCl}$ (3 mol/L) system. Both of them are connected to the sample solution by a salt bridge. The latter has a double junction system with an exchangeable electrolyte system. The electrode potential of the saturated calomel electrode is 0.2444 V at 25 °C with the following reaction,



Silver/silver chloride electrode has a potential of 0.199 V at 25°C with the half-reaction,



6.3.1.3. Auxiliary (Counter) Electrode. It minimizes the errors due to the cell resistance by controlling the potential of the working electrode. The auxiliary electrode can be any inert conduction electrode including mercury pool, a platinum wire, a graphite surface and glassy carbon. The auxiliary electrode is coupled to the working electrode but plays no part in determining the magnitude of the potential being measured. The current flows between the working and auxiliary electrode and it serves to conduct electricity from the source through the solution to the microelectrode [39].

6.3.2. Supporting Electrolyte

In voltammetry, theoretical treatment for deriving equations for the peak current needs minimization of migration of the metal ion caused by the electrical field. Thus, an excess of an inert supporting electrolyte is introduced into the sample solution, which lowers the transference number of the ions measured. Supporting electrolyte provides an efficient conducting medium that voltammetry requires and suitable pH value when it is necessary.

The composition of the supporting electrolyte may affect the selectivity and sensitivity of the measurement. The ideal electrolyte should give well-separated and well-shaped peaks and should be in such concentration range that it should provide high conductivity but low contamination. The choice of supporting electrolyte depends on the chemical identity and composition of analyte solution. The supporting electrolyte can be an inorganic salt, a mineral acid, and a base or a buffer system. Inorganic salts are widely used in metal analysis, mineral acids are used in the determination of organic analytes and buffer systems are used when pH control is important [39].

6.3.3. Oxygen Removal

The dissolved oxygen in the analyte solution is reduced at the surface of various electrodes forming two distinct waves during the electrolysis (Figure 6.9). The first wave corresponds to the formation of hydrogen peroxide,



and the second wave corresponds to the reduction of the peroxide,



Therefore, the resulting large background current interferes with the measurement of many reducible analytes. Also, the products of the oxygen reduction may affect the electrochemical process under investigation.

The most common method for oxygen removal is purging the solution with inert gas usually purified nitrogen, for 4-8 minutes prior to recording the voltammogram. Longer purge times may be required for large sample volumes or for trace measurements [37].

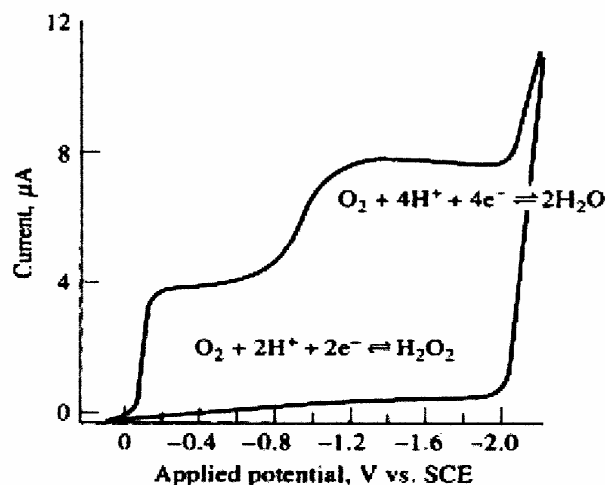


Figure 6.9. Oxygen peaks in voltammetry [37]

6.4. Stripping Methods

Stripping analysis is an electro-analytical technique that utilizes an electrolytic step to preconcentrate the analyte from the sample solution into or onto the working electrode. The working electrode may be either a mercury electrode or solid electrode such as rotating disc electrodes with gold or platinum tips. Determination of some metals like silver, gold and mercury with oxidation potentials more anodic than that of the mercury requires the use of solid electrodes with a wide anodic potential range such as gold, platinum and carbon. With those electrodes potential range can be increased up to +0.7 V values. Also, for metal analysis that cannot be based on amalgam formation with mercury, solid electrodes should be used.

The preconcentration step can be assumed as an effective electrochemical extraction and it is followed by redissolving or stripping the analyte from the microelectrode. During the analysis, electrolysis is discontinued, after a certain time stirring is stopped and the

analyte is determined by one of the voltammetric methods that have been described previously. In Figure 6.10 a linear-scan voltammetric method for anodic stripping of two different metal ions is illustrated. First peak corresponds to the least readily reduced metal ion.

The method is characterized by running extremely favorable signal to background ratio and the analysis in the 10^{-6} to 10^{-9} M range can be performed. The method is both simple and rapid [40]

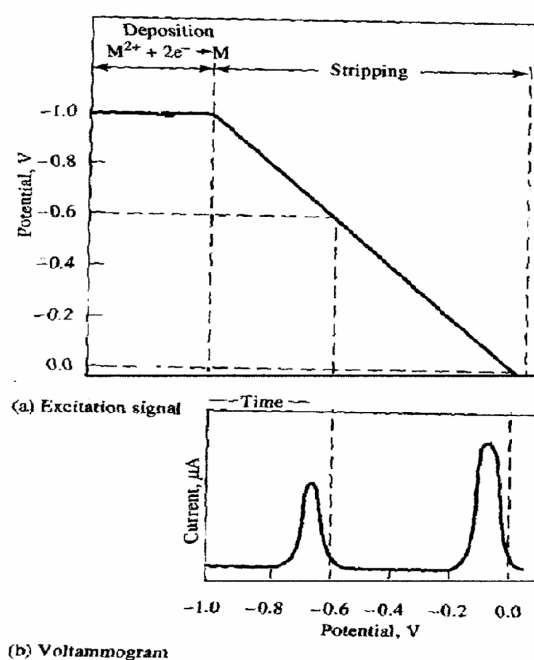


Figure 6.10. a) Excitation signal of stripping voltammetry, b) Corresponding voltammogram [37]

6.4.1. Anodic Stripping Voltammetry

Anodic Stripping Voltammetry (ASV) is the most widely used form of stripping analysis. The metals are preconcentrated by cathodic deposition on microelectrode surface by either on mercury or solid electrodes at a controlled time and potential. The deposition potential is usually 0.3-0.5 V more negative than the standard reduction potential of the

least readily reduced metal ion to be determined. At the mercury electrode, for the amalgam forming metals, the reaction is



At solid electrodes, for measurement of ions with positive redox potentials, the corresponding electrochemical reaction is



which results in a metallic film on the surface. The deposition step in stripping analysis is usually facilitated by convective transport of the metal ions to the surface of the working electrode. The convective transport is achieved by electrode rotation, solution flow or by solution stirring.

Following the deposition step there is a small rest period where convection is stopped, deposition current drops to almost zero and a uniform concentration distribution is established. During the rest period, electrodeposition, which facilitated by diffusion transport, is continued.

After the rest period, the stripping step is employed. This step consists of scanning the potential anodically. When the potential reaches the standard reduction potential of a metal-metal ion couple, that particular metal is reoxidized back into solution and a corresponding current develops;



The resulting voltammograms recorded during the stripping step provides the analytical information of interest. The stripping current is proportional to the concentration of the metal that is built in during the deposition step on the electrode surface and to its concentration in the sample solution. Peak potentials or the half-wave potentials are used to identify the metals in the sample solution and they give the qualitative information.

Elements that are commonly determined by anodic stripping are Ag, Au, Bi, Cd, Cu, Ga, Ge, Hg, In, Pb, Sn, Tl, Zn, Sb, Ba, Bi, K, Mn, Ni, Pt, Hg and As.

6.4.2. Cathodic Stripping Voltammetry

Cathodic Stripping Voltammetry (CSV) can be assumed as the mirror image of ASV. It involves anodic deposition of the analyte, followed by stripping with a negative potential scan.

CSV is used for the determination of organic and inorganic compounds and anions that form insoluble salts mercury or silver. Some species that can be determined by CSV are arsenate, chloride, bromide, iodide, sulfate, sulfide, thiocyanate and mercaptans. The application of a relatively positive deposition potential to the working electrode in the presence of those compounds results in the formation of an insoluble film of the salt on the electrode surface. This mainly can be performed on mercury working electrode, although silver electrodes can be used for some species such as halides or sulfides [40].

The reaction in the deposition step can be represented as



where M is the electrode material, A^{n-} is the analyte, and MA is the soluble salt in the form of a film on the electrode surface [40].

As in the ASV, the solution containing the analyte is usually stirred continuously during the deposition step. Following the preconcentration step, the deposit is stripped off and measured during a cathodic potential scan with the following reaction.



6.5. Evaluation of Data

A voltammogram and the representative standard addition curve are shown in Figure 6.11. The bold curves show the two replications of the analyte measurement whereas the dashed curves show the standard addition curves which were performed as two replicates.

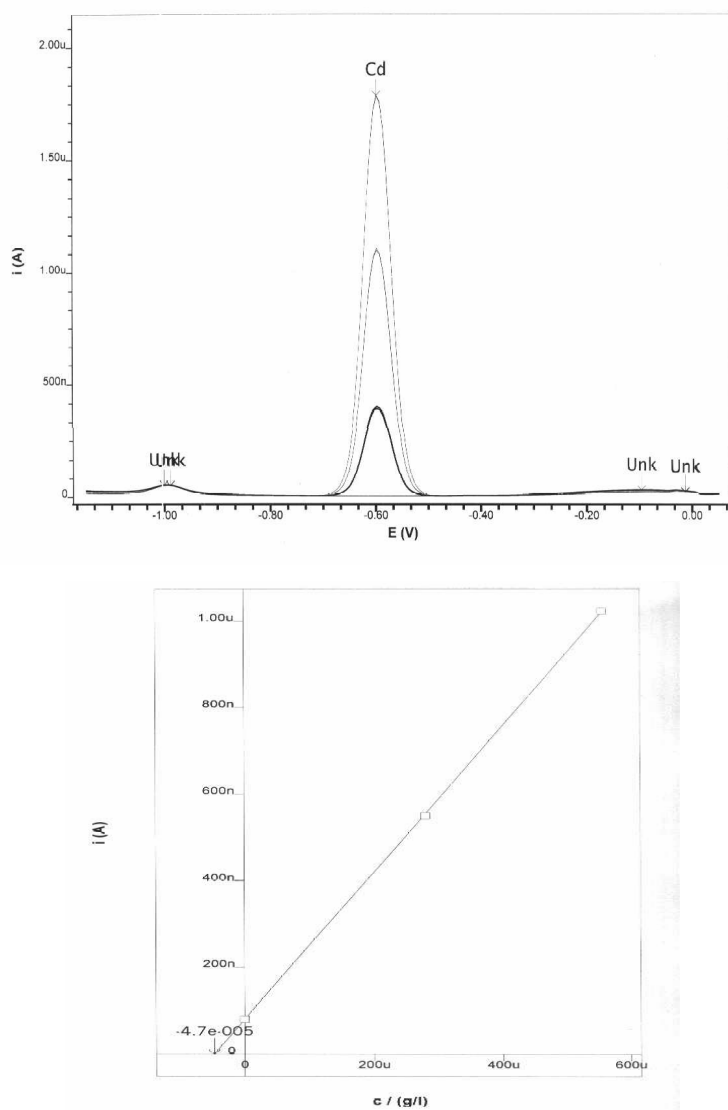


Figure 6.11. A voltammogram and standard addition curve

In this study, the evaluation of data was performed by standard addition method. Standard addition method requires single or multiple addition of a standard solution. The following procedure was used to calculate the concentration of the sample:

Measurement of sample solution: The sample solution with unknown mass concentration $c(s)$ was measured twice.

Measurement of spiked sample solutions: The sample solution was spiked twice with a standard solution of known mass concentration. Each of these spiked solutions were measured twice.

7. REAGENTS AND INSTRUMENTS

7.1. Reagents

7.1.1. Surfactants

7.1.1.1. Sodium Dodecyl Sulfate (SDS). SDS was supplied from Sigma Chemicals Company. As an anionic surfactant it was found in white powdered form with 99 per cent purity. It was used in the adsorption experiments on soil with different concentrations ranging from 2 to 12 mM. In the experiments considering the interaction between polluted soil and SDS, 6, 8, 10, and 12 mM SDS were used.

7.1.1.2. Hyamine 1622 (Benzethonium Chloride). Hyamine 1622 was supplied from Sigma Chemicals Company. As a cationic surfactant it was used in the two phase titration experiments to determine the amount of adsorbed anionic surfactant by the soil. 4 mM Hyamine 1622 solution was used as a titrant in the two phase titration.

7.1.2. Chloroform

Chloroform with purity between 99 and 99.4 per cent was supplied from Merck. It was used in the two phase titration experiments to form the second phase other than the aqueous phase.

7.1.3. Indicator Solution

Dimidium Bromide-Disulphine Blue solution was used in the two phase titration experiments as an indicator. It was supplied from BDH Laboratory Chemicals Inc. It was prepared by mixing 20 mL of stock solution with 20 mL of 2.5 M H_2SO_4 and diluting to the final volume of 500 mL with distilled water.

7.1.4. Sulphuric Acid (H_2SO_4)

H_2SO_4 was supplied from Merck. Its purity was between 95.0 and 98.0 per cent. It was used for the preparation of the indicator solution. A 2.5 M H_2SO_4 solution was prepared by taking 13.8 mL from the stock solution and diluting to the final volume of 100 mL with distilled water.

7.1.5. Acetate Buffer Solution

Acetate buffer solution was prepared by using concentrated acetic acid (CH_3COOH) and aqueous ammonia (NH_3) which were both supplied from Merck. This buffer solution was used in the voltammetric measurements. It was prepared by mixing a 11.76 mL of CH_3COOH with a 7.47 mL of aqueous NH_3 and diluting to 100 mL. The final pH measurement registered between 4.60 and 4.80.

7.1.6. Phosphate Buffer Solution

It was prepared by dissolving 12.8 g monopotassium phosphate (KH_2PO_4) and 15.8 g dipotassium phosphate (K_2HPO_4) in 1 L deionized water and the pH of the prepared buffer solution was 6.94. Both KH_2PO_4 and K_2HPO_4 were supplied from Merck.

7.1.7. Carbonate Buffer Solution

It was prepared by dissolving 8.4 g sodium bicarbonate (NaHCO_3) and 10.6 g sodium carbonate (Na_2CO_3) in 1 L deionized water and the pH of the prepared buffer solution was 10.03. Both NaHCO_3 and Na_2CO_3 were supplied from Merck.

7.1.8. Cadmium (Cd) Standard Solution

$\text{Cd}(\text{NO}_3)_2$ solution of a 1000 ppm concentration was supplied from Merck. A 4, 6, and 8 ppm of cadmium solutions were prepared from this stock solution to pollute the soil artificially. These concentrations for the cadmium solutions were chosen according to soil

pollution parameters taken from Turkish Ministry of Environments. 10 and 30 ppm of solution was also prepared for use in voltammetric measurements.

7.1.9. Potassium Chloride Solution (KCl)

KCl solution (3 M) was supplied from Metrohm. It was used in the voltammetric measurements.

7.1.10. Titriplex III (EDTA)

Titriplex III known as EDTA was supplied from Merck. It was used as a chelating agent during the heavy metal-SDS-ligand interaction experiments. EDTA is a hexadentate ligand. It has six potential sites for bonding a metal ion: the four carboxyl groups and the two amino groups. Cadmium has formation constant for EDTA complex equals to 2.9×10^{16} .

7.1.11. Ethylene Diamine (EN)

EN was supplied from Merck and it was used as a chelating agent in the heavy metal-SDS-ligand interaction experiments. EN is a bidantate ligand with two amine groups which are the potential sites for bonding a metal ion. Cadmium has formation constant for EN complex equals to 1.2×10^{12} .

7.1.12. Hydrochloric Acid (HCl)

10 per cent HCl, which was supplied from Merck, was used in cleaning the glasswares and analyte cell during the voltammetric measurements.

7.1.13. Potassium Dichromate ($K_2Cr_2O_7$)

$K_2Cr_2O_7$, which was used in the analysis of organic carbon content of soil, was supplied from Merck.

7.1.14. Ferrous Sulfate (FeSO_4)

FeSO_4 also used in the analysis of organic carbon content of soil was supplied from Merck.

7.1.15. Calcium Chloride (CaCl_2)

CaCl_2 used both in the pH and cation exchange capacity analysis of soil and it was supplied from Merck.

7.1.16. Barium Chloride (BaCl_2)

BaCl_2 used in the cation exchange capacity analysis of soil and it was supplied from Merck.

7.1.17. Ferroin Indicator Solution

Ferroin indicator solution which was used in the titration part of the organic carbon content analysis of soil was prepared by dissolving 1.485 g O-phenanthroline monohydrate which was supplied from Merck and 0.695 g ferrous sulfate in approximately 80 mL deionised water. Then it was diluted to 100 mL. The prepared solution was stored in a dark bottle away from light.

7.2. Instruments**7.2.1. 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.

7.2.2. Mechanical Shaker

Two mechanical shakers MRC Water Bath Shaking BT-350 and Memmert WB 14 were used to equilibrate the soil and the reactants.

7.2.3. Analytical Balance

Gec Avery analytical balance with maximum load of 200 g and a precision of 0.1 mg was used.

7.2.4. Voltammetric Analyser

Voltammetric measurements were carried out by using Metrohm 757 VA Computrace Voltammetric Analyser with a three electrode cell system. Rotating Disc Gold Electrode with a gold tip was used as the working electrode where Glassy Carbon and Ag/AgCl electrodes were served as the auxiliary and reference electrodes, respectively.

As a voltammetric method, DPASV was used in order to determine the amount of heavy metal (Cd) in the sample solutions. The Cd determination method was developed by optimizing the deposition time, stirring rate and deposition potential parameters.

The analytes for the voltammetric measurements were prepared by taking 10 mL of sample solution, 0.5 mL of acetate buffer solution and 0.1 mL of 3 M KCl solution. Dilutions of the sample solutions were done by using deionized water. The cleanliness of the analyte cell and the glasswares were both very important for the voltammetric measurements. Therefore, the analyte cell of voltammetry and the glassware used during the experiments were kept in 10 per cent HCl solution between the runs.

7.2.5. Atomic Absorption Spectrophotometer (AAS)

AAS was used to determine the cation exchange capacity of soil in terms of its calcium content. The instrument was Varian SpectrAA 250 Plus and the working conditions were given in Table 7.3.

Table 7.1. Working conditions of AAS for Calcium determination

Lamp Current	10 mA
Fuel	Acetylene
Support	Air
Flame Stoichiometry	Reducing:red cone 1-1.5 cm high
Wavelength	422.7 nm
Spectral Band Pass	0.2 nm

In normal conditions, for the analysis of calcium the supporting gas should nitrous oxide but the concentration of calcium was very high therefore the interferences coming from acetylene-air combination were ignored.

8. EXPERIMENTAL METHODS

8.1. Methodology for Soil Analysis

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.

Soil analysis were carried out in order to specify its characteristics such as its pH value, texture, water, organic matter content, and its cation exchange capacity. The initial heavy metal content of soil was determined by wet ashing followed by voltammetric measurements.

8.1.1. pH Analysis

The pH analysis of soil was carried out by two different procedures. Samples were prepared in two replicates.

8.1.1.1. Soil:Water (1:5) Suspension. A 10.0 g air-dry soil was weighed into a bottle and 50 mL of deionised water was added. The prepared soil suspension was mechanically shaken for 1 hour at 15 rpm. After 1 hour, the electrode of the pH-meter was immersed into the soil suspension and the measured pH values were recorded as the equilibrium was reached while stirring with a mechanical shaker [41].

8.1.1.2. Soil: 0.01 M CaCl₂ (1:5) Suspension. A 10.0 g air-dry soil was weighed into a bottle and 50 mL of 0.01 M CaCl₂ solution was added. The soil suspension was shaken by hand and then it was allowed to settle for 30 minutes. After 30 minutes, the electrode was immersed into the supernatant part of the soil suspension and the measured pH values were recorded when the pH-meter became steady [41].

8.1.2. Soil Texture Analysis

In order to determine the gravel, sand, silt and clay content in the soil used in our experiments, the soil texture analysis was carried out. Before applying the soil texture analysis procedure, the soil was dried at 60⁰C for one day. Higher temperatures were avoided not to damage the organic content of the soil. After the drying step, the soil was passed through the sieves with number 4, 10, 20, 40, 70 ,100 and 200. The soil remaining under the sieve number 10 gave the gravel percentage and the soil under the sieve number 200 gave the silt and clay percentage of the soil. The remaining percentage indicated the sand amount in the soil [41].

8.1.3. Water Content Analysis

The water content experiment was done with two replicate soil samples. Weighing bottles were brought to a constant weight at 105⁰C prior to analysis. Soil samples were placed into the weighing bottles. The weight of the soil samples and the weighing bottles were recorded together before and after drying in the oven at 105⁰C for 24 hours. They were cooled in a dessicator prior to weighing procedure. The difference in weights indicated the amount of water in the soil [42].

$$\text{Water Content (\%)} = (M_w - M_d) / M_d \times 100 \quad (8.1)$$

where:

M_w = Mass of wet soil sample (wet weight – tare weight)

M_d = Mass of dry soil sample (dry weight – tare weight)

8.1.4. OMC Analysis

Soil samples were weighed between 0.5 and 1.0 g and placed into a 250 mL conical flask. A 10 mL of 1 N K₂Cr₂O₇ was added to the soil sample and the flask was swirled gently to disperse the soil in the solution. Concentrated H₂SO₄ was added into the suspension and the flask was swirled immediately until the solution and the reagent were

mixed. The flask contents were heated up to 135°C by swirling the flask. The suspension was set aside to cool for 20 or 30 minutes and then it was diluted to 200 mL with deionized water and the experiment proceeded by FeSO₄ titration using the ferroin indicator. In the titration part, three or four drops of ferroin indicator were added and the solution was titrated with 0.4 N FeSO₄. When the end point was reached, the solution had greenish color and then changed into a dark green. At this point, FeSO₄ was added drop-by-drop until the color changed sharply from blue-green to reddish-grey. This OMC was carried out with two replicate soil samples and a blank solution. The reaction of this titration is given below [43].



According to this reaction, 1 mL of 1 N dichromate solution is equivalent to 3 mg of carbon. The percentage of organic carbon is determined from the following equation:

$$\text{Organic Carbon (\%)} = \frac{0.003 \text{ g} \times \text{N} \times 10 \text{ ml} \times (1 - \text{T} / \text{S}) \times 100}{\text{ODW}} \quad (8.3)$$

$$= \frac{3(1 - \text{T} / \text{S})}{\text{W}} \quad (8.4)$$

where:

N = Normality of K₂Cr₂O₇

T = Volume of FeSO₄ used in the sample titration (mL)

S = Volume of FeSO₄ used in the blank titration (mL)

ODW = Oven-dry sample weight (g)

8.1.5. CEC Analysis

A 2.0 g dried soil samples were weighed and placed in the centrifuge tubes and 15 mL of 0.1 M CaCl₂ solution were added into the tubes. The tubes were shaken in the mechanical shaker with water bath for 24 hours at 25°C, and were centrifuged at 6000 rpm for 30 minutes to separate liquid and soil phase. The liquid was discarded and the soil was

subsequently saturated with Ca^{2+} by repeating the above operation two more times. Salt was washed with distilled water repeatedly until free of Cl^- , and Ca^{2+} was extracted with 15 mL 0.1 M BaCl_2 solution three times [44]. The concentration of the Ca^{2+} was determined by AAS according to the parameters given in the section 7.2.5. The experiments were run in two replicates.

8.1.6. Wet Ashing Procedure for the Initial Heavy Metal Content in Soil

A 1.0 g of dry soil sample was weighed and equal volumes (5 mL) of concentrated HNO_3 and concentrated HCl were added. The sample was allowed to sit at room temperature for at least one hour before heating. Then the sample was digested for two hours at a temperature of $90 \pm 5^\circ\text{C}$ on a hot plate [45]. The digested sample was washed with 100 mL of deionized water in order to measure the zinc (Zn), cadmium (Cd), lead (Pb) and copper (Cu) content in the soil sample by voltammetric analysis. The experiments were run in two replicates.

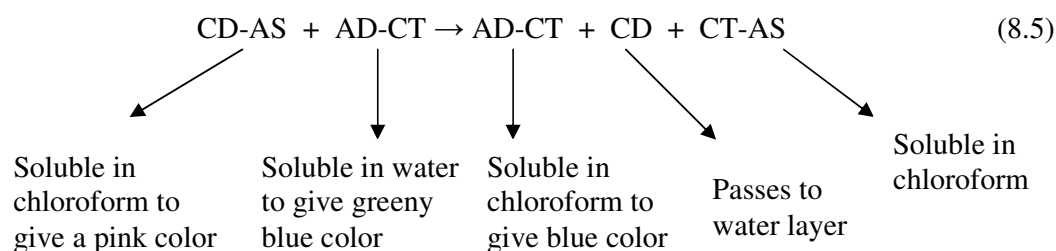
8.2. Methodology for Surfactant-Soil Interaction

The interaction between surfactant and soil was investigated by using the two-phase titration method.

Soil samples of 10 g each were taken and a 40 mL of 2, 4, 6, 8, and 12 mM SDS solutions were added. The surfactant-soil suspensions were shaken on the mechanical shaker with water bath at $(25 \pm 2^\circ\text{C})$ for 72 hours to establish equilibrium [46].

In the two-phase titration, anionic-active matter is determined by titration with a standard cationic-active solution. The solution for anionic surfactant determination (indicator) consists of a mixture of a cationic dye (Dimidium Bromide) and an anionic dye (Disulphine Blue VN) and the titration process is carried out in a two-phase aqueous-chloroform system. During two-phase titration, the anionic surfactant forms a salt with the cationic which dissolves in the chloroform layer to give this layer a red-pink color. At the end point, the Hyamine 1622 cation displaces the Dimidium cation from the chloroform

soluble salt and the pink color leaves the chloroform layer as the dye passes to the aqueous phase. Hyamine 1622 in excess forms a salt with the anionic dye Disulphine Blue VN which dissolves in the chloroform layer and colors it blue [47].



where:

AS = Anionic Sample (SDS)

CT = Cationic Titrant (Hyamine 1622)

CD = Cationic Dyestuff (Dimidium Bromide)

AD = Anionic Dyestuff (Disulphine Blue VN)

According to the procedure of a two-phase titration method, a 10 mL of unknown sample was taken above the soil after the shaking for 72 hours and mixed with 5 mL of distilled water, 7.5 mL of chloroform and 5 mL of indicator in order to form the two phases. The titration was done by using 4 mM Hyamine 1622 and the concentration of the anionic surfactant, SDS, was determined. By taking the difference between the initial concentration of SDS and the concentration in the solution, the amount of SDS adsorbed by the soil was found. According to the results of two-phase titration, C_e , the concentration of SDS remaining in the aqueous solution after the surfactant is adsorbed on the soil at equilibrium, and C_s , the content of SDS adsorbed per gram of soil, were calculated. The plots of C_e versus C_s , were investigated to determine the CMC of SDS [48].

8.3. Optimization of Method Parameters for Voltammetry

To develop a method for cadmium determination, the pH of the analyte cell and the parameters of the method like deposition time, stirring rate and deposition potential should be determined.

To decide the pH of the media, 4 ppm Cd sample solution was analysed with different buffer solutions like acetate buffer with pH of 4.76, phosphate buffer with pH of 6.92 and carbonate buffer with pH of 10.03. The suitable buffer was selected for the experiments of Heavy Metal-Soil and Polluted Soil-SDS Interactions.

Other than pH of the analyte cell; deposition time, stirring rate and deposition potential of the method were optimized for each cadmium concentrations used in the experiments. The parameters with suitable results for HMDE which was the working electrode were selected for the method developed.

8.4. Methodology for Cadmium (Cd)-Soil Interaction

Cd-soil interactions were investigated to determine the time needed to establish the equilibrium between soil and the pollutant, cadmium. The samples were prepared according to (V/m) ratio where V represents the volume of Cd solution added to the soil sample at 4, 6, and 8 ppm concentration levels and m stands for the mass of soil sample used. To determine the equilibrium time, samples with a (V/m) ratio of 20, 30, and 40 mL/g were prepared and placed on a mechanical shaker to be shaken for 2, 6, 16, 20, 25, 30 and 36 hours. The soil mass (m) was taken as both 1.0 g and 2.0 g weight. Amount of cadmium that was not retained by the soil was determined by DPASV technique. These data obtained by voltammetry were plotted versus experiment time to determine the equilibrium time between the soil and the Cd solution. According to these experiments, the equilibrium time was found to be 25 hours at 4, 6, and 8 ppm concentration levels of cadmium.

To see the difference of the Cd adsorbed by soil at 25 hours and 5 days, another set of experiment was prepared. Samples were shaken for 5 days again at the same

temperature and the same concentration levels of cadmium. Then the concentrations of Cd adsorbed by soil after 25 hours and 5 days were compared at each V/m ratio and Cd concentration whether the concentration values were different or not for each experiment time.

In order to indicate the effect of water on the polluted soil, another set of experiments for each concentration of cadmium were prepared. In these experiments, the polluted soils with cadmium for 25 hours were collected and dried in the oven at around 100°C. Water according to (V/m) ratios was added on the dried polluted soils and these left in the mechanical shaker for again 25 hours.

8.5. Methodology for Polluted Soil and SDS Interaction

The procedure of this part includes two steps to be followed. In the first step, 2.0 g soil samples were polluted with 4, 6 and 8 ppm Cd solutions in the ratios of 20, 30 and 40 mL/g for 25 hours shaking in the mechanical shaker like in Section 8.4. The polluted soil was separated from the supernatant by using filter papers and dried in the oven at 100°C. When the soils got dried, they were tried to be cleaned by anionic surfactant, SDS, of different concentrations again with the same ratios used during polluting the soil. The soils polluted with each Cd concentrations were allowed to interact with three different SDS concentrations (6, 8 and 10 mM) which were determined according to the CMC value of SDS found in the “Surfactant-Soil Interaction” part.

8.6. Methodology for Polluted Soil, Surfactant SDS and Ligand Interactions

To increase the effect of SDS on cadmium desorption from polluted soil, commonly known ligand EDTA was used. When a ligand is used, it forms a complex with the metal ion and the formed complex has low hydrophilicity. With this low hydrophilicity the metal-ligand complex enters easily into the micelle formed by anionic surfactant SDS.

Initially, standard solutions with 4 ppm cadmium and changing EDTA concentrations were prepared and analysed with acetate buffer (under acidic conditions) by

DPASV. Also cadmium-EDTA mixtures were analysed by using different buffer solutions like phosphate and carbonate buffer with neutral and basic conditions, respectively.

Another ligand was also searched when EDTA gave no reproducible results with any buffer solutions. EN was used as a ligand in place of EDTA. The prepared solutions by using 4 ppm cadmium and 0.1 mM EN were analysed with phosphate buffer (under neutral conditions) by DPASV and then cadmium solutions with higher EN concentrations were also analysed to see the effect of EN concentration. When reproducible results were obtained, the same Cd-EN solutions were prepared in the presence of SDS analysed by again DPASV in order to determine whether SDS and EN were suitable for each other to decontaminate the soil from cadmium.

9. RESULTS AND DISCUSSION

9.1. Soil Analysis

9.1.1. pH Analysis

9.1.1.1. Soil:Water (1:5) Suspension. Two 10 g of soil samples were weighed and mixed with deionized water. After shaking for 1 hour, the pH of the suspensions were measured by immersing the electrodes into the suspensions. The data collected for the two soil samples are given in the Table 9.1.

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

	Soil Sample 1	Soil Sample 2	Avarage 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.

9.1.1.2. Soil: 0.01 M CaCl₂ (1:5) Suspension. In this procedure, again two 10 g of soil samples were weighed and mixed with 0.01 M CaCl₂ solution. After waiting for 30 minutes, the pH values of the settled suspensions were recorded and the values are given in Table 9.2.

Table 9.2. pH values of soil samples according to the soil:0.01 M CaCl₂ (1:5) suspension procedure

	Soil Sample 1	Soil Sample 2	Avarage pH
pH	5.02	4.95	4.98

This procedure also indicated that the soil used in the experiments was acidic.

When the data collected from two different procedures are compared, the average pH values are slightly different from each other but as a result both procedures determined that the soil is acidic.

9.1.2. Soil Texture Analysis

A 300 g of soil weighed and reduced to small particles in size. After leaving the sample in the oven for one day at 60⁰C, soil was passed through the different sieves with numbers 4, 10, 20, 40, 70, 100, 200. By taking the weight of the sample remained under the sieves, the percentage content of soil was calculated. According to data given in Table 9.3, it was determined that the soil type was sand with the heighest percentage equals to 85.71 per cents.

Table 9.3. Soil texture percentages

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

9.1.3. Water Content Analysis

In the water content analysis, initially the two jars for the replicate soil samples were weighed and again they were weighed when approximately 5 g of soil samples were placed in. The jars containing the soil samples were placed in the oven for one day at 115°C. After removing the jars from the oven, their final weights were taken when they cooled. The wet and dry weights of soil samples are shown in the Table 9.4.

Table 9.4. Wet and dry weights of the two soil samples

	Soil Sample 1	Soil Sample 2	Average
Wet Weight (g)	5.00	5.01	5.00
Dry Weight (g)	4.89	4.89	4.89

The water content was determined by using the average values of the two soil samples and it was calculated as 2.39 per cent.

9.1.4. OMC Analysis

In the OMC determination, the important parameters are the volumes of FeSO₄ used in the sample titration and in the blank titration. In the Table 9.5, the volumes of FeSO₄ are presented for the calculation of the OMC in percentages.

Table 9.5. Volumes of FeSO₄ used in the blank and sample titrations to determine the OMC

	Volume of FeSO ₄ used in the titration (mL)
Average of Blank Solutions	23.05
Average of Sample Solutions	6.20

According to these titrations results, the OMC of the soil was determined as 2.73 per cent by using the OMC equation given in section 8.1.4.

9.1.5. CEC Analysis

The determination of cation exchange capacity was carried out by saturating the soil sample with Ca^{2+} . When the saturation was completed, the amount of Ca^{2+} taken by the soil was determined by using AAS. To prepare the calibration curve for AAS, 25, 50, and 100 ppm calcium standard solutions were used and absorbances of these concentrations were recorded (Table 9.6).

Table 9.6. Absorbances of the standard calcium solutions used to prepare the calibration curve

Standard Calcium Solution (ppm)	Absorbance
25	0.114
50	0.203
100	0.427

The absorbance values of the standard solutions were plotted versus their concentrations to prepare the calibration curve.

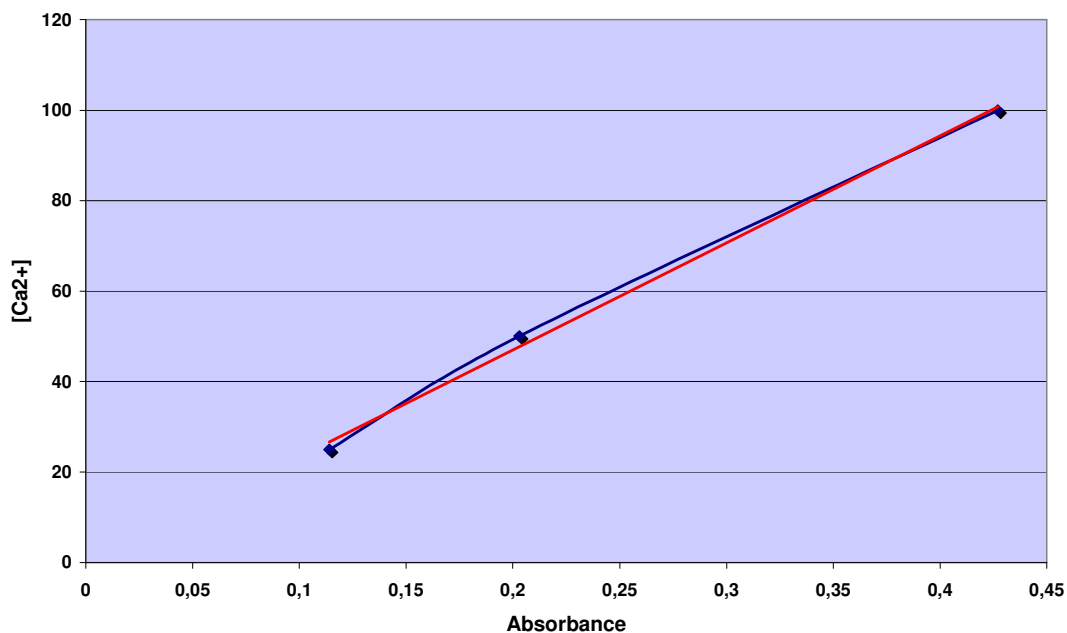


Figure 9.1. Plot of Ca^{2+} concentration of standard solutions versus their absorbance values for calibration curve with R^2 equals to 0.9971.

After the preparation of calibration curve, replicate sample solutions, with dilution factor 4, were analyzed by AAS and the absorbance of these samples were found to be 0.408 and 0.452, which corresponds to the Ca^{2+} concentrations of 96.16 and 106.57 ppm, respectively. Therefore, it was concluded that the original soil samples had 384.66 and 426.27 ppm Ca^{2+} .

The CEC is generally expressed in the cmol/kg unit [2]. When the ppm values of Ca^{2+} concentrations were converted into this unit, the average CEC of the soil was found to be 22.81 cmol/kg.

9.1.6. Wet Ashing Procedure for the Initial Heavy Metal Content in Soil

This procedure was carried out by using three soil samples with 1 g weight. The digested samples were washed with 100 mL of deionized water and analysed by voltammetry to determine the amount of metals (Zn, Cd, Pb and Cu) in the initial content

of soil. The concentration of each heavy metal in 100 mL of solution for each soil sample is given in Table 9.7.

Table 9.7. The initial Zn, Cd, Pb and Cu content in the soil sample 1, 2 and 3

	Zn (ppb)	Cd (ppb)	Pb (ppb)	Cu (ppb)
Soil Sample 1	120.00	11.37	124.53	73.08
Soil Sample 2	100.00	12.23	117.27	33.71
Soil Sample 3	105.00	13.24	118.65	41.15

These data indicated that the soil used was vertically clean of heavy metals in the beginning.

9.2. Surfactant-Soil Interaction

The interaction of SDS with the acidic soil was investigated to see the exact value of CMC of SDS when it was in the interaction with acidic media. As it was mentioned in the experimental methods part, different concentrations of SDS (2, 4, 6, 8, and 12 mM) solutions and soil left in mechanical shaker at $(25 \pm 2^{\circ}\text{C})$ for three days for the establishment of the equilibrium between the soil and the anionic surfactant. The samples taken from above the soils were analysed by the two-phase titration procedure and the concentration of SDS remaining in the aqueous solution after the adsorption, C_e , and the content of SDS adsorbed per gram of soil, C_s , were calculated. The soil-SDS interaction experiments were done in replicates to compare the results. In Table 9.8., C_e and C_s results obtained from two experiments are given.

Table 9.8. Soil-SDS Interaction Data of Experiment 1 and 2 for 72 hours

SDS (mM)	C_e (mg/L)		C_s (mg/g)	
	Experiment 1	Experiment 2	Experiment 1	Experiment 2
2	0.75	0.72	2.26	2.31
4	12.52	11.96	4.60	4.61
6	24.11	24.60	6.90	6.90
8	43.65	44.66	9.20	9.20
12	81.67	99.91	13.78	13.76

The values of C_e and C_s were plotted to see the soil-SDS interaction. As it is shown in Figure 9.2 and Figure 9.3, a breaking point was observed in the C_e versus C_s graph. When the graph was examined, it was determined that the breaking point occurred at 8×10^{-3} mM of SDS concentration. As a result, it is found that SDS gave approximately the same CMC value during the interaction with acidic soil with the theoretical one which is equal to 8.2×10^{-3} mM [48].

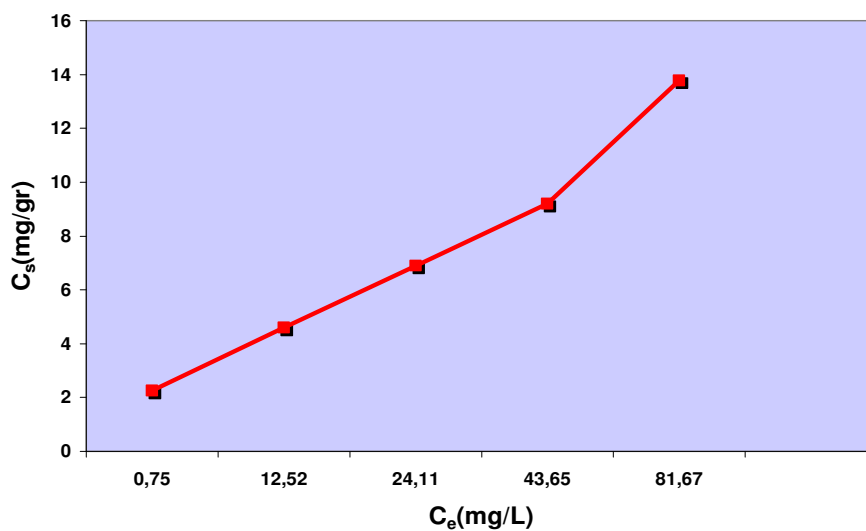


Figure 9.2. Plot of C_s versus C_e for adsorption isotherm of SDS (2, 4, 6, 8, and 12 mM) on soil (Experiment 1)

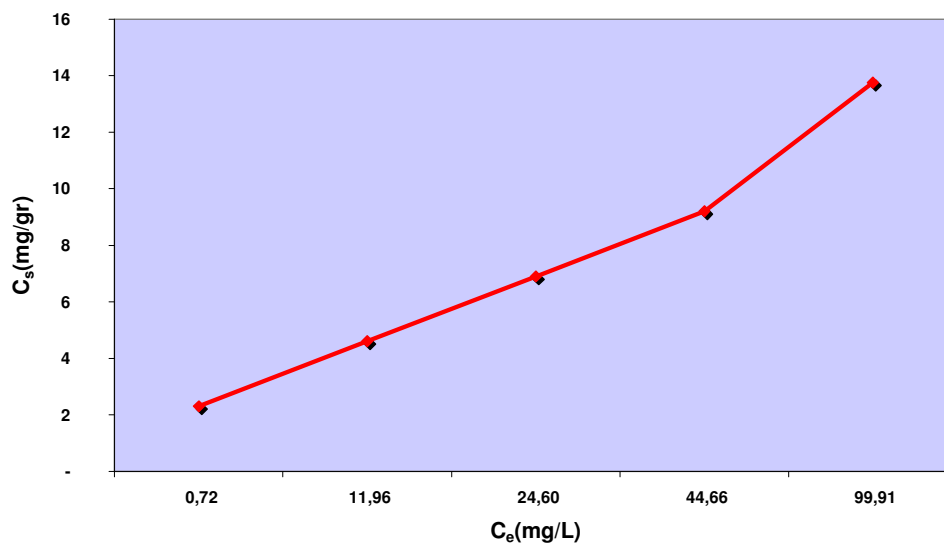


Figure 9.3. Plot of C_s versus C_e for adsorption isotherm of SDS (2, 4, 6, 8, and 12 mM) on soil (Experiment 2)

9.3. Optimization of Method Parameters for Voltammetry

9.3.1. Optimization of the Electrolyte

In order to decide which pH condition was suitable for the cadmium determination, 4 ppm cadmium sample solution was analysed with three different buffer solutions which were acetate buffer with pH of 4.76, phosphate buffer with pH of 6.92 and carbonate buffer with pH 10.03.

Table 9.9. Results obtained for 4 ppm cadmium standard solution with different buffer solutions

Buffer Type	Half-wave Potential(V)	Concentration (ppb)
Acetate Buffer(acidic)	-0.598	3965±6.49
Phosphate Buffer(neutral)	-0.609	3619±2.75
Carbonate Buffer(basic)	-0.645	3274±3.54

According to the results given in Table 9.9, the experiments for Heavy Metal-Soil and Polluted Soil-SDS Interactions were carried out under acidic conditions by using acetate buffer during the voltammetric analysis because it gave the closest concentration value to the real one. Another reason for having acidic condition was that the soil used in the experiments had acidic pH value therefore the experiments with soil were carried out under acidic conditions.

By using acetate buffer during the voltammetric analysis, the other parameters like deposition time, stirring rate and deposition potential were optimized according to the working electrode (HMDE) used during the experiments.

9.3.2. Optimization of Deposition Time

Table 9.10. Deposition time optimization for Cd determination

Deposition Time (s)	Current (nA)		
	4 ppm Cd	6 ppm Cd	8 ppm Cd
60	324	493	678
90	452	698	956
120	590	898	1230
140	690	1060	1420

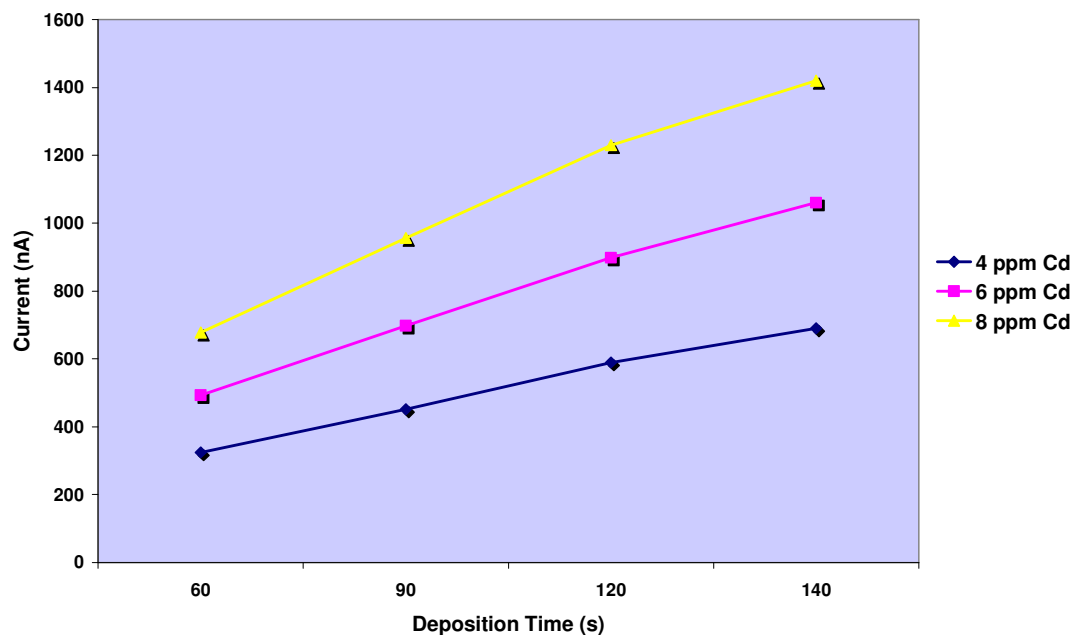


Figure 9.4. Plot of current versus deposition time for optimization of Cd analysis

When the currents obtained for the deposition time values were concerned, it was determined that when the deposition time was above 90 seconds during 8 ppm Cd determination, the current values became greater than 1000 nA which were above the current limits of HMDE, the electrode used during the voltammetric analysis. Therefore, for each concentration of cadmium the deposition time were taken as 90 seconds.

9.3.3. Optimization of Stirring Rate

Table 9.11. Stirring rate optimization for Cd determination

Stirring Rate (rpm)	Current (nA)		
	4 ppm Cd	6 ppm Cd	8 ppm Cd
1600	415	640	862
1800	444	666	876
2000	484	698	956
2200	512	777	1020
2400	532	818	1070

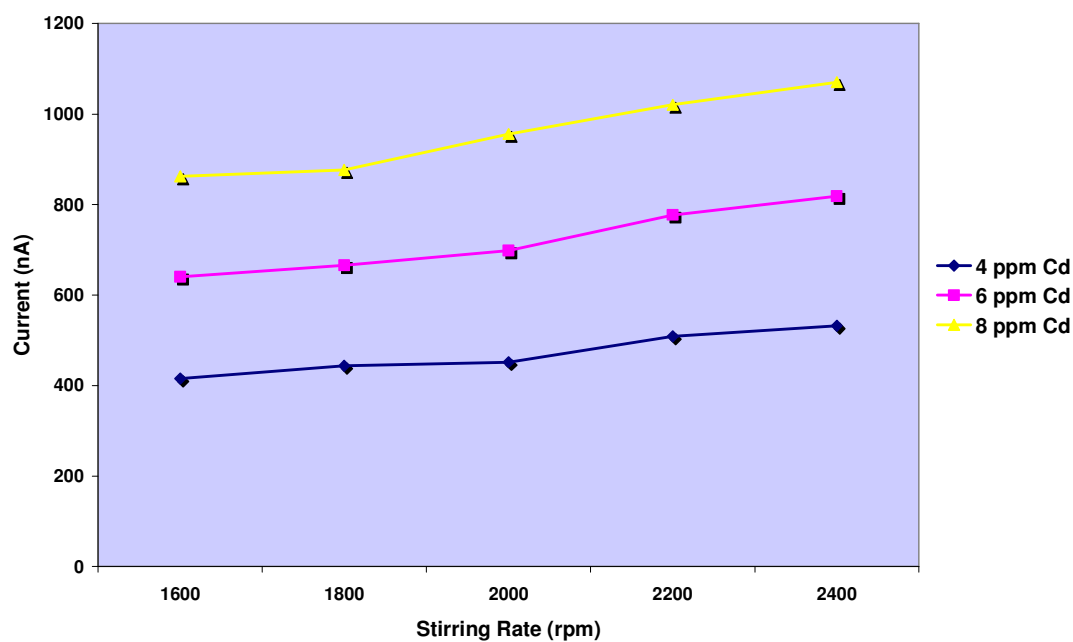


Figure 9.5. Plot of current versus stirring rate for optimization of Cd analysis

As the stirring rate increased the current values obtained also increased. In the 8 ppm Cd determination when the stirring rate applied at the values above 2000 rpm, the currents determined became higher than 1000 nA. Because of the same discussion carried out in the deposition time optimization, the stirring rate was taken as 2000 rpm for each cadmium concentrations.

9.3.4. Optimization of Deposition Potential

Table 9.12. Deposition potential optimization for Cd determination

Deposition Potential (V)	Current (nA)		
	4 ppm Cd	6 ppm Cd	8 ppm Cd
-1.0	467	676	1060
-1.2	479	712	1140
-1.4	468	710	1120

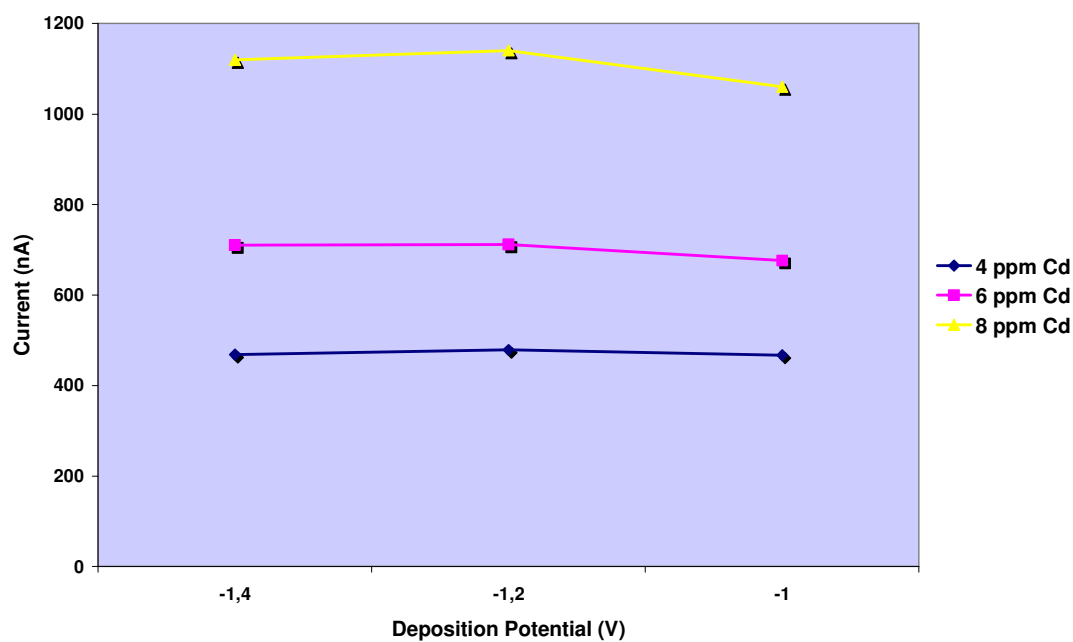


Figure 9.6. Plot of current versus deposition potential for 4, 6, and 8 ppm Cd determination

In optimization of deposition potential, it was observed that as the deposition potential exceeded -1.2 V, the current obtained decreased for each cadmium concentration since the deposition value became far away from the half-way potential of cadmium which is equal to -0.56 V. Therefore, the deposition value was taken as -1.10 V which is the mean of -1.0 and -1.2 V

After the optimization step, the determination and voltammetric parameters for the analysis of cadmium were given in Table 9.13 and 9.14, respectively.

Table 9.13. Determination Parameters

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

Table 9.14. Voltammetric Parameters

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 Amplitude (V)	0.05
Pulse Time (s)	0.04
Voltage Step Time (s)	0.1
Sweep Rate (V/s)	0.0595
Stirring Rate (rpm)	2000

9.4. Cadmium (Cd)-Soil Interaction

9.4.1. Cd-2 g Soil Interaction

2 g soil experiments were carried out by using cadmium solutions in different concentration levels (4, 6, and 8 ppm) and (V/m) ratios (20,30, and 40 mL/g) for 2, 6, 16, 20, 25, 30, and 36 hours in order to find the equilibrium time for cadmium-soil interactions.

The amount of metal that was not adsorbed by the soil was determined by analysing the solution above the soil with DPSPV under previously specified voltammetric and determination conditions in Section 9.3. An example for the voltammogram of the results of polluting the soil for 25 hours is given in Figure 9.7.

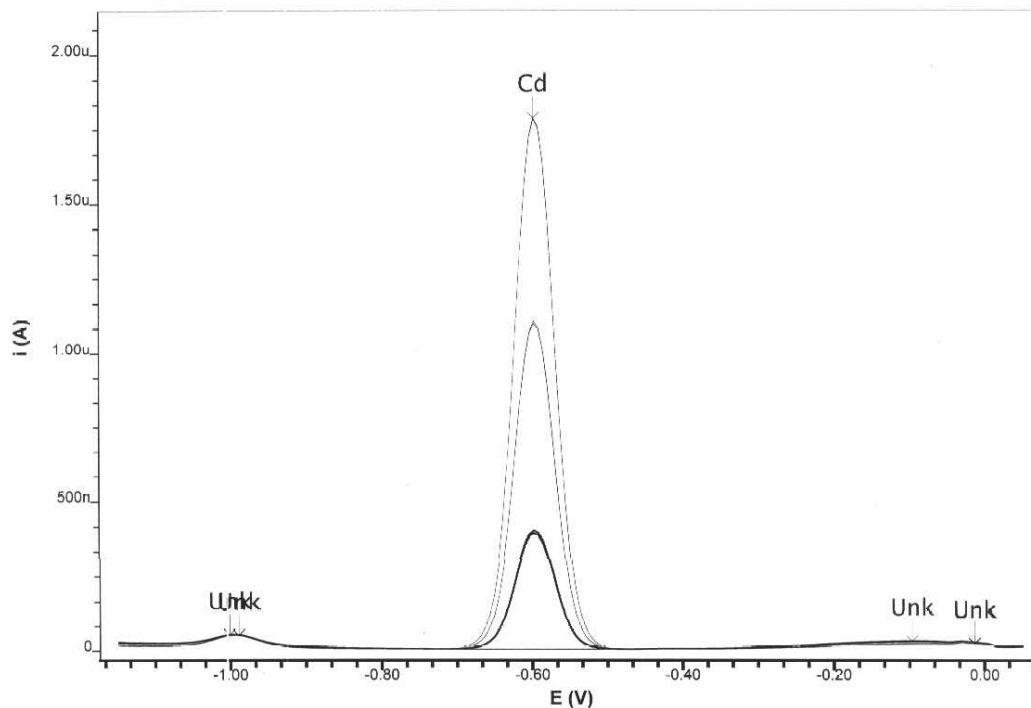


Figure 9.7. Voltammogram of polluting the soil with 8 ppm Cd for 25 hours at 20 mL/g ratio

Experimental results indicated that when 2 g soils were used, the equilibrium between the cadmium and soil was established at 25 hours for each cadmium concentrations at each (V/m) ratios. The graphs that show the equilibrium time are given in Figure 9.8, 9.9, and 9.10.

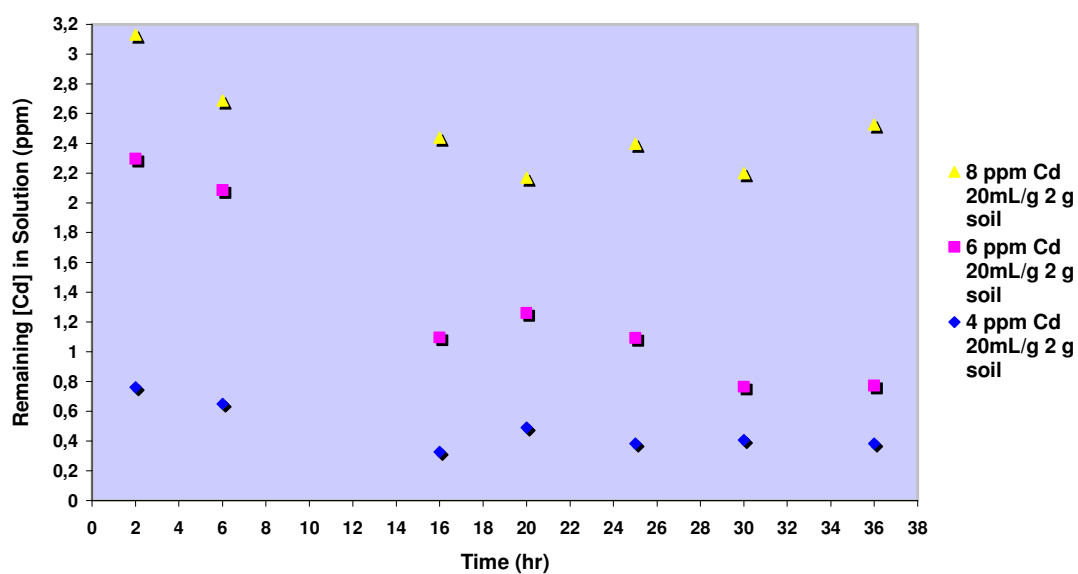


Figure 9.8. Plot of remaining [Cd] in the solution versus time for 4, 6, and 8 ppm Cd interaction with 2 g soil at 20 mL/g

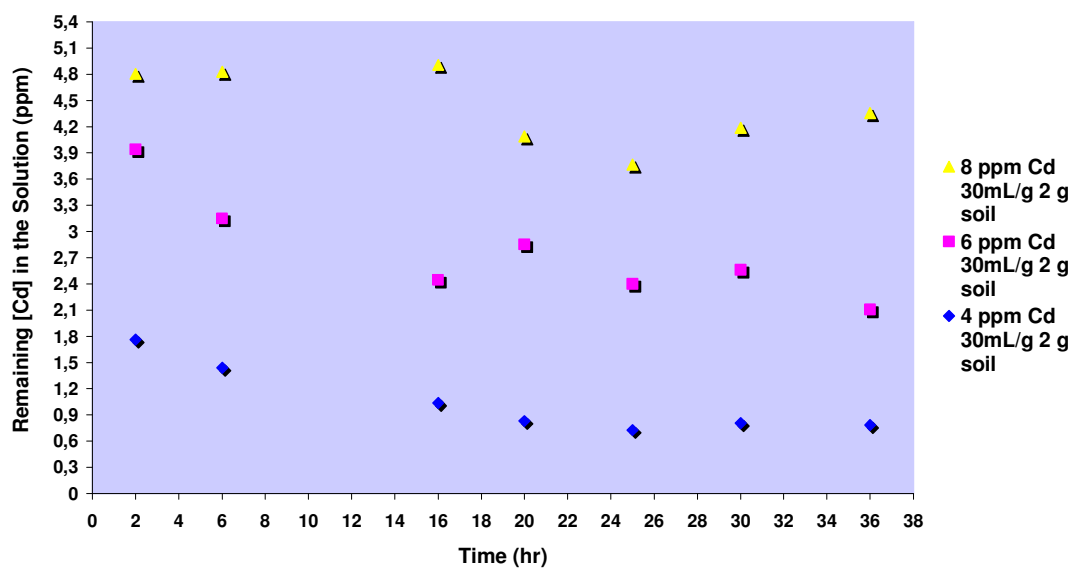


Figure 9.9. Plot of remaining [Cd] in the solution versus time for 4, 6, and 8 ppm Cd interaction with 2 g soil at 30 mL/g

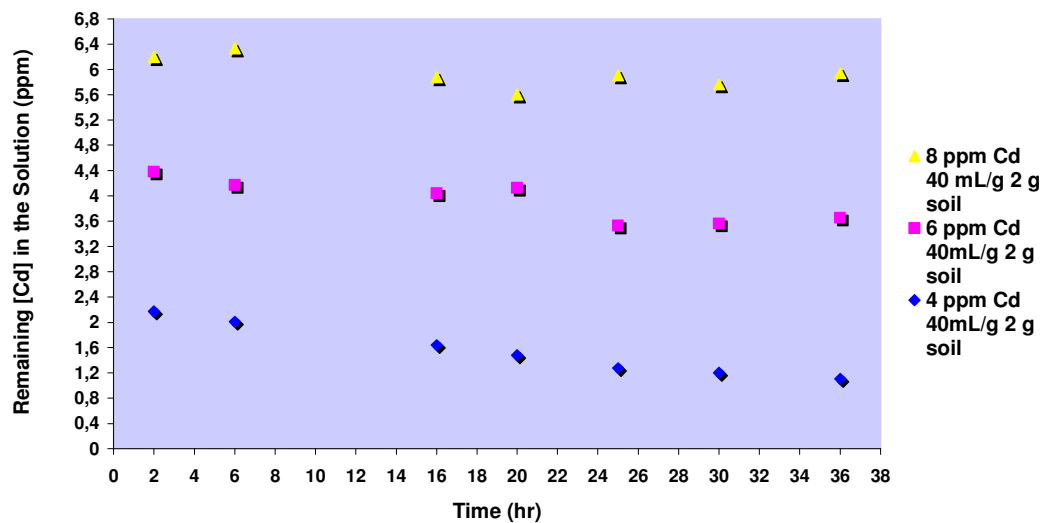


Figure 9.10. Plot of remaining [Cd] in the solution versus time for 4, 6, and 8 ppm Cd interaction with 2 g at 40 mL/g

9.4.2. Cd- 1g Soil Interaction

The same procedure in 2 g soil experiments with the same parameters were carried out for 1 g soil experiments.

When the experimental results were considered, again the equilibrium time was determined as 25 hours. The interactions between 1 g soil and cadmium with different concentrations and (V/m) ratios are given in Figure 9.11, 9.12, and 9.13.

When the results of 1 g and 2 g soil experiments were compared, it was observed that 2 g soil experiments stated the equilibrium time as 25 hours more clearly at each concentration of cadmium with each (V/m) ratio. Therefore, the proceeding steps of this study were carried out by using 2 g soil weight in all experiments.

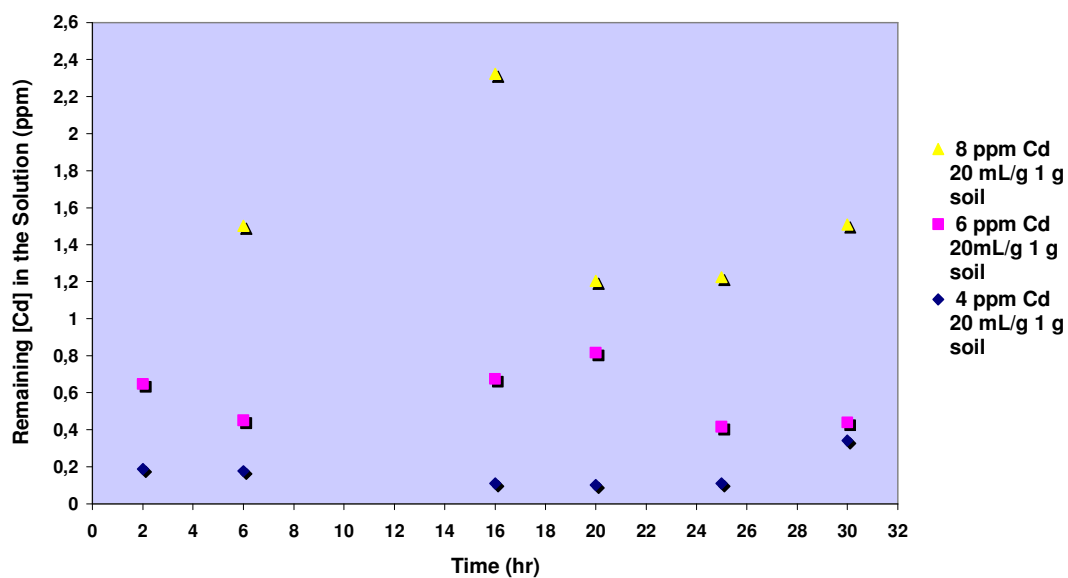


Figure 9.11. Plot of remaining [Cd] in the solution versus time for 4, 6, and 8 ppm Cd interaction with 1 g soil at 20 mL/g

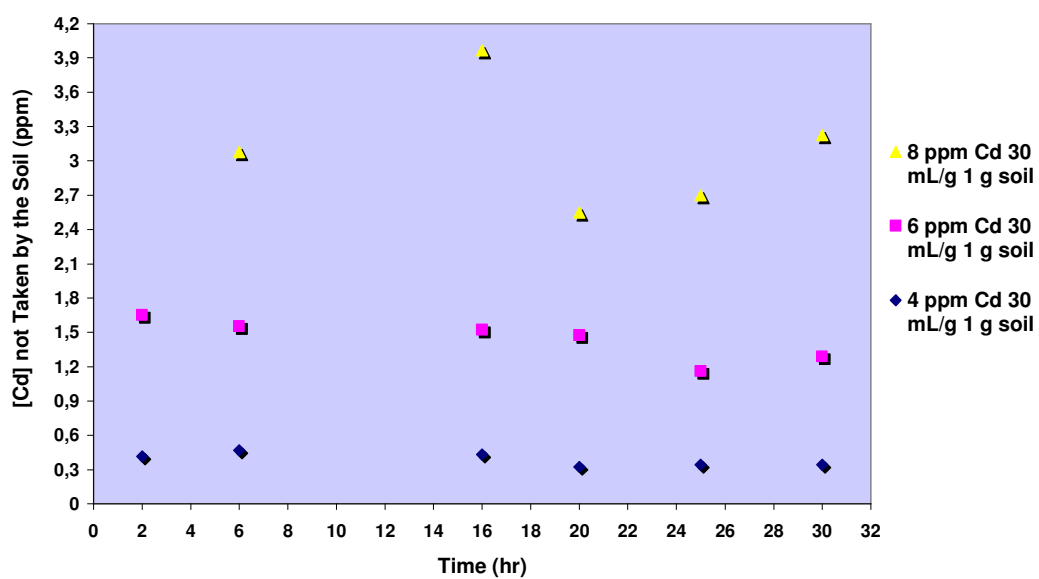


Figure 9.12. Plot of remaining [Cd] in the solution versus time for 4, 6, and 8 ppm Cd interaction with 1 g soil at 30 mL/g

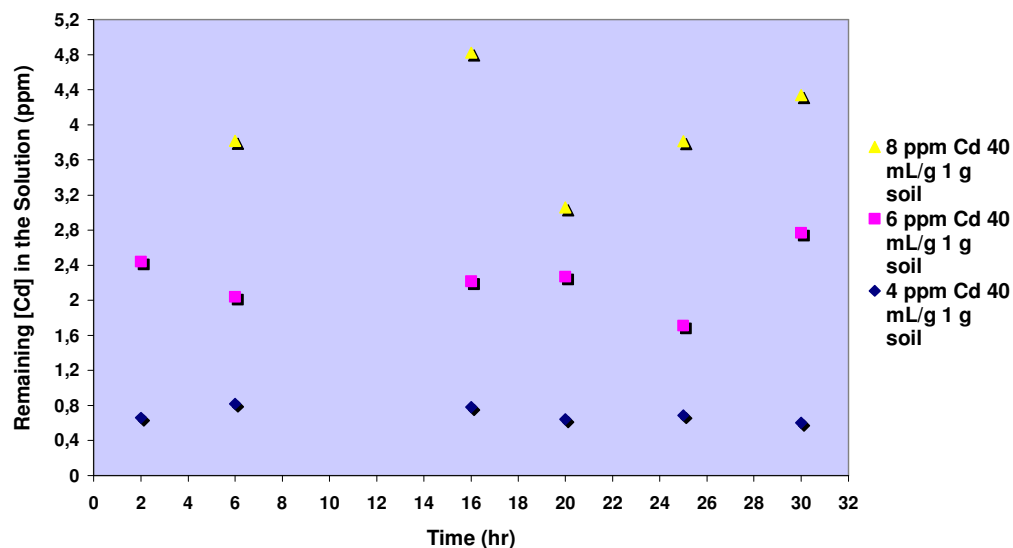


Figure 9.13. Plot of remaining [Cd] in the solution versus time for 4, 6, and 8 ppm Cd interaction with 1 g soil at 40 mL/g

Table 9.15. The concentration of Cd not retained by the soil at 4, 6, and 8 ppm Cd solutions added to 2 g soil samples at the given (V/m) ratios

V/m (mL/g)	4 ppm Cd (ppm)	6 ppm Cd (ppm)	8 ppm Cd (ppm)
20	0.44 (11.00%)	0.96 (16.00%)	2.01 (25.12%)
30	0.67 (16.75%)	2.07 (34.50%)	3.45(43.12%)
40	1.32 (33.00%)	3.21 (53.50%)	4.43 (55.37%)

When the results given in Table 9.15 were concerned, it was clearly determined that the amount of metal intake of soil decreases as the V/m ratio increases which means as we increase the volume of cadmium solution added on the soil, the amount of cadmium retained by the soil decreases.

9.4.3. Comparison of the Results of 25-hour and 5-Day Experiments

After setting the equilibrium time as 25 hours, experiment sets for each concentration of cadmium were prepared to pollute 2 g soils for 5 days. The results of 25-hour and 5-day experiments are given in Table 9.16, 9.17 and Figure 9.14, 9.15 for comparison.

Table 9.16. Comparing the amount of Cd not taken by the soil after 25 hours and 5 days

V/m (mL/g)	4 ppm Cd		6 ppm Cd		8 ppm Cd	
	25 hrs (ppm)	5 days (ppm)	25 hrs (ppm)	5 days (ppm)	25 hrs (ppm)	5 days (ppm)
20	0.44	0.15	0.96	0.47	2.01	1.66
30	0.67	0.44	2.07	1.29	3.45	2.74
40	1.32	0.81	3.21	2.28	4.43	3.96

Table 9.17. Comparing the amount of Cd taken by the soil after 25 hours and 5 days

V/m (mL/g)	4 ppm Cd		6 ppm Cd		8 ppm Cd	
	25 hrs (ppm)	5 days (ppm)	25 hrs (ppm)	5 days (ppm)	25 hrs (ppm)	5 days (ppm)
20	3.56	3.85	5.04	5.53	5.99	6.34
30	3.33	3.56	3.93	4.71	4.55	5.26
40	2.68	3.19	2.79	3.72	3.57	4.04

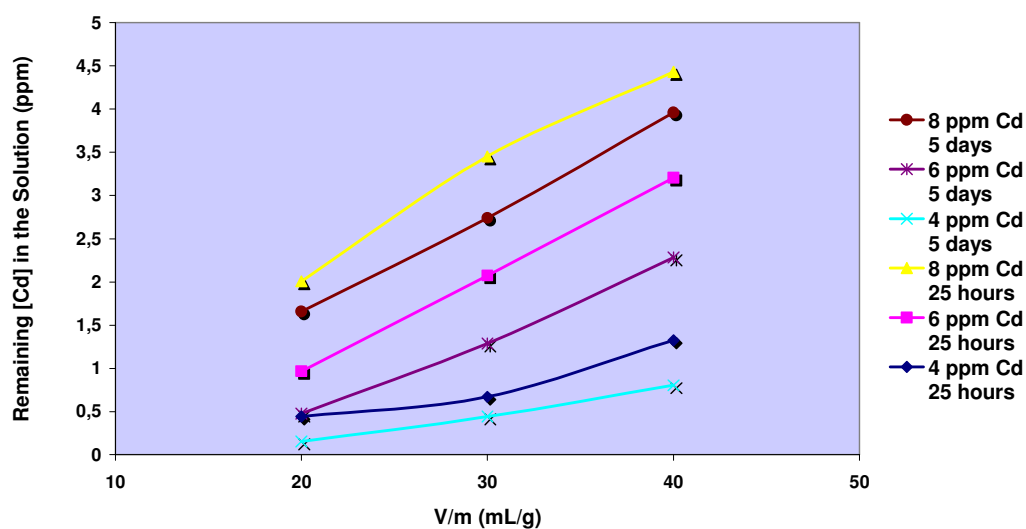


Figure 9.14. Plot of [Cd] in the solution versus (V/m) to compare the results of 25-hour and 5-day experiments for 4, 6, and 8 ppm Cd

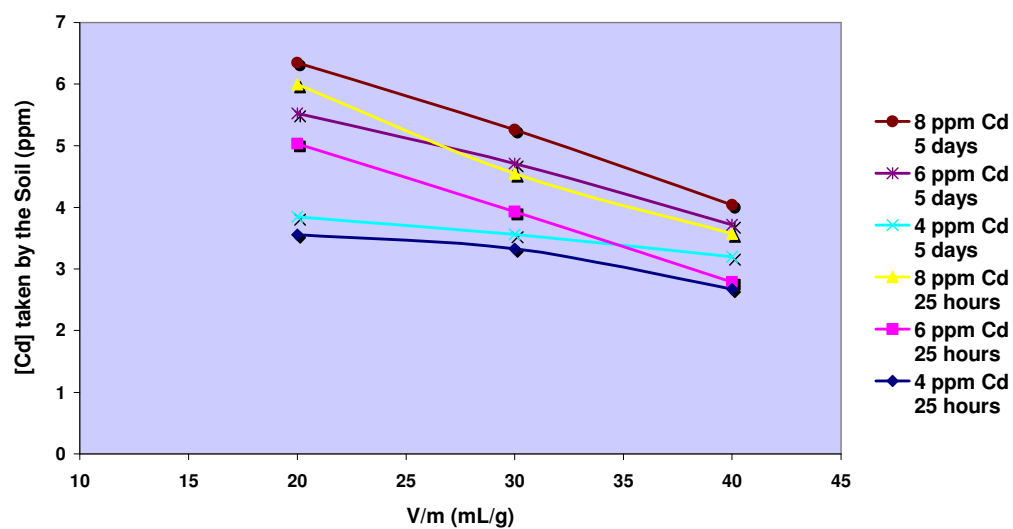


Figure 9.15. Plot of [Cd] in the soil versus (V/m) to compare the results of 25-hour and 5-day experiments for 4, 6, and 8 ppm Cd

The results obtained from 25 hours and 5 days experiments indicated that the amounts of metal uptake by the soil were only slightly different from each other. Thus, the equilibrium time for cadmium-soil interaction remained as 25 hours.

9.4.4. Water-Polluted Soil Interaction (Blank Trials)

According to the procedure given in Section 8.4, 2 g initially polluted soil with cadmium at 4, 6 and 8 ppm levels were left in deionized water for 25 hours. After 25 hours, the concentration of cadmium released to the aqueous layer from soil was determined with DPASV. The results are given in Table 9.18.

Table 9.18. The percentage of cadmium taken from soil contaminated with 4, 6, and 8 ppm Cd by water at ratio of 20, 30, and 40 mL/g

Volume/mass (mL/gr)	4 ppm Cd polluted soil (%)	6 ppm Cd polluted soil (%)	8 ppm Cd polluted soil (%)
20	0.33	0.78	0.53
30	0.49	0.76	1.75
40	0.30	0.79	2.24

The experimental results (very low percentage of cadmium uptake) indicated that water could not manage to clean up the cadmium contaminated soil after 25 hours.

9.5. Polluted Soil and SDS Interaction

The polluted soils with 4, 6, and 8 ppm Cd were interacted with 6, 8, and 10 mM SDS on a shaker for 25 hours at $25 \pm 2^\circ\text{C}$. The concentration range of SDS used was determined according to the CMC value which was found as approximately 8 mM in Section 9.2. These concentrations were selected on purpose to compare the behavior of SDS below, above and at the CMC value. The presence of SDS in the analyte cell did not cause any problem for the analysis of free cadmium in the solution. In Figure 9.16, an example of a voltammogram for the interaction between polluted soil and SDS is given.

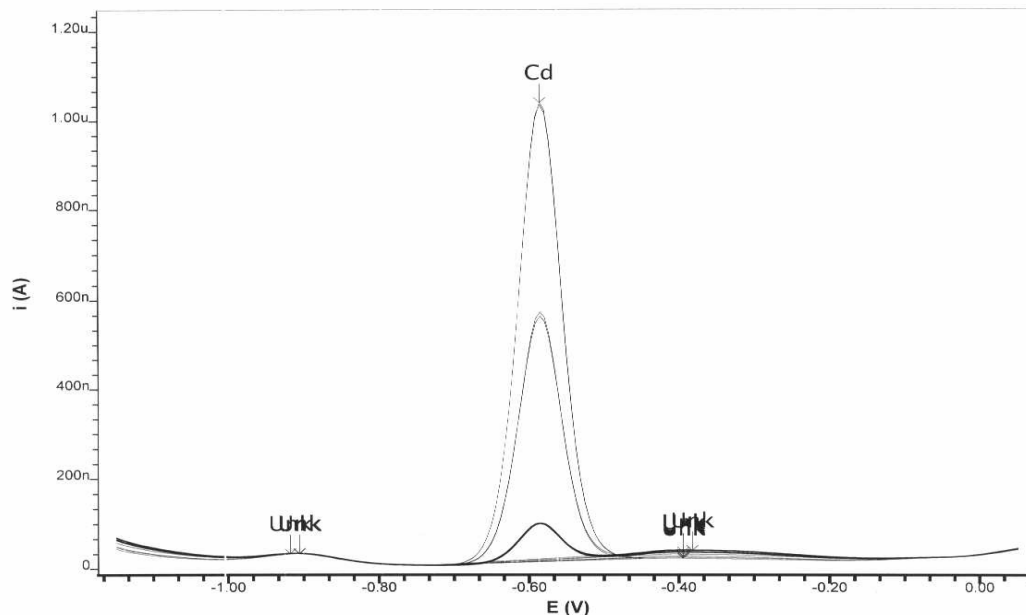


Figure 9.16. Voltammogram of interaction between the polluted soil with 8 ppm Cd and 6 mM SDS at 20 mL/g ratio.

When the Figure 9.17, 9.18 and 9.19 were considered, it was determined that as the concentration of the SDS increases, the cadmium amount taken from the polluted soil increases for each V/m ratio. This statement was all confirmed by each cadmium concentration (4, 6, and 8 ppm) used during the experiments.

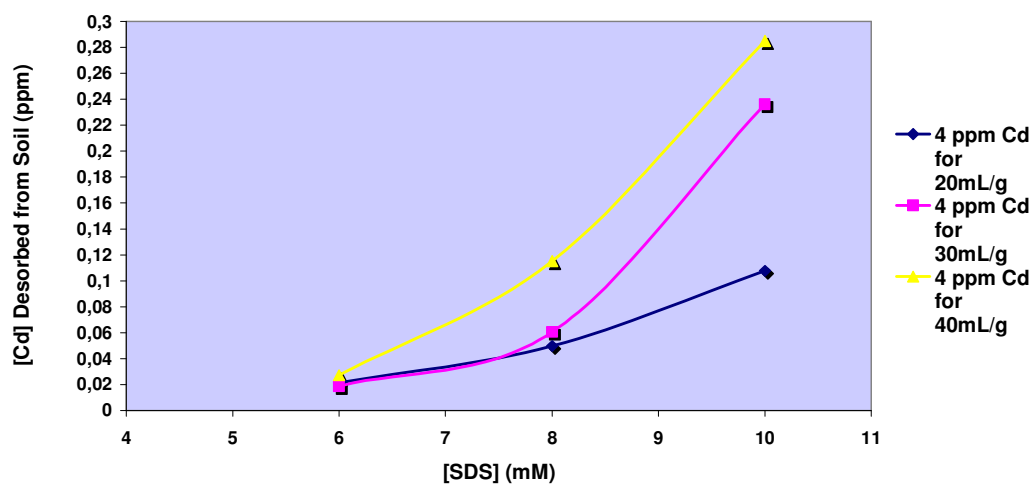


Figure 9.17. Plot of [Cd] desorbed from polluted soil with 4 ppm Cd versus [SDS] at 20, 30, and 40 mL/g by 6, 8, and 10 mM SDS

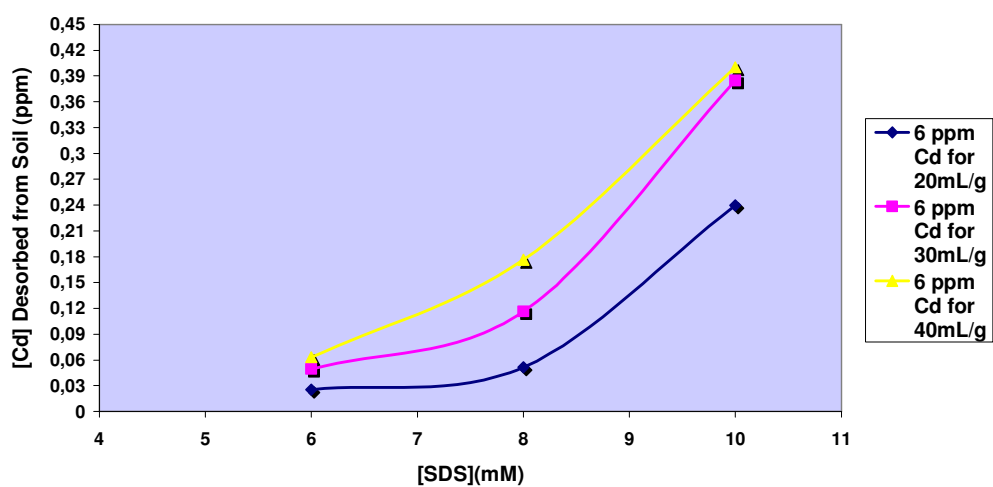


Figure 9.18. Plot of [Cd] desorbed from polluted soil with 6 ppm [Cd] versus [SDS] at 20, 30, and 40 mL/g by 6, 8, and 10 mM SDS

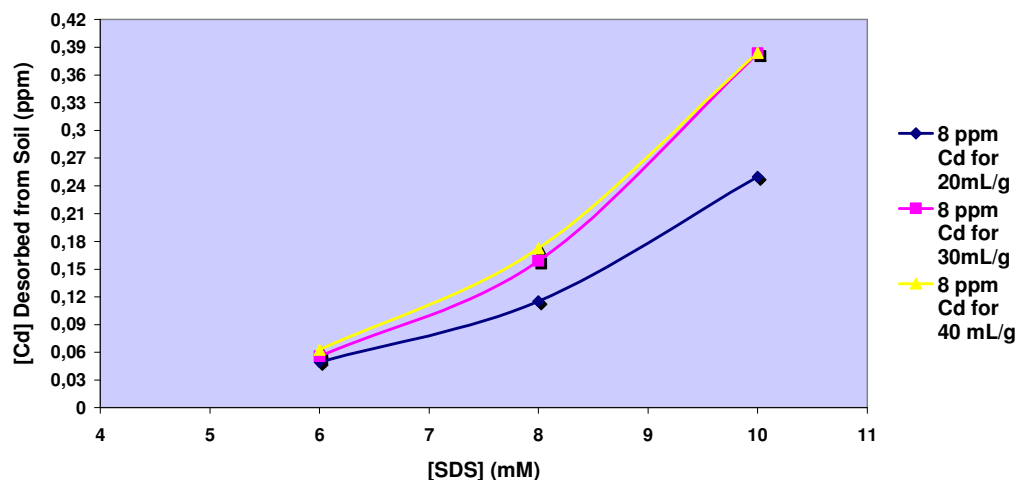


Figure 9.19. Plot of [Cd] desorbed from polluted soil with 8 ppm Cd versus [SDS] at 20, 30, and 40 mL/g by 6, 8, and 10 mM SDS

Figure 9.20, 9.21 and 9.22, indicated that the cadmium uptake from the polluted soil increases as the V/m ratio of SDS added on the polluted soil increases. For example, in Figure 9.20, three different soil samples polluted with 4, 6, and 8 ppm cadmium solutions were left to interact with 6 mM SDS in the ratios of 20, 30, and 40 mL/g. As a result of this interaction, it was observed that the uptake of cadmium from polluted soils increases as the V/m ratio of SDS increases. This result can be generalized for the experiments carried out by both 8 mM and 10 mM SDS, shown in Figure 9.21 and 9.22, respectively.

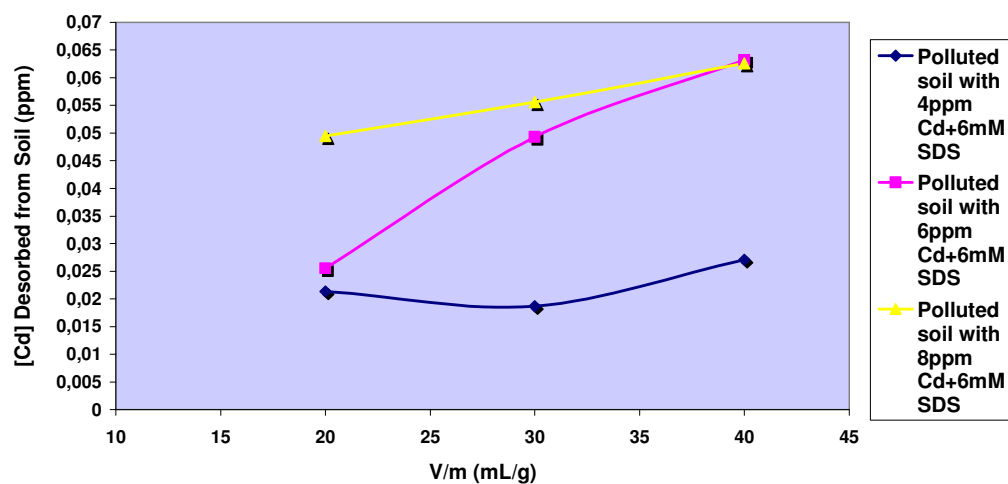


Figure 9.20. Plot of [Cd] desorbed from the polluted soil by 6 mM SDS versus (V/m)

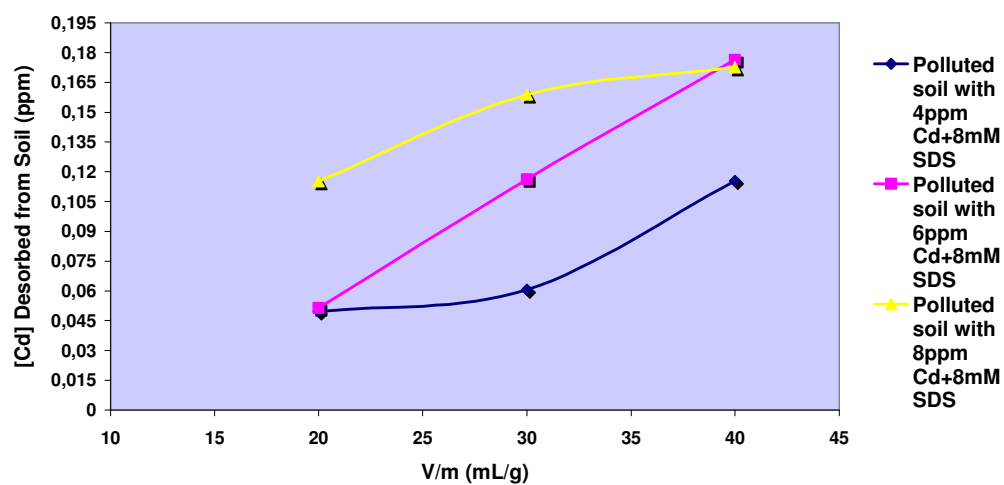


Figure 9.21. Plot of [Cd] desorbed from the polluted soil by 8 mM SDS versus (V/m)

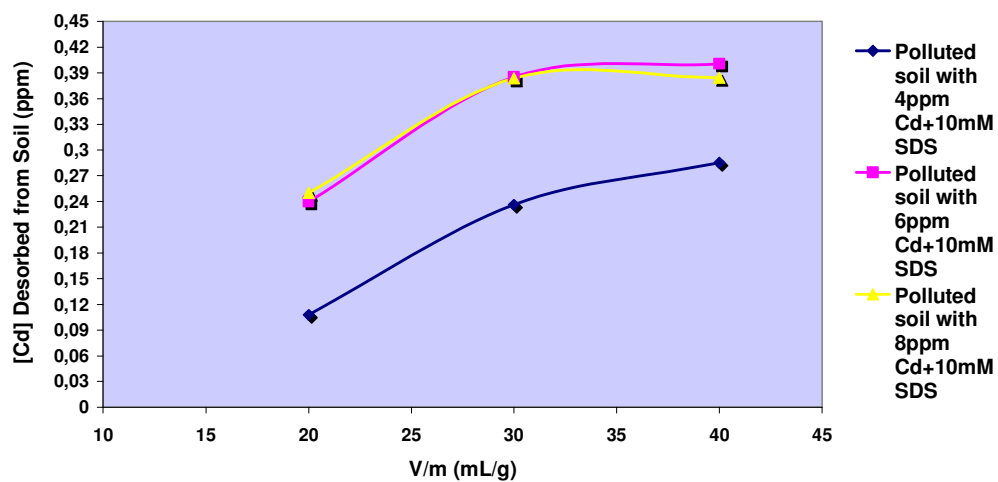


Figure 9.22. Plot of [Cd] desorbed from the polluted soil by 10 mM SDS versus (V/m)

Table 9.19. The cadmium percentage taken from 4 ppm Cd polluted soil by 6, 8, and 10 mM SDS at each (V/m) ratio

SDS concentration (mM)	Soil polluted with 4 ppm Cd		
	20 mL/g	30 mL/g	40 mL/g
6	0.57	0.55	0.89
8	1.34	1.75	3.82
10	2.92	7.01	9.60

Table 9.20. The cadmium percentage taken from 6 ppm Cd polluted soil by 6, 8, and 10 mM SDS at each (V/m) ratio

SDS concentration (mM)	Soil Polluted with 6 ppm Cd		
	20 mL/g	30 mL/g	40 mL/g
6	0.50	1.15	1.79
8	0.99	2.64	4.60
10	4.78	10.69	11.50

Table 9.21. The cadmium percentage taken from 8 ppm Cd polluted soil by 6, 8, and 10 mM SDS at each (V/m) ratio

SDS concentration (mM)	Soil Polluted with 8 ppm Cd		
	20 mL/g	30 mL/g	40 mL/g
6	0.79	1.13	1.51
8	1.85	2.95	3.80
10	3.77	7.43	8.44

Finally, we also compared the percentages of cadmium taken from the polluted soil by SDS. The results are given in Table 9.19, 9.20, and 9.21 for soils polluted with 4, 6, and 8 ppm Cd, respectively. When the given results were taken into account, it was concluded again that the increase in the SDS concentration increases the amount of cadmium taken from the polluted soil increases and also the cadmium uptake from the polluted soil increases as the V/m ratio increases when the same concentration of SDS used.

Other than the SDS concentrations used during the experiments, one set of experiment also carried out by using 12 mM SDS. The results are given in Table 9.22.

Table 9.22. The cadmium percentage taken from polluted soil with 4 ppm Cd by 12 mM SDS

V/m (mL/g)	Cd % taken from polluted soil with 4 ppm Cd by 12 mM SDS
20	3.90
30	8.40
40	12.16

The percentages of cadmium taken from 4 ppm polluted soil at each V/m ratios by 12 mM SDS were greater than the other results obtained from the experiments carried out with 6, 8, and 10 mM where the soil was polluted with the same concentration of cadmium. Therefore, it was generalized that as the SDS concentration increases, the degree of cleaning the soil increases.

In order to see what would happen when the interaction time of polluted soil and SDS increases, another set of experiment prepared. The soil samples were polluted for 5 days and then they were placed in contact with SDS solutions for another 5 days. To see the effect of 5 days interaction time, sample of 4 ppm Cd polluted soil and one sample of 6 ppm Cd polluted soil for 5 days in replicates were tried to be cleaned by 10 mM SDS for 5 days and the average results obtained from replicate samples are given in Table 9.23.

Table 9.23. Cadmium uptake from 5-day polluted soil by 10 mM SDS after 5 days of interaction and 25-hour polluted soil by 10 mM SDS after 25 hours of interaction time

Concentration used to pollute the soil (ppm)	Cd % uptake after 5 days with 10 mM SDS	Cd % uptake after 25 hours with 10 mM SDS
4 ppm Cd 30mL/g	12.07	7.01
6 ppm Cd 30mL/g	12.85	10.69

When the 5 days and 25 hours experiments with the soil samples polluted by the same concentration of cadmium at the same V/m ratio were compared, it was concluded that after 5 days the amount of cadmium taken from soil was greater in amount than the 25 hours experiment by using the same concentration of SDS in each experiment.

9.6. Polluted Soil, Surfactant SDS and Ligand Interaction

Initially, 4 ppm Cd solutions with different EDTA concentrations were analysed with acetate buffer by DPASV in order to determine the level of EDTA concentration enough to form a stable complex with cadmium. According to the results given in Table 9.24, it was determined that the concentration of uncomplexed cadmium ion in test media in comparison to its initial concentration did not decrease with the increasing concentration of EDTA. This was the expected situation, since the complexes of cadmium and EDTA partially dissociate in an acidic media.

Table 9.24. Results obtained when the standard solutions of EDTA with 4 ppm cadmium were analysed with acetate buffer by DPASV

[EDTA] in 4 ppm Cd Standard Solution (mM)	[Cd] not Complexed by the EDTA complex (ppb)
10	3324.30
20	2724.62
30	2590.24
40	2996.74
50	3621.18
60	2999.85
70	3364.34
80	3166.00
90	2956.39
100	2763.80
200	2978.12

Two other buffer combinations, carbonate and phosphate which made the media basic and neutral, respectively were also tested under the same experimental conditions. At these pH values where a stable complex formation occurred between cadmium and EDTA,

very low current values, i. e. 2.00-2.60 nA were registered. This was attributed to the fact that cadmium might have been totally complexed by EDTA. However, the corresponding current values were almost the same for all EDTA concentrations tested between 0.1 mM and 100 mM levels. Also, the half-wave potential value for the cadmium peak was shifted and the standard addition curves were not reproducible. Yet, an unidentified separate peak appeared in the voltammogram. Thus, the analysis with EDTA at neutral and basic pH values did not give reproducible results as shown in Figure 9.23. Therefore, another ligand was searched that can work with DPASV.

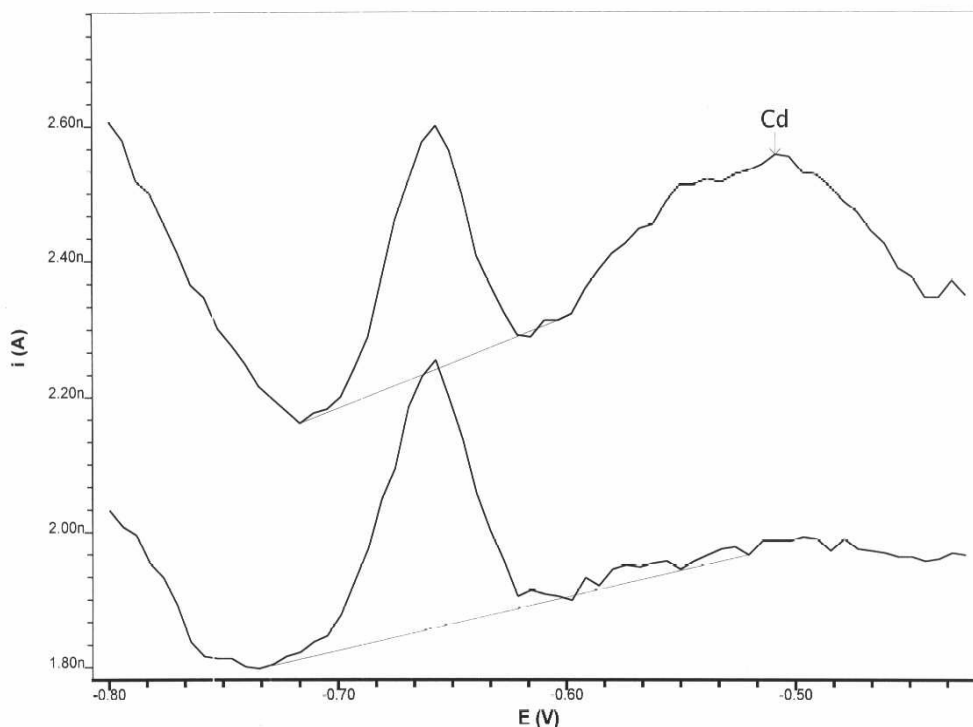


Figure 9.23. Voltammogram of 8 ppm Cd with 0.1 mM EDTA in the presence of phosphate buffer solution

The organic ligand EN was used instead of EDTA. In order to see the effect of EN as a ligand, 4 ppm (4000 ppb) Cd solutions were prepared with different EN concentrations. The experiments were run in the presence of a phosphate buffer. Results are given in Table 9.25.

Table 9.25. Results obtained when 4 ppm Cd solution was analysed with different EN concentrations and phosphate buffer by DPASV

EN concentration (mM)	Half-wave Potential (V)	Cd remained in the solution (ppb)	Cd taken by EN complex (ppb)
1	-0.615	2257.90	1742.10
10	-0.615	2425.74	1574.26

Ligand EN was suitable for complexing the cadmium in a phosphate buffer and the DPASV method was run successfully. However, no obvious enhancement effect on the removal of cadmium from media was observed as the concentration of EN was increased from 1 mM to 10 mM.

As it was determined that the ligand EN worked with voltammetry, combining SDS with EN was tested in order to determine that whether the formed complexes between cadmium and EN enter into the micelles formed by SDS or not. A solution containing 4 ppm Cd, 1 mM EN and 10 mM SDS was prepared and analysed by DPASV. In Figure 9.24, the voltammogram of the solution prepared by 4 ppm Cd, 1 mM EN and 10 mM SDS is given. According to the current values, the cadmium remaining in the solution was found to be 3516.8 ppb. When this result was compared with the result of 4 ppm Cd and 1 mM EN (Table 9.25), it was determined that the ligand EN and cadmium complex was not taken into the SDS micelles.

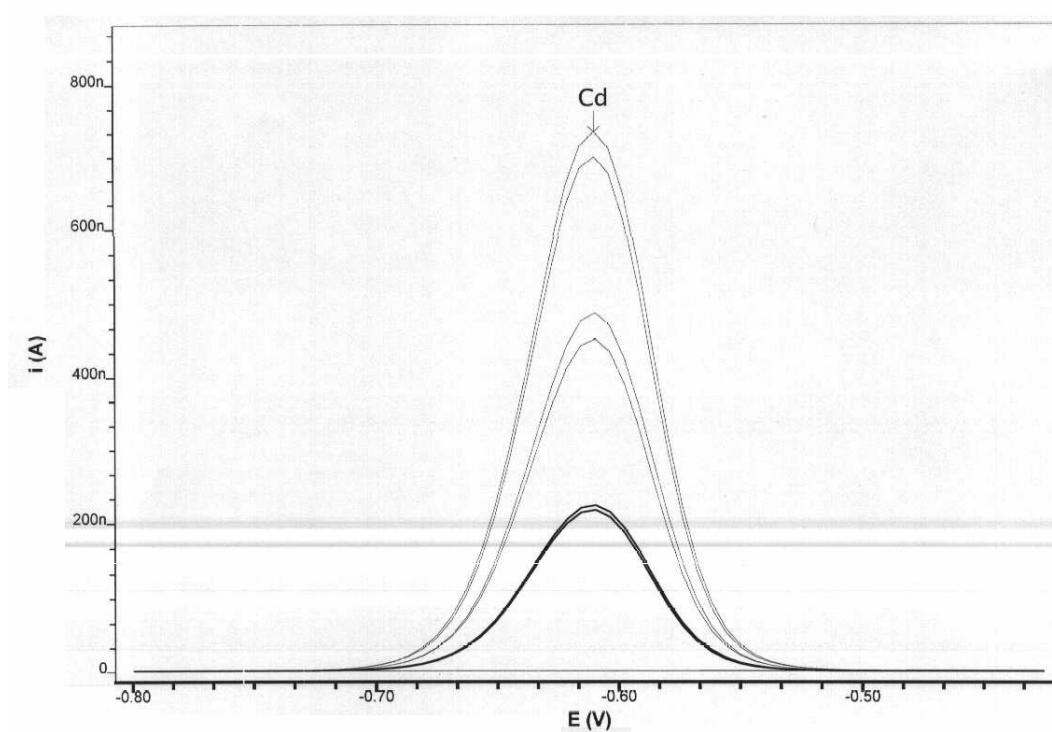


Figure 9.24. Voltammogram of 4 ppm Cd-1 mM EN-10 mM SDS with phosphate buffer solution

It was concluded that EN and SDS could not work together for the aim of having Cd-EN complexes entering into the micelles of SDS and also the presence of SDS prevented partially the complex formation of EN with cadmium ions.

10. CONCLUSIONS

1. A new method, DPASV, has been used successfully in the study of heavy metal-soil and heavy metals-soil-surfactant interactions. Although only one type of surfactant (SDS) and only one heavy metal (Cd) has been studied, the DPASV promised to be a useful method in these types of works. A ligand-surfactant system was also investigated by this method.
2. In order to get best quantitative results, method parameters like deposition time, stirring rate of the working electrode and deposition potential were optimized. In addition to this, the optimum pH environment was determined using acidic, neutral and basic buffer solutions. The acidic acetate buffer was found to work best for heavy metal-soil and heavy metal-soil-surfactant interactions. Since the soil used in this study was also determined to be acidic, the acetate buffer was thought to create a similar environment to the “real” systems. The neutral phosphate buffer was a better choice for heavy metal-ligand system.
3. Soil, artificially polluted with cadmium, could be decontaminated using anionic surfactant SDS. Studies showed that when the SDS concentration was below or at the CMC value of this surfactant, the cleansing process was much less efficient than when the SDS concentration was above the CMC. Decontamination ability it increased as the concentration of SDS in the solution and the contact time it had with the contaminated soil were increased. Therefore, the result suggested that the decontamination process was successful if SDS formed micelles in the solution.
4. As the volume of the SDS solution in contact with the constant weight of soil increased (i. e. V/m ratio), percent decontamination was observed to increase.
5. An attempt to decontaminate the soil with surfactant-ligand systems was also made. The ligands used were hexadentate EDTA and bidentate EN. In the preliminary studies, metal-ligand interaction was studied initially with EDTA in the presence of

acidic acetate buffer which was determined to be the ideal working environment for DPASV. However, the EDTA-metal complex dissociated due to the acidity of the media. When the buffer was changed and neutral and basic environments were created, voltammetric peaks did not give satisfactory results.

6. The second ligand used, EN, was found to work best in the presence of neutral phosphate buffer. The complex formation of heavy metal with EN was successfully observed with DPASV. However, when SDS was introduced to this environment, emulsions formed and EN-metal interactions were disturbed. No satisfactory results could be obtained for EN-SDS-heavy metal system.

11. SUGGESTIONS FOR FUTURE WORK

1. Since DPASV proved to be a successful method for heavy metal-soil and heavy metal-soil-surfactant interactions, it can be used to study other metal-soil interactions. Soil texture can be changed. Soil with different clay, silt and sand contents can be used. Further work should include metal ions such as Cu, Zn, Ni, Pb or metal mixtures.
2. SDS can be changed with an other anionic or non-ionic surfactants. Cationics are not suitable for decontamination processes.
3. A suitable ligand should be found to develop an effective surfactant-ligand system for the decontamination of soil.

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