

**SURFACTANT SORPTION & DESORPTION ON SOIL
SURFACES OF VARYING CLAY CONTENT**

by

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ABSTRACT

In this research, sorption and desorption behavior of selected surfactants were investigated on a soil sample that was mixed with different clays at different ratios. The surfactants investigated were a cationic surfactant Benzethonium chloride (Hyamine 1622) and an anionic surfactant Sodium Dodecyl Sulphate (SDS). The clays were Kaolin, Attapulgite, and Calcium-Montmorillonite.

The sorption and desorption isotherms of soils were fitted to the Langmuir and Freundlich isotherm equations, and related sorption and desorption constants were calculated from these isotherms. It was found that the sorption capacities for all of the three different types of clay at different mixing ratio for Hyamine were higher compared to those of SDS. On the other hand, desorption capacities for SDS is better than those of Hyamine.

ÖZET

Bu çalışmada, seçilmiş yüzey aktif maddelerin 3 farklı kilin değişik karışım oranlarıyla harmanlanması sonucu oluşan toprak karışımlarındaki sorpsiyon ve dezorpsiyon davranışları incelenmiştir. Yüzey aktif maddelerden anyonik yüzey aktif madde olan Sodyum Dodesil Sulfat ve katyonik yüzey aktif madde olan Hyamine incelenmiştir. Kil örnekleri ise Kaolin, Attapulgit, ve Kalsiyum-Monmorilonit'dir.

Toprakların sorpsiyon ve dezorpsiyon izotermeleri, Langmuir ve Freundlich eşitliklerine konarak ilgili sorpsiyon ve dezorpsiyon sabitleri hesaplanmıştır. Üç kilin toprakla olan değişik tüm karışım oranlarında Hyamin'in sorpsiyon kapasitesinin SDS'ten daha iyi olduğu gözlemlenmiştir. Öte yandan, SDS'in dezorpsiyon kapasitelerinin Hyamin'inkilerden daha iyi olduğu gözlemlenmiştir..

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1. INTRODUCTION

Adsorption of surface-active-agents (surfactants) has been of increasing interest because of their many applications in processes such as detergency, cosmetics, enhanced oil recovery, soil washing, and enhanced subsurface remediation. The products known under the general name surfactants mainly do not exist in nature, they are manufactured by chemical reaction, therefore they are synthetic.

Surfactants are amphiphilic molecules having two major components (moieties); a hydrophilic, or water soluble, head group, and a hydrophobic, or water insoluble, tail group. This dual nature causes surfactants to adsorb at interfaces thereby reducing the interfacial energies (Rosen, 1989). The classification of surface active agents are done according to their head group :

1. Ionic
2. Nonionic

The ionic head group is also subdivided into anionic, cationic, and zwitterionic categories referring the anion, cation, or both attached to the low affinity portion of the molecule.

Soils are composed of mineral matter (sand, silt, clay), air, water, organic matter, and organisms. There are two general types of soils: mineral soils and organic soils. Mineral soils form from decomposed rocks or sediment derived from rocks. Organic soils form from the accumulation of plant material, usually in water-saturated, anaerobic conditions that retard decomposition. Mineral matter is described as texture and comprises half the volume of mineral soils. The other half of the soil volume is composed of voids or holes. Soil is a biologically active matrix. It is a home for plant roots, seeds, animals, bacteria, fungi, algae, and viruses.

Experimentally, the investigation of adsorption from solution is much simpler than that of gas adsorption. A known mass of adsorbent solid is shaken with a known volume of solution at a given temperature until there is no further change in the concentration of the supernatant solution. This concentration can be determined by a variety of methods involving chemical or radiochemical analysis, colorimetry, refractive index, etc. The experimental data are usually expressed in terms of an apparent adsorption isotherm in which the amount of solute adsorbed at a given temperature per unit mass of adsorbent - as calculated from the decrease (or increase) of solution concentration - is plotted against the equilibrium concentration.

In this research, the adsorption and desorption behavior of a cationic surfactant (Hyamine 1622) and an anionic surfactant (SDS, Sodium Dodecyl Sulfate) have been studied on the soil samples which have different clay contents. The types of clay were Kaoline, Calcium-Montmorillonite (Ca.Mon.) and Attapulgitite (Atta.). The data obtained from the experiments are put into the adsorption isotherms (Langmuir and Freundlich) to describe the behavior of these surfactants.

2. SURFACE-ACTIVE-AGENTS (SURFACTANTS)

From the point of view of a chemist, a surface or interface is the boundary between two phases. In any heterogeneous system the boundaries are of fundamental importance to the behavior of the system as a whole. For example, the phenomenon of adhesion is an effect of the surface or interface between two solid phases, or in some instances between a liquid and a solid phase. Similarly, wetting, emulsification, foaming, detergent effects, adsorption effects, and various combinations of these are conditioned by what goes on in the interfaces between two phases (Schwartz, Perry, 1978).

Certain solutes, even in very low concentrations, have the startling property of altering the surface energy of their solvents to an extreme degree. The effect is invariably a lowering rather than an increase of the surface energy. Solutes having such properties have come to be known as the surface active agents. The most important characteristic of surface active agents is the presence of a strongly hydrophilic group and a strongly hydrophobic group linked together in the same molecule.

The word surfactant is a shortened form of the term surface-active-agents and denotes the outstanding property of these compounds : They tend to concentrate at the surface and interfaces of an aqueous solution and to alter the surface properties. Because of the presence of the hydrophilic group a surfactant is more or less readily soluble in water. However, the hydrophobic group is repelled by water, giving a tendency for that portion of the molecule to leave the aqueous phase. This leads to a higher concentrations at the surfaces or boundaries than in the main body of the solution. At the surface, the air water interface, the surfactant molecules orient themselves with the hydrophilic groups in the water and the hydrophobic groups extending as far as possible in the other direction, still consistent with the molecular dimensions and geometry and with the intermolecular forces acting upon them. The result of this oriented surface film is the lowering of the surface tension of the water and a greater tendency toward bubble and foam formation. A large number of surfactants are characterized by a molecular structure which is

essentially linear, i.e., considerably longer than it is wide. One end of the linear structure is composed of radicals, which are compatible with the solvent system, and the opposite end of incompatible radicals. Usually one end comprises a hydrocarbon radical of hydrophobic nature characterized by weak residual valence forces, whereas the other end is of a hydrophilic nature with strong residual or secondary valence forces.

2.1 Micelles

Solutions of highly surface active materials exhibit unusual physical properties. In dilute solution the surfactant acts as a normal solute. At fairly well defined concentrations, however, abrupt changes in several physical properties, such as osmotic pressure, turbidity, electrical conductance and surface tension take place. The rate at which osmotic pressure increases with concentration becomes abnormally low and the rate of increase of turbidity with concentration is much enhanced, which suggests that considerable association is taking place. The conductance of ionic surfactant solutions, however, remains relatively high, which shows that ionic dissociation is still in force. This characteristic of surfactants in aqueous solution is the aggregation of their molecules into larger, oriented groups called micelles. These seemingly anomalous behaviors could be explained in terms of these organized aggregates of the surfactant ions in which the lipophilic hydrocarbon chain are oriented towards the interior of the micelle, leaving the hydrophilic groups in contact with the aqueous medium. Micellisation is, therefore, an alternative mechanism to adsorption by which the interfacial energy of a surfactant solution might decrease.

When one considers the energetics of micellisation in term of the hydrocarbon chains of the surfactant molecules, the following factors are among those, which must be taken into account :

1. The intermolecular attractions between the hydrocarbon chains in the interior of the micelle represent an energetically favorable situation; but it is not one which results from the alternative hydrocarbon-water attraction in the case of single dissolved surfactant molecules.
2. Micellisation permits strong water-water interaction (hydrogen bonding) which would otherwise be prevented if the surfactant was in solution as single molecules wedged between the solvent water molecules. This is a most important factor in micelle formation and also, of course, in any adsorption process at an aqueous interface. It is often referred to as the hydrophobic effect.

In very dilute solutions, the individual single molecules or their ions are present. Further increments of surfactants also dissolve to form separate molecules or ions up to certain point known as the critical micelle concentration, abbreviated CMC. Beyond this point the concentration of single molecules remains relatively constant. Much more surfactant may still be dissolved to give clear solutions, but the added increments then form micelles instead of appearing as single molecules. At some higher concentration, often much higher, the solubility limit for that particular surfactant may be reached. Further increments no longer dissolve in the saturated solution but instead form a new phase, solid or liquid, usually hydrated. In the micelles in an aqueous solution the molecules are oriented with their hydrophobic portions clustered together, the hydrophilic ends extending outward. Such ordering results from repulsion, or at least from absence of attraction, of the hydrophobe groups by the water molecules, further aided by any attraction that might exist between hydrophobes. The micelles are in equilibrium with the monomers, and one may picture relatively free passage of surfactant molecules back and forth between the two states (Shaw, 1980).

Depending on such factors as the chemical nature and architecture of the surfactant, the salt content of the solution, and the temperature, the micelles may be spheres, ellipsoids, or cylinders, and may average tens or hundreds of molecules per micelle.

Micelle formation is opposed by thermal agitation and, in the case of micelles of ionic surfactants, by repulsion between the charged head groups on the surface of the micelle. Consequently, a low critical micelle concentration would be expected to be favored by :

1. Increasing the hydrophobic part of the surfactant molecules. In aqueous medium the CMC of ionic surfactants is approximately halved by the addition of each CH_2 group. For nonionic surfactants the CMC may be reduced by a factor of as much as 10 for each additional CH_2 group. Between about C_{16} and C_{18} members the rate of change of CMC in a homologues series tends to decrease and above the C_{18} member it tends to remain approximately constant. This is probably the result of coiling of the long hydrocarbon chains in the water phase.
2. Lowering the temperature.
3. The addition of simple salts (in the case of ionic surfactants). The repulsion between the charged groups at the surface of the micelle is reduced by the screening action of the added ions (Shaw, 1980).

2.2 Characteristic Features of Surface Active Agents

Most surface-active-agents are characterized structurally by an elongated portion of low residual affinity, and one end of high residual affinity. Chemically, there are two great classes; the ionic and the non-ionic. The non-ionic class has non-ionizable high-affinity end groups, usually containing a number of oxygen, nitrogen, or sulfur atoms in nonionizing configurations. This class is of primary importance in non-aqueous systems but a number of non-ionic surfactants have been widely and successfully used in aqueous systems, both as emulsifiers and as straight detergents (Schwartz, Perry, 1978).

The ionic class of agents has two main divisions. If the elongated, low-affinity portion of the molecule is included in the anion in aqueous solution, the substance is called anion active or simply anionic. It gives negatively charged surfactant ions in aqueous solution, usually originating in sulfonate, sulfate, or carboxylate groups. Sodium stearate is a typical anionic surface-active-agent since it ionizes in solution to form Na^+ and the long-chain stearate anion, $\text{C}_{17}\text{H}_{35}\text{COO}^-$, which may be considered responsible for the surface activity. The cation active or cationic surfactants form a cation that contains the elongated low-affinity portion of the molecule. Cetylpyridinium chloride is an example of this class. A third class of lesser importance exists wherein the molecule as a whole forms a zwitterion. Cetyl aminoacetic acid is an example to this group. The anionic and cationic classes can be subdivided according to the nature of the ionic group. In the anionic class the most important ionic groups are the carboxy ($-\text{COOH}$), sulfonic acid ($-\text{SO}_3\text{H}$), and sulfuric ester ($-\text{OSO}_3\text{H}$). The free bond indicated in the various group formulas is attached directly or indirectly to the elongated low-affinity portion of the molecule. In the cationic class the most prevalent ionic groups are the primary, secondary and tertiary amino groups and the quaternary ammonium groups. Phosphonium and sulfonium groups are sometimes encountered but they are of far less importance (Schwartz, Perry, 1978).

2.3 Cationic – Anionic Interactions

Cationic and anionic surfactants neutralize each other when present together in the same solution. The oppositely charged surfactant ions join each other to form neutral ion pairs, bonded together not only by Coulombic forces but also possibly by forces between their two hydrophobes, resulting in micellization and/or precipitation depending on the conditions. Precipitation occurs when anionic and cationic surfactants are mixed in stoichiometric amounts, but progressive solubilization if one or the other is added in

excess. It is interesting that, despite this neutralization effect, addition of the opposite type can cause a marked increase in surface adsorption and hence marked decrease in surface tension and critical micelle concentration. Likewise, the aquatic toxicity characteristic of many anionic and cationic surfactants is usually neutralized when both type are present together (Swisher, 1987).

2.4 Detergency

Detergency is the theory and practice of dirt removal from solid surfaces by surface chemical means. It accounts for the bulk of all surfactant usage. A satisfactory detergent must possess the following properties :

1. Good wetting characteristics in order that the detergent may come into intimate contact with the surface to be cleaned.
2. Ability to remove or to help remove dirt into the bulk of the liquid.
3. Ability to solubilize or to disperse removed dirt and to prevent it from being redeposited on to the cleaned surface or from forming a scum.

The solid substrate to be cleaned may be a hard surface (e.g. glass, metal, plastics, ceramic), or fibrous (e.g. wool, cotton, synthetic fibres), or a part of the body (skin, hair, teeth). The dirt may be liquid or solid (usually it is a combination of both); it has many possible origins (e.g. skin, food, the atmosphere); it may be polar or nonpolar; of small or large particle size; chemically reactive or inert towards the substrate and/or the detergent.

The best wetting agents are not necessarily the best detergents, and vice versa. In textile washing, especially, diffusion of the surfactant molecules plays an important role.

The choice of surfactant, therefore, involves a compromise between a small hydrocarbon chain length for rapid diffusion and a longer hydrocarbon chain length for better dirt removal and dispersion characteristics. The removal of solid dirt can be considered in terms of the surface energy changes involved. If the dirt is fluid (oil or grease), its removal can be considered as a contact-angle phenomenon. The addition of detergent lowers the contact angle at the triple solid-oil-water boundary. Surfactants which adsorb at the solid-water and dirt-water interfaces will be the best detergents. Adsorption at the air-water interface with the consequent lowering of surface tension and foaming is, therefore, not necessarily an indication of detergent effectiveness; for example, nonionic detergents usually have excellent detergent action yet are poor foaming agents. Redeposition of dirt can be prevented by the charge and hydration barriers which are set up as a result of detergent molecules being adsorbed on the cleaned material and on to the dirt particles. Since the substrate and dirt surfaces tend to be negatively charged, anionic detergents tend to be more effective than cationic detergents. The most successful detergents are those forming micelles, and this originally led to the opinion that micelles are directly involved in detergent action, their role probably being that of solubilising oily material. However, detergent action is dependent upon the concentration of unassociated surfactant and practically unaffected by the presence of micelles (other than as a reservoir for replenishing the unassociated surfactant adsorbed from solution). It appears, therefore, that the molecular properties of surfactants associated with good detergent action also lead to micelle formation as a competing rather than as a contributing process (Shaw, 1980).

2.5 Cationic Surfactants

The cation active or cationic surface active agents are characterized by the fact that the hydrophobic group forms part of a cation when the compound is dissolved in

water. The class may be regarded as consisting broadly of those bases which contain a typical hydrophobic group, and may be subclassified according to the essential nature of the functional basic group. The amines and quaternary ammonium salts constitute by far the largest groups of cationic surface active agents. Since the amines are readily converted to quaternary ammonium compounds by very simple synthesis the two groups will be discussed together. They differ from each other in one very important physical property, namely, solubility. The primary, secondary, and tertiary amines containing a hydrophobic group sufficiently large to be in the surface active range are usually insoluble in water or aqueous alkaline solutions. They are soluble in acidic solutions where the pH is low enough to convert the bases to their conjugate soluble cations. The quaternary ammonium compounds by contrast are soluble in basic as well as in acidic aqueous media. This is accordance with the strong basicity of the quaternary ammonium hydroxides. Aside from the amines and quaternary ammonium compounds there is a group of nitrogenous bases including guanidines, hydrazines, amine oxides, basic nitrogen heterocyclic substances, etc. around which surface active agents have been synthesized. Finally, there is the group of non-nitrogenous bases, of which the most noteworthy are the sulfonium compounds.

In general, the cationic and anionic surface active agents will mutually precipitate when brought together in aqueous solution. This is due to the formation of the high molecular weight, poorly ionizable salt of the hydrophobic anion with the hydrophobic cation. In some cases, however, where both anion and cation are at the lower end of the hydrophobic range, the salts are soluble and have been used as surface active agents. In these cases, it cannot be truly said that the product is anion active or cation active since both ions are active. Cationic surfactants are effective anti-bacterial agents. Thus these are generally employed as disinfectants and antiseptic agents and used in germicide and sanitizer products but seldom as cleansers (Schwartz, Perry, 1978).

2.5.1 Hyamine

It belongs to quaternary ammonium salts and hydrates class. Below is an example of the produced sample of hyamine cationic surfactant (Sisley, 1964)

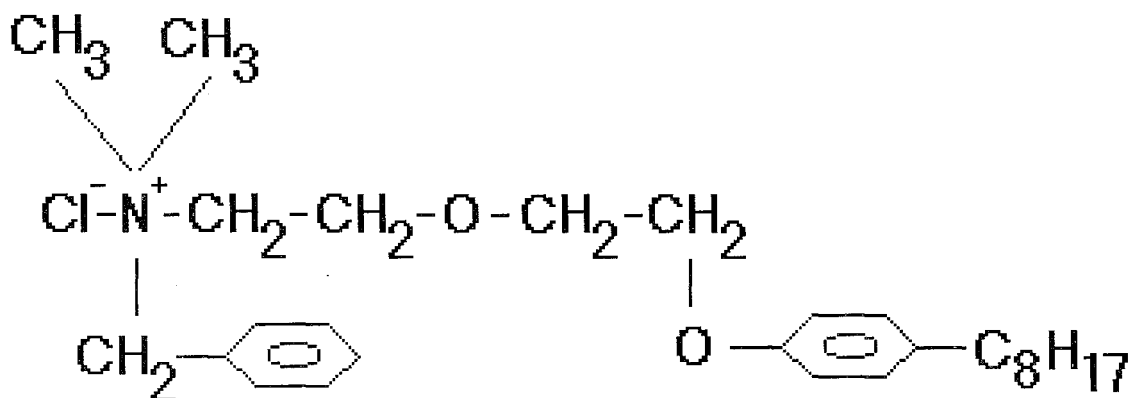


Figure 2.1 : Chemical composition of Hyamine 1622 (Sisley, 1964)

2.5.1.1 Hyamine 1622, R&H

Composition: Condensation product of para tertiary octylphenol with dichloroethyl ether and conversion of the monochloro derivative into a quaternary ammonium compound by reaction with benzyl dimethylamine chloride:

Class : II/E

Form : Powder

Properties: Stable in the presence of alkali

References : J. Am. Water Works Assoc., 39, 1035-45 (1948); Soap, Sanit, Chemicals, 1949, p. 139; A. J. Hall, Skinner's Silk & Rayon Rec., Vol. 4, 1951, p. 514.

Patterns: British 494,766; U.S. 2,170,111; 2,229,024.

Application: Used in making sanitized finish on textiles; substantive; renders articles treated immune to bacterial attack; active against the fungi *Chaetomium Globosum* and *Metarrhizium Glutinosum* which have a particular bad effect on cellulose. And some more possible uses are:

1. Destruction or diminution of the effects of bacteria
2. Elimination of moulds, algae in aquaria, etc.
3. Disinfection of dishes, plates, cloths, glasses, in hotels, canteens, restaurants, bars, etc.
4. Disinfection of dishcloths, hand towels, etc.
5. Sterilization of articles by destroying bacteria that cause putrefaction or moulds
6. Washing sheets, linens, etc.
7. Deodorization of cooking utensils
8. Washing fruits and vegetables
9. Sterilization of fish markets and equipment used in preserving works
10. Preserving fish
11. Gold sterilization of surgical instruments
12. Cleaning wounds and the skin, preparation of areas for operations
13. Deodorization of eating places
14. Sanitation of fruit stores
15. Sanitary control for baths and showers
16. Preventing development of mould on foods
17. Preservative treatment for leather
18. Destruction of algae in the refrigeration systems of air conditioning apparatus.
19. Sterilization of bathrooms and toilet utensils
20. Cleaning meat before refrigeration

(Sisley, 1964)

2.6 Anionic Surfactants

The anionic series has been applied mainly for wetting, detergency, emulsification, and the other functions which are usually associated with the term surface activity.

Anionic surfactants are used as active ingredients in products like hair shampoo, hand dish washing liquids and washing powders and flakes. Anionic surfactant may cause skin irritation and other skin ailments through the removal of natural oils especially to those who are sensitive (Schwartz, Perry, 1978).

2.6.1 SDS (Sodium Dodecyl Sulphate)

In the class of Products obtained by sulfonation of fatty bodies without previous treatment. Below are two examples of the produced samples of the sodium dodecyl sulphate surfactants (Sisley, 1964).

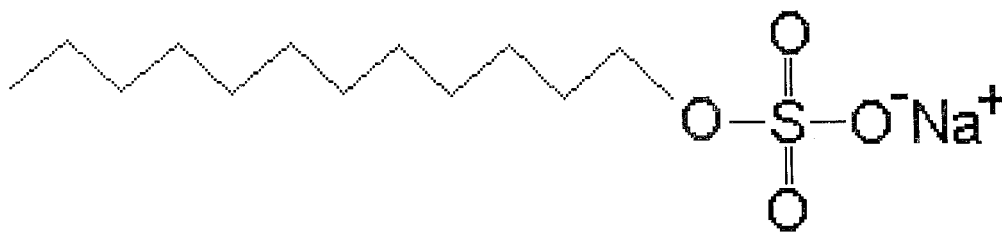


Figure 2.2 : Chemical composition of SDS (Sisley,1964)

2.7 Nonionic Surfactants

2.7.1 Water soluble types

The most strongly hydrophilic groups encountered in surface active agents are the ionic groups, and the majority of water soluble surface active agents are in fact ions. There are, however, certain configurations which are hydrophilic, but nonionic. The two best known radicals in this class are ether oxygen and hydroxyl. Other groups containing oxygen, such as carboxylic ester, and those containing non basic nitrogen, such as the amide group are also distinctly hydrophilic. It is very unusual for groups other than hydroxyl or ether to occur in sufficient number in a single large molecule to render the molecule water soluble. This is particularly true when the molecule contains a typical hydrophobic groups. Modern synthetic methods allow the introduction of a controlled number of ether or hydroxyl group into a hydrophobic molecule, thereby conferring on it any desired degree of compatibility with water. Thus it is possible to start with a substance such as octadecyl alcohol (which has more hydrophilic character than octadecane but is still water insoluble) and progressively introduce ethylene ether groups by means of ethylene oxide. The products become more and more hydrophilic, and finally completely soluble in water when about twelve to fifteen ethylene ether groups have been introduced.

The nonionic surface active agents are usually considered to include only those compounds which are soluble in water. There is a large number of compounds which are dispersible in water and which have surface active properties but do not have enough hydrophilic character to be fully soluble in water. The water insoluble compounds are for the most part oil soluble and are sometimes grouped under the name oil soluble emulsifying agents (Schwartz, Perry, 1978)

2.7.2 Oil Soluble Emulsifying Agents

A class of compounds which is very widely used commercially consists of those nonionic substances containing too few hydrophilic groups to render them water soluble, but enough such groups to give them a distinct polar character. These substances are for the most part soluble in oxygenated, aromatic, and halogenated solvents and in some cases in mineral oils. They have in general a powerful emulsifying effect, usually forming W/O (water-in-oil) emulsions when introduced into an oil-water system. In themselves they are often dispersible to form O/W (oil-in-water) systems in water. Their water solubility increases progressively with the number of hydrophilic groups present and inversely with the relative size of the hydrophobic group. The best known oil soluble nonionic emulsifying agents are the fatty acid esters of polyhydric alcohols or of ether alcohols (Schwartz, Perry, 1978).

2.8 Mixed Surfactant Types – Zwitterionics

Products are also in use which do not fit precisely into one of the three main categories – anionic, nonionic, or cationic – or which belong to more than one. These have been designated with a variety of special properties for specialty uses and are produced in relatively small quantities. Prominent among these are the zwitterionic or amphoteric surfactants, wherein the molecule contains both anionic and cationic centers. Frequently they are derivatives of methylated glycine such as sarcosine, or betaine with the hydrophobe group linked to the N. In the zwitterionic surfactants the hydrophobe is generally a fatty alkyl group

3. SOIL

Soil is a complex mixture of mineral matter, air, water, organic matter, and living organisms (<http://interactive.usask.ca/skinteractive/modules/agriculture/soils>).

3.1 Soil Composition

Soil is a three phase system. It is made up of solids, liquids and gases. The solid part is the mineral (non-living or inorganic) material and the living (organic) matter components. Water and air make up the liquid and gas parts of the soil. The amounts of each type of matter in the soil determine the type of soil as classified by scientists. An "average" mineral soil sample consists of about 45% mineral matter, 25% air, 25% water and 1% - 5% organic matter.

3.1.1 Inorganic Substances

Mineral particles are formed from rock by physical and chemical weathering processes. The size and grouping of the various particles affect the characteristics of soil such as texture. Primary minerals come directly from rock such as quartz, feldspars and micas. Secondary minerals such as clays and salts are formed from primary particles by weathering. Gases occupy pores or spaces between the many particles in soil; most commonly found gases in soil include nitrogen, oxygen and carbon dioxide. In its liquid or gaseous form, water may occupy pore spaces not occupied by gases. Water acts as a medium where nutrients from the minerals and decaying organic matter are released and

made available to plant roots other organisms Water is also an effective temperature regulator of the soil, giving the living organisms a more stable environment to grow and reproduce (<http://interactive.usask.ca/skinteractive/modules/agriculture/soils>)

3.1.2 Organic Substances

Remains of plants, animals and their wastes provide most nutrients for soil organisms and plant growth; the constant cycling of matter maintains the nutrient content in soil. Well-decomposed matter is called humus. The amount of organic matter affects soil fertility, water carrying capacity, and tilth (looseness of soil-- allows plant roots room to grow and breathing space for soil organisms).

Living organisms - billions of tiny plants and animals, such as bacteria, fungi, worms, insects and protozoa, live in the soil. A single gram of fertile topsoil may contain a trillion bacteria or more! These organisms, along with larger plants and animals affect the amount of characteristics of soil such as the amount of organic matter present.

The solid crust of the earth, lithosphere is made up largely of eight chemical elements. Table 3.1 shows the composition of the solid crust of earth to a depth of 10 miles (Miller, 1958).

Table 3.1 Composition of Soil. (Miller, et.al., 1958)

| | % |
|------------|-------|
| OXYGEN | 47.33 |
| SILICON | 27.74 |
| ALUMINUM | 7.85 |
| IRON | 4.5 |
| CALCIUM | 3.47 |
| SODIUM | 2.46 |
| POTASSIUM | 2.26 |
| MAGNESIUM | 2.24 |
| TITANIUM | 0.46 |
| HYDROGEN | 0.22 |
| CARBON | 0.19 |
| PHOSPHORUS | 0.12 |
| SULFUR | 0.12 |
| OTHERS | 0.84 |

3.1.3 Characteristics of Different Soil Types

Soils are classified according to the proportions of different sized particles they contain. (<http://interactive.usask.ca/skinteractive/modules/agriculture/soils>)

3.1.3.1 Sand, loamy sand, sandy loam

These are well drained and aerated and workable for most of the year. They are very light to handle and quick to warm up in spring. Unless they have a very high organic matter content they are prone to drying out too quickly, and additional watering will be needed. This extra watering will also help to wash out the plant foods and lime from the soil, so they are likely to be acid (except for some coastal soils). They are often referred to as “hungry” soils and need lots of extra feeding. With careful management however, they can be amongst the most productive soil types.

3.1.3.2 Medium loam, sandy clay loam, silt loam

These are the “average” soil types. They achieve a good balance between the ability to be very productive and the minimum of attention. The medium loam group is probably the best in this respect.

3.1.3.3 Clay, sandy clay, clay loam, silty clay loam, silty clay, Silt

Although these soils are difficult to work and manage, they usually have good supplies of plant foods and lime. The main drawbacks are the high water holding capacity (which means they are late to get going in spring) and the effort required to work them. It will be needed to catch just the right weather conditions to avoid hard work and damage to the soil structure. The use of heavy machinery (and especially rotavators) should be avoided at all costs, particularly when the soil is wet.

3.1.3.4 Peat moss or fen soils

Provided they are not too acid and have effective sub drainage, these are probably the best natural soils available. They are rich in plant foods, are easily workable and early. It is possible to convert existing soil into peat type soil by adding large amounts of organic matter. Some of the keenest exhibition growers do just this. It can be time consuming and costly at first, but once you get there life becomes much easier. It must be avoided making the soil too acid though, and careful choice of organic matter is needed.

3.1.3.5 Chalk soils and limestone soils

These are the soils that contain a high proportion of chalk or lime. So much in fact, that it overrides their normal particle size classification. They are often very shallow soils, and severely limit the types of plants that can be grown successfully in them.

A three sided chart which is widely used to classify soil types. The diagram shows a three sided grid with each side representing the content of a particular particle on a scale from 0% to 100%. The bottom line is the sand content, starting at 0% at the bottom right hand corner, and rising to 100% in the bottom left hand corner. Moving clockwise around the triangle, the line from the bottom left corner to the top point of the triangle is the clay content, starting at 0% in the bottom left corner and rising to 100% at the top. Continuing clockwise, silt starts at 0% at the top of the triangle and increases to 100% at the bottom right hand corner. By following the percentage lines for sand silt and clay to wherever they meet inside the triangle it can be determined which category soil falls into.

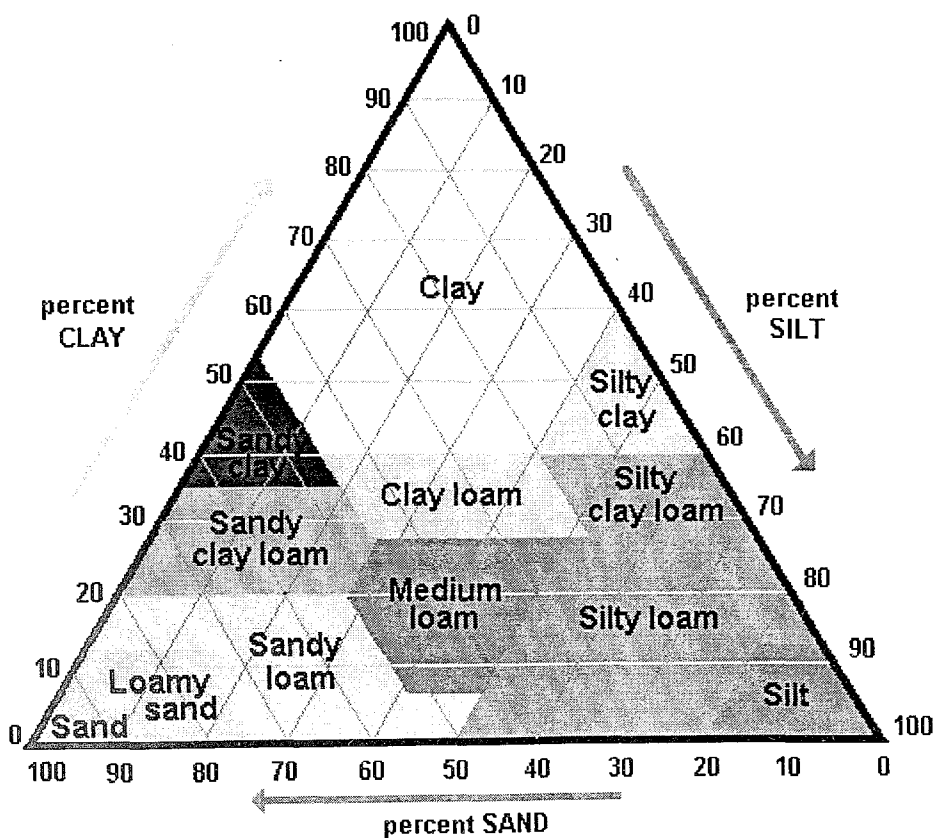


Figure 3.1 3-side grided diagram that helps locating the type of soil

To locate the exact point on the grid it should be first calculated the percentage of sand, silt and clay in the total sample without including the organic matter in the total. Then the percentage of sand, as your starting point, is taken and, using the bottom of the triangle grid to find the corresponding percentage, a line upwards is drawn and to the left (parallel with the right hand side of the triangle) at the exact percentage.

Next the percentage of clay is taken and, using the left hand slope of the triangle grid the percentage point is found. Starting at that point, a line horizontally across (parallel with the bottom of the triangle) toward the right slope of the triangle is drawn. It will cross the sand line at some point.

The final confirmation is done is that the percentage of silt, located by the same process on the right hand slope of the triangle and following a line drawn downwards toward the bottom left will cross in the same point as the other two.

The intersection of these three lines will fall within one of the coloured areas on the grid, and this is the soil type.

3.2 Soil and Environment

Soils were considered as a natural body by Russian and US scientists in the late 1800s. This allowed scientists to study and classify soils with the objective of trying to understand soil formation from an environmental perspective. They recognized that soils were formed by weathering of surface deposits or "parent materials" by processes that were :

1. physical
2. chemical
3. biological

The concept of soil forming factors allows scientists to understand and classify soils more clearly

3.2.1 Parent Materials

Soils are formed by weathering of "parent materials". These materials have many origins such as bedrock surfaces, aeolian (wind blown), lacustrine (from glacial lake beds), alluvium (river) and organic (peat) deposits. Many of our soils have been developing since the last ice age. The soil profile is in a dynamic equilibrium. As wind and water erode particles from the surface of the profile, weathering produces more soil from the parent material. (<http://interactive.usask.ca/skinteractive/modules/agriculture/soils>)

3.2.1.1 Physical Weathering

The conversion of large rock matter into small (mineral) particles is mainly the result of physical weathering. Glacial erosion, wind, water and are the major physical forces involved in this type of weathering. The action of freezing water (and expanding in rock cracks or fissures), gravity movements (earthquakes and landslides), the burrowing actions by organisms or the movement animals across the land, are also physical forces.

3.2.1.2 Chemical Weathering

Processes which break down rock matter to produce smaller, chemically different substances are included in this category. Oxidation, carbonation and hydration are major chemical actions which break-down and change rocks from one form to another. Examples of chemical weathering include

- the reaction of iron and oxygen to form iron oxide (rust)
- dissolving of limestone (a base) in water which contains carbon dioxide, making the water slightly acidic

3.2.1.3 Biological Actions

Biological action begins the process of weathering at the very early stages as lichens and mosses desperately cling to the barren surfaces of rocks. They open up fissures and scrounge nutrients where they can, producing acids and chelating agents in an attempt to dissolve nutrients from the hostile environment. As the soil develops further the microfauna and microflora play their part in the development of humus. Billions of tiny plants and animals live, reproduce, grow and die in the soil, constantly adding organic matter to its composition.

The soil is a habitat for living things that carry out the biological actions. Without these living things, soil would not be soil as we know it. These living organisms in the soil provide (<http://interactive.usask.ca/skinteractive/modules/agriculture/soils>)

- a cover of vegetation to protect the soil.
- nutrients (through decomposition, there is the addition of organic matter).
- roots to help bind soil particles.
- mixing of soil components (by the action of animal organisms such as ants, worms).
- cycling of nutrients.

3.3 Soil profile

Soils develop over long periods of time, perhaps ten thousand years, as a response to the soil forming factors. With time, soils generally become deeper and develop distinct layers. Soil is composed of three distinct horizontal layers which often are discernible by differences in color. These layers are called horizons, and their sequence (downward from the soil surface) is referred to as the soil profile. The soil profile in mineral soils has three horizon types, from the surface downwards called A, B and C. Horizons can usually be distinguished by color differences, but closer study also shows differences in chemical and physical properties. Individual horizons have defining characteristics designated by a subscript such as Ah, Bt or Cca.

A horizon - is the top layer of soil (topsoil). This thin layer (usually less than 20 centimeters) is usually the most fertile because of the organic matter which has accumulated from plant and biological activity. In this layer, roots are most dense and exude nutrients which stimulate microorganisms which results in a high biological activity. Topsoil is very precious and can be easily eroded by water and wind and it is in

this layer that the most leaching occurs. This downward movement of percolating water moves small mineral particles and salts giving rise to a process called "eluviation". Forested soils frequently show a lighter coloured A horizon or Ae (e = "eluviated") , as organic matter and iron compounds are leached downward whereas grassland soils are darker, resulting from an accumulation of more organic matter giving the characteristic Ah (h = "humic") horizon. A horizons are distinguished by adding a second letter after the capital "A" - for example Ah, Ap, Ae. The A horizon can be subdivided into A₀₁ (litter), A₀₂ (duff), A₀₃ (leaf mold), A₁ (humus), and A₂ (leached zone). Each of these subdivisions represents a stage of progressive humification increasing from A₀₁ to A₂.

B horizon - The soil under the top layer is called subsoil. It is usually lighter in colour because it does not contain as much humus, making it less fertile. This layer can vary in thickness from a few centimetres to a metre or more. The B horizon shows accumulations of mineral particles such as clay and salts due to leaching from the topsoil. This process is called "illuviation". The B horizon usually has a denser structure than the A horizon, making it more difficult for plants to extend their roots. B horizons are distinguished on the basis of colour, structure and the kind of material that has accumulated in by leaching the horizons above. A Bt horizon has blocky structure with an accumulation of clay. A Bnt horizon accumulates both clay and sodium from salty parent material and has an easy to recognize columnar structure. The reddish Bf horizon has a significant accumulation of iron and aluminum. Whereas, the only differences in a Bm horizon are perhaps colour and structure.

C horizon - This horizon lies under the subsoil and is called the "parent material". This is the original material from which the soil developed. This layer has deposits of sand, gravel, pebbles, boulders and rock in various mixtures. The original parent material could be deposits from glacial activity (Till), from sand and silt carried by the wind (Aolean), from sediments carried by flowing water (Fluvial), including water in flood plains, or from gravity moving material down a slope.

Another source of parent material forms at the bottom of lakes (Lacustrine). Aquatic plants die, and sink to the lake floor, then decay, forming a rich organic soil. The lake bed is also a collector of silt, clay and fine sand deposited by the processes of water and wind erosion. After a long period of time, the lake is filled with soil and a very fertile field is formed. This layer is relatively unaffected by actions in the other horizons, although some accumulations of calcium, magnesium and other salts can occur. Chernozemic C horizons usually have a parent material rich in calcium and magnesium carbonates designated Cca. C horizons that contain salts: sodium, magnesium, calcium sulphates and chlorides) are designated as Csa. Cg horizons are gleyed and show dull grey colours, sometimes with mottles - typical of poorly drained areas

3.4 Soil forming factors

The action of weathering and biological activity on surface deposits eventually led to the formation of a soil profile. The kind of soil profile that developed was thought to be the result of six natural factors acting together: parent material, climate, vegetation, topography, time and man. In many instances only one or two factors dominate allowing us to understand and classify soils more easily.

3.4.1 Parent Material

Parent material refers to the surface deposits which have undergone weathering to produce the soil present today. Through the weathering process, parent material has been broken down, moved, sorted and deposited. The type of soil that has developed was, in large part, determined by the origin and type of parent material. The nature of the

underlying parent material influences the characteristics of soil formation on the surface. Such characteristics include soil structure, texture, porosity, minerals present and water holding capacity. (<http://interactive.usask.ca/skinteractive/modules/agriculture/soils>)

3.4.2 Climate

The climatic characteristics which have the greatest influence on soil formation are temperature, precipitation and wind. The effects of weathering and hence soil development may be increased with warmer temperatures and higher moisture levels. These conditions enhance chemical reactions such as hydrolysis and oxidation. Conversely, cooler temperatures and lower moisture amounts would slow down the effects of weathering. To be effective in soil development the moisture must penetrate the soil to act on the parent material. If the temperature is too warm and there is only a little moisture which may evaporate from the soil surface when the wind blows then there is very little soil development. Conversely, cooler temperatures with more and frequent rainfall and low wind speeds allow more moisture to penetrate the soil profile and enhance soil development

3.4.3 Vegetation

Vegetation is very important in soil formation from five main aspects. First it protects the soil from wind and water erosion. Second the roots of grasses and trees penetrate downwards to break up the parent material and add structure. Third plants provide organic matter which improves structure and the ability of the soil to hold moisture. Fourth plants cycle nutrients that would otherwise be washed out of the profile. Five, plant roots provide a nutrient rich habitat for soil microorganisms often called the

rhizosphere effect. Symbiotic relationships with bacteria and fungi help the plant obtain nutrients such as nitrogen and phosphorus.

3.4.4 Topography

It affects water movement in soil as well as physical, chemical, and biological processes

3.4.5 Time

It is obvious that the longer the soil forming processes have to act on the parent material the more development of the soil profile

3.5 Soil Physics

Soil physical properties are extremely important from both an agriculture and engineering standpoint. The way in which a soil is put together, or its architecture, is related to its structure which in turn is a reflection of texture, aggregation and porosity. The movement of air, water and solutes through the soil is dependent on the spaces and their configuration among the soil particles. This will also affect soil temperatures and the soil's ability to store water. Physical properties such as colour, texture and structure are used in soil classification, particularly in horizon definitions. All these properties will affect how easy the soil will support living organisms or how easy the soil will support a building.

3.5.1 Soil Separates

Soils are made up of a mixture of particles ranging from clay size of less than $2\mu\text{m}$ to gravels and stones. Smaller particles are often cemented together by organic matter, iron oxides, plant roots etc. and form the fundamental structure of soils as aggregates. Table 3.2 shows the particle size limits for soils

Table 3.2 Particle size limits for soils (Miller, et al., 1958)

| TYPE | PARTICLE SIZE |
|-------------|----------------------|
| Coarse sand | 2 mm – 0.2 mm |
| Fine Sand | 0.2 mm- 0.02 mm |
| Silt | 0.02 mm – 0.002 mm |
| Clay | Less than 0.002 mm |

3.5.2 Density and Porosity

Bulk density is the mass of 1 cm^3 of the soil which includes both solid particles plus the voids among particles or the pore space. Porosity is derived mathematically from bulk density and the density of the soil solid particles or particle density. The size of soil particles and how they are clumped together or aggregated largely determines the bulk density and porosity.

3.5.3 Structure

The term structure refers to grouping of the primary soil particles into secondary clumps or aggregates-often called peds. Structure is important to components that flow such as water, air, heat, nutrients. Chemical conditions such as salinity can severely affect structure.

3.5.4 Texture

Soil texture is a reflection of the distribution of particle size fractions in soils or the relative amounts of sand silt and clay. Fine textured soils contain more clay size minerals and have relatively high porosity but the pores are small and often discontinuous. In contrast, coarse textured soils contain sand sized minerals and have more porosity but bigger pores that are connected.

3.5.5 Colour

The colour of soil surface horizons is related to how much organic matter is present. In sub surface horizons mineral composition becomes important. Accumulations of oxidized iron compounds give red colours, loss of organic matter and iron compounds gives light coloured grey horizons.

3.6 Soil Chemistry

Soil chemistry studies the chemical characteristics of soil which depends on their mineral composition, organic matter and environment

3.6.1 Cation Exchange

An example of chemical properties in soils is the way in which positively and negatively charged particles (ions) within the soil react to one another. The colloidal mineral and organic matter particles in soils usually have a net negative charge. Clays have more charge or cation exchange capacity than sands. Many natural soil nutrients and those from applied fertilizers have positive ions (cations) (e.g K^+ , Ca^{2+} , Mg^{2+}). These nutrients are attracted to, and held by, the soil particles so balancing the charge. This is important to soil fertility as some nutrients remain available in the soil and are not leached readily. Eventually, in humid regions, basic cations on the surface such as Ca^{2+} are gradually replaced by acidic cations such as H_3O^+ , $Al(OH)^{2+}$ and $Al(OH)^+$

3.6.2 Soil pH

pH is a measure of the hydrogen ion activity within the soil. Soils range from acidic (low pH or high free hydrogen ions) to alkaline or basic (high pH). Most soils are within a pH range from 4.5 (considered strongly acidic for soils) to 8.5 (medium alkaline). Soils which are higher in acidity or alkalinity levels can result in deficiencies or

excesses (that may be toxic) of certain kinds of elements. For instance, higher alkalinity can make elements such as iron, manganese and zinc less soluble.

4. ADSORPTION

An understanding of sorption processes is very important to environmental engineers to aid in understanding the fate and transport of contaminants in the environment and the removal of contaminants in engineered reactors. Sorption is most often defined as the concentration or movement of contaminants from one phase to another. The general term sorption is often used for the natural process rather than adsorption or absorption because the exact manner in which partitioning to solid occurs is often not known. Adsorption is the process by which ions or molecules present in one phase tend to condense and concentrate on the surface of another phase. The material being concentrated is the adsorbate, and the adsorbing solid is termed the adsorbent (Sawyer, et al., 1994).

4.1 Surface chemistry and Adsorption

Even most carefully polished surfaces are not smooth in a microscopic sense, but are irregular, with valleys and peaks alternating over the area. The regions of irregularity are particularly susceptible to residual force fields. At these locations the surface atoms of the solid may attract other atoms or molecules in the surrounding gas or liquid phase. Similarly, the surfaces of pure crystals have nonuniform force fields because of the atomic structure in the crystal. Such surfaces also have sites or active centers where adsorption is enhanced. Two types of adsorption may occur (Smith, 1981)

4.1.1 Physical Adsorption

Physical adsorption is nonspecific and somewhat similar to the process of condensation. The forces attracting the fluid molecules to the solid surface are relatively weak, and the heat evolved during the exothermic adsorption process is of the same order of magnitude as the heat of condensation, 0.5 to 5 kcal/g.mol, since the forces involved in physical adsorption are weak. The amount of physical adsorption decreases rapidly as the temperature is raised and is generally very small above the critical temperatures of the adsorbed component. This is further evidence that physical adsorption is not responsible for catalysis. Physical adsorption is not highly dependent on the irregularities in the nature of the surface, but is usually directly proportional to the amount of surface. However, the extent of adsorption is not limited to a monomolecular layer on the solid surface, especially near the condensation temperature. The adsorbed material may condense and form several superimposed layers on the surface of the adsorbent. As the layers of molecules build up on the solid surface, the process becomes progressively more like one of condensation. Physical adsorption is quite reversible; i.e., a decrease in concentration the material is desorbed to the same extent that it was originally adsorbed (Smith, 1981).

4.1.2 Chemisorption

The second type of adsorption is specific and involves forces much stronger than in physical adsorption that lead to the formation of chemical compounds. Normally, the adsorbed material forms a layer over the surface which is only one molecule thick, and the molecules are not considered free to move from one surface site to another. When the surface is covered by the monomolecular layer, the capacity of the adsorbent is essentially exhausted. Also, chemical adsorption is seldom reversible. The adsorbent

must generally be heated to higher temperatures to remove the adsorbed materials. According to Langmuir's pioneer work, the adsorbed molecules are held to the surfaces by valence forces of the same type as those occurring between atoms in molecules. Further evidence for the theory that such adsorption involves valence bonds is found in the large heats of adsorption. When the critical temperature of the component is exceeded, physical adsorption approaches a very low equilibrium value. An important feature of chemisorption is that its magnitude will not exceed that corresponding to a monomolecular layer. This limitation is due to the fact that the valence forces holding the molecules on the surface diminish rapidly with distance. These forces become too small to form the adsorption compound when the distance from the surface is much greater than usual bond distances. Langmuir proposed simple formulations for rates of adsorption and desorption of gases and liquids on solid surfaces (Smith, 1981).

4.2 Adsorption Isotherms

When the measured adsorption data are plotted against the concentration value of the adsorbate at equilibrium, a graph is obtained called adsorption isotherm. A useful relationship between the shape of the adsorption isotherm and the adsorption mechanism for a solute-solvent adsorption system.

The S-curve isotherm is characterized by an initial slope that increases with the concentration of a substance in the soil solution. This suggests that the relative affinity of the soil solid phase for the solute at low concentrations is less than the affinity of the soil for the solvent.

The L-curve isotherm is characterized by an initial slope that does not increase with the concentration of the substance in the soil solution. This behavior points out the

high relative affinity of the soil solid phase at low concentration and a decrease of the free adsorbing surface.

The H-curve isotherm is characterized by a large initial slope, which indicates the high affinity of soil solid phase for the adsorbate.

The C-curve isotherm exhibits an initial slope that remains independent of the substance concentration in the solution under the possible experimental condition. This type of isotherm looks like a constant partitioning of a solute between the solvent and the adsorbing surface. It may be due to proportional increase of the adsorbing surface as the surface excess of an adsorbate increase. (Montell, 1951).



Figure 4.1 Adsorption Curves (Myers, 1998)

4.2.1 Langmuir Isotherm

The derivations may be carried out by using as a measure of the amount adsorbed either the fraction of the surface covered or the concentration of the gas or liquid adsorbed on the surface. The important assumptions are as follows :

1. All the surfaces of the catalyst has the same activity for adsorption; i.e., it is energetically uniform. The concept of nonuniform surface with active centers can be employed if it is assumed that all the active centers have the same activity for adsorption and that the rest of the surface has none, or that an average activity can be used.
2. There is no interaction between adsorbed molecules. This means that the amount adsorbed has no effect on the rate of adsorption per site.
3. All the adsorption occurs by the same mechanism, and each adsorbed complex has the same structure.
4. The extent of adsorption is less than one complete monomolecular layer on the surface.

In the system of solid surface and liquid, the molecules of liquid will be continually striking the solid surface and a fraction of these will adhere. However, because of their kinetic, rotational, and vibrational energy, the more energetic molecules will be continually leaving the surface. An equilibrium will be established such that the rate at which molecules strike the surface, and remain for an appreciable length of time, will be exactly balanced by the rate at which molecules leave the surface (Smith, 1981)

Since the adsorption is limited to complete coverage by a monomolecular layer, the surface may be divided into 2 parts; the fraction Φ covered by the adsorbed molecules and the fraction $1-\Phi$, which is bare. Since only those molecules striking the uncovered part of the surface can be adsorbed, the rate of adsorption per unit of total surface will be proportional to $1-\Phi$; that is,

$$r_a = k_a C_e (1-\Phi) \quad (1)$$

the rate of desorption will be proportional to the fraction of covered surface

$$r_d = k_d \Phi \quad (2)$$

The amount adsorbed at equilibrium is obtained by equating r_a and r_d and solving for Φ .

$$\Phi = \frac{K_L * C_e}{1 + K * C_e}, \quad (3)$$

where ,

$$K_L = k_a/k_d \quad (4)$$

And,

$$\Phi = \frac{C_s}{C_{s,max}} \quad (5)$$

The general formula for Langmuir isotherm at equilibrium is :

$$\frac{1}{C_s} = \frac{1}{C_{s,max}} + \frac{1}{K_L * C_{s,max} * C_e} \quad (6)$$

Where,

- Φ = fraction of occupied sites
- k_a = rate constant for adsorption
- k_d = rate constant for desorption
- C_s = amount of adsorbate adsorbed per unit mass of soil
- $C_{s,max}$ = concentration required for monolayer coverage
- C_e = concentration of adsorbate remaining in solution at equilibrium
- K_L = Langmuir adsorption equilibrium constant

4.2.2 Freundlich Isotherm

Freundlich studied the adsorption phenomenon extensively and showed that adsorption from solutions could be expressed by the equation :

$$C_s = K_f * C_e^{\frac{1}{n}} \quad (7)$$

Where C_e is the equilibrium concentration of solute remaining in solution after adsorption, C_s is the mass of adsorbate adsorbed per unit weight of adsorbent, and K and n are constants which must be evaluated for each solute and temperature.

The Freundlich Isotherm is often expressed in its logarithmic form,

$$\ln C_s = \ln K_f + \frac{1}{n} \ln C_e \quad (8)$$

Adsorption data, when plotted according to Equation (8), yield a straight lines. Experimental data are often plotted in this manner as a convenient way of determining whether removal of materials from solution is accomplished by adsorption, and as a means of evaluating the constants K and n . (Smith, 1981)

4.3 Factors Effecting Adsorption

The adsorption isotherms are equilibrium equations and apply to conditions resulting after the adsorbate-containing phase has been in contact with the adsorbent for sufficient time to reach equilibrium. However, in any practical process for the removal of a contaminant from a gas or liquid, the rate at which the material is adsorbed onto the solid becomes an important consideration. Essentially three steps can be identified in the removal of a contaminant by adsorption. First, it must move from the liquid or gaseous phase through a boundary layer in the fluid to the exterior of the adsorbent. Next, it must pass by diffusion into and through the pores of the adsorbent. If the phase containing the adsorbent is quiescent, then diffusion through the boundary layer may be the slowest and rate determining step. In this case, if the fluid is agitated, the thickness of the boundary layer becomes reduced and the rate of adsorption will increase. At increase turbulence, however, a point will be reached where diffusion through the pores becomes the slowest step so that increased turbulence will not result in increased rates of adsorption. Thus, depending upon the general characteristics of the material being adsorbed and the relative rates of diffusion through the boundary layer and into the pores, increased agitation of the fluid containing the material may or may not increase the rate of adsorption. Both the rate and the extent of adsorption are dependent upon the characteristics of the molecule being adsorbed and of the adsorbent. The extent of adsorption is governed to some extent by the degree of solubility of the substance in water. The less soluble material, the more likely it is to become adsorbed. With molecules containing both hydrophilic (water liking) and

hydrophobic (water disliking) groups, the hydrophobic end of the molecule will tend to become attached to the surface. Next, the relative affinity of the material for the surface is a factor to the general types of adsorption. Finally, the size of the molecule is of significance, as this affects its ability to fit within the pores of the adsorbent, and its rate of diffusion to the surface. Generally, adsorption is increased at pH ranges where the species is neutral in charge. In addition, pH affects the charge on the surface, altering its ability to adsorb materials.

5. MATERIALS AND METHODS

5.1 Materials

5.1.1 Soil

Soil sample was taken from Trakya, Tekirdağ region. It was also used as a filling soil especially as a bottom layer in the flower pots. It was a soil collected from rocky regions of the mountains.

5.1.2 Surfactants

5.1.2.1 Sodium Dodecyl Sulphate (SDS)

SDS was supplied from BDH Laboratory Chemicals Inc. As an anionic surfactant it was used in powdered form of 99.9 percent purity. 2, 4, 6, 8, 9, 12 milimolar aqueous solutions of SDS were used in the sorption and desorption experiments. 40 mM SDS solution was used as titrant in two phase titration of Hyamine 1622.

5.1.2.2 Hyamine 1622

Hyamine 1622 was supplied from Sigma Chemical Company. As an cationic surfactant it was used in powdered form of 99.9 percent purity. 5, 10, 15, 20, 30, 40 milimolar aqueous solutions of Hyamine were used in the sorption and desorption experiments. 0.004 M hyamine solution was used as titrant in two phase titration of SDS.

5.1.3 Clays

The clays used in this research which are Kaoline, Calcium-Montmorillonite and Attapulgitite were supplied from University of Missouri, Columbia They were used in powdered form of 99.9 percent purity. The physical and chemical properties are given in Appendix B

5.1.4 Mechanical Shaker

The mechanical shaker Memmert WB 14 model was used in the experiments for shaking the samples.

5.2 Methods

5.2.1 Particle Size Analysis

100 gram of soil sample was sieved wet so as to get rid of all clay content that the soil has through the sieve which has the number 200. Sieving was performed under tap water until the clear water passing through the sieve is obtained. Then the soil remaining on the sieve was weighed. After that, the sand and clay contents of soil sample was found : 54.35 g sand and 45.65 g clay.

5.3 Sorption & Desorption Experiments

5.3.1 Sorption Experiments

8, 7, 6, 5 gram of soil samples without any clay content were weighed and mixed

concentrations which were ranged from 2 mmol/L to 12 mmol/L for SDS and 5 mmol/L to 40 mmol/L for Hyamine . The suspensions were then shaken with a mechanical shaker with 90 revolutions per minute at constant temperature ($25 \pm 2^\circ\text{C}$) for 72 hours. The suspensions were filtered. Then the solutions were titrated using the two phase titration method using a cationic surfactant in the titration of Sodium Dodecyl Sulfate and an anionic surfactant in the titration of Hyamine 1622 as the titrant. Using calibration equations (Asutay,M.,2000) , the concentration of the surfactant left in the solution was found. Taking difference between the initial concentration and the concentration left in solution, the amount of the surfactant sorbed was found. Then, data were fitted to the Langmuir and Freundlich Isotherms

5.3.2 Desorption Experiments

40 ml distilled water was added to each filtered suspension that came from sorption experiments. The samples were re-equilibrated with a mechanical shaker with 90 revolutions per minute at constant temperature ($25 \pm 2^\circ\text{C}$) for 72 hours. Suspensions were filtered again. The filtrates were then titrated using the two phase titration method as described in sorption experiments. Then desorption data was fitted to the Langmuir and Freundlich Isotherms

5.3.3 Two Phase Titration

Anionic-active matter is determined by titration with a standard cationic-active solution. The indicator consists of a mixture of a cationic dye (Dimidium Bromide) and an anionic dye (Disulphine Blue VN) and titration is carried out in a two-phase aqueous-chloroform system. The anionic surfactant forms a salt with the cationic which dissolves in the chloroform layer to give this layer a red-pink colour. At the endpoint the Hyamine 1622 cation displaces the Dimidium cation from the chloroform soluble salt and the pink colour leaves the chloroform layer as the dye passes to the aqueous phase. Hyamine

system. The anionic surfactant forms a salt with the cationic which dissolves in the chloroform layer to give this layer a red-pink colour. At the endpoint the Hyamine 1622 cation displaces the Dimidium cation from the chloroform soluble salt and the pink colour leaves the chloroform layer as the dye passes to the aqueous phase. Hyamine added in excess forms a salt with the anionic dye Disulphine Blue VN which dissolves in the chloroform layer and colours it blue. The amount of cationic surfactant is determined by using an anionic surfactant and the reaction applies the opposite. The procedure includes placing 20 ml. of the solution with unknown amount of anionic/cationic surface active agent into a vessel, add 10 ml of distilled water, 15 ml chloroform and 10 ml of acid indicator solution and titrating this solution with Hyamine 1662 for anionic and with SDS for cationic active agents (Reid , et. al., 1967)

6. RESULTS AND DISCUSSION

The results of sorption experiments were obtained according to the methods described in materials and methods section. C_i , C_e and C_s values are given in Tables A.1 – A.24 in Appendix A section. C_i is the initial SDS and Hyamine 1622 concentration, C_e is the concentration of SDS and Hyamine 1622 remaining in the aqueous solution after the surfactant is sorbed on the soil at equilibrium. C_s is the content of the surfactant sorbed per gram of soil. C_s was calculated from the difference between the initial C_i and the equilibrium C_e concentrations of the surfactants. The adsorption parameters of Langmuir and Freundlich isotherms are given in Tables 6.1 – 6.12 and the plots of C_e versus C_s are given in Figures 6.1- 6.24

Table 6.1 Langmuir adsorption parameters for Kaolin/Soil ratios in SDS

| Kaolin/Soil | $C_{s,max}$ | K_L | R^2 |
|-------------|-------------|-----------|-------|
| 20% | -27.08 | -0.000369 | 0.987 |
| 30% | -16.89 | -0.00049 | 0.987 |
| 40% | -8.25 | -0.000727 | 0.975 |
| 50% | -6.74 | -0.00075 | 0.95 |

Table 6.2 Langmuir adsorption parameters for Ca.Mon/Soil ratios in SDS

| Ca.Mon./Soil | $C_{s,max}$ | K_L | R^2 |
|--------------|-------------|----------|------------|
| 20% | 14.4 | 0.00127 | No fitting |
| 30% | 0.46 | -0.00076 | No fitting |
| 40% | 1.43 | -0.00084 | No fitting |
| 50% | 1 | -0.00044 | No fitting |

Table 6.3 Langmuir adsorption parameters for Atta./Soil ratios in SDS

| Atta./Soil | $C_{s,max}$ | K_L | R^2 |
|------------|-------------|----------|------------|
| 20% | -14.43 | -0.00143 | 0.876 |
| 30% | -27.55 | -0.00113 | 0.85 |
| 40% | -7.06 | -0.00314 | No fitting |
| 50% | 93.45 | 0.00066 | No fitting |

Table 6.4 Langmuir adsorption parameters for Kaolin/Soil ratios in Hyamine

| Kaolin/Soil | $C_{s,max}$ | K_L | R^2 |
|-------------|-------------|--------|-------|
| 20% | 69.4 | 0.028 | 0.951 |
| 30% | 92.84 | 0.0126 | 0.92 |
| 40% | 68.8 | 0.152 | 0.982 |
| 50% | 82.36 | 0.021 | 0.991 |

Table 6.5 Langmuir adsorption parameters for Ca.Mon./Soil ratios in Hyamine

| Ca.Mon./Soil | $C_{s,max}$ | K_L | R^2 |
|--------------|-------------|---------|-------|
| 20% | 63.08 | 0.0286 | 0.975 |
| 30% | 58.36 | 0.00818 | 0.946 |
| 40% | 63.84 | 0.0062 | 0.95 |
| 50% | 110.8 | 0.0014 | 0.992 |

Table 6.6 Langmuir adsorption parameters for Atta./Soil ratios in Hyamine

| Atta./Soil | $C_{s,max}$ | K_L | R^2 |
|------------|-------------|-------|-------|
| 20% | 47.96 | 0.131 | 0.926 |
| 30% | 50.84 | 0.123 | 0.963 |
| 40% | 41.72 | 0.159 | 0.882 |
| 50% | 191.48 | 0.005 | 0.991 |

Table 6.7 Freundlich adsorption parameters for Kaolin/Soil ratios in SDS

| Kaolin/Soil | n | K_F | R² |
|--------------------|----------|----------------------|----------------------|
| 20% | 0.947 | 0.00849 | 0.984 |
| 30% | 0.876 | 0.00458 | 0.980 |
| 40% | 0.759 | 0.00136 | 0.976 |
| 50% | 0.735 | 0.00093 | 0.970 |

Table 6.8 Freundlich adsorption parameters for Ca.Mon./Soil ratios in SDS

| Ca.Mon./Soil | n | K_F | R² |
|---------------------|----------|----------------------|----------------------|
| 20% | 1.39 | 0.0696 | No fitting |
| 30% | -0.221 | too big | No fitting |
| 40% | -0.524 | too big | No fitting |
| 50% | 0.243 | too small | No fitting |

Table 6.9 Freundlich adsorption parameters for Atta./Soil ratios in SDS

| Atta./Soil | n | K_F | R² |
|-------------------|----------|----------------------|----------------------|
| 20% | 0.756 | 0.00568 | 0.823 |
| 30% | 0.827 | 0.01416 | No fitting |
| 40% | 0.659 | 0.00344 | No fitting |
| 50% | 1.18 | 0.1236 | No fitting |

Table 6.10 Freundlich adsorption parameters for Kaolin/Soil ratios in Hyamine

| Kaolin/Soil | n | K_F | R² |
|--------------------|----------|----------------------|----------------------|
| 20% | 1.817 | 4.126 | 0.953 |
| 30% | 1.649 | 2.916 | 0.950 |
| 40% | 1.578 | 2.208 | 0.990 |
| 50% | 1.434 | 2.748 | 0.991 |

Table 6.11 Freundlich adsorption parameters for Ca.Mon./Soil ratios in Hyamine

| Ca.Mon./Soil | n | K_F | R^2 |
|--------------|-------|-------|-------|
| 20% | 1.607 | 3.064 | 0.985 |
| 30% | 1.519 | 1.108 | 0.977 |
| 40% | 1.404 | 0.816 | 0.976 |
| 50% | 1.360 | 0.46 | 0.982 |

Table 6.12 Freundlich adsorption parameters for Atta./Soil ratios in Hyamine

| Atta./Soil | n | K_F | R^2 |
|------------|-------|-------|-------|
| 20% | 1.796 | 6.16 | 0.975 |
| 30% | 1.997 | 7.04 | 0.968 |
| 40% | 1.968 | 5.96 | 0.920 |
| 50% | 1.064 | 1 | 0.973 |

Table 6.13 Langmuir desorption parameters for Kaolin/Soil ratios in SDS

| Kaolin/Soil | $C_{s,max}$ | K_L | R^2 |
|-------------|-------------|---------|------------|
| 20% | 27.4 | 0.00124 | No fitting |
| 30% | 13.44 | 0.00257 | 0.944 |
| 40% | 11.84 | 0.0104 | 0.866 |
| 50% | 8.92 | 0.0097 | 0.963 |

Table 6.14 Langmuir desorption parameters for Ca.Mon/Soil ratios in SDS

| Ca.Mon./Soil | $C_{s,max}$ | K_L | R^2 |
|--------------|-------------|----------|------------|
| 20% | 15 | 0.00255 | No fitting |
| 30% | 1.372 | -0.00268 | No fitting |
| 40% | 1.936 | -0.002 | No fitting |
| 50% | 1.252 | -0.00079 | No fitting |

Table 6.15 Langmuir desorption parameters for Atta./Soil ratios in SDS

| Atta./Soil | $C_{s,max}$ | K_L | R^2 |
|------------|-------------|---------|------------|
| 20% | 5.85 | 0.0243 | No fitting |
| 30% | -21.96 | -0.002 | No fitting |
| 40% | -17.76 | -0.0024 | 0.946 |
| 50% | 86.2 | 0.00074 | 0.824 |

Table 6.16 Langmuir desorption parameters for Kaolin/Soil ratios in Hyamine

| Kaolin/Soil | $C_{s,max}$ | K_L | R^2 |
|-------------|-------------|-------|-------|
| 20% | 60.96 | 0.102 | 0.975 |
| 30% | 54.04 | 0.113 | 0.973 |
| 40% | 42.52 | 0.491 | 0.914 |
| 50% | 101.52 | 0.018 | 0.971 |

Table 6.17 Langmuir desorption parameters for Ca.Mon./Soil ratios in Hyamine

| Ca.Mon./Soil | $C_{s,max}$ | K_L | R^2 |
|--------------|-------------|--------|-------|
| 20% | 43 | 0.151 | 0.900 |
| 30% | 52.08 | 0.0545 | 0.964 |
| 40% | 58.6 | 0.018 | 0.950 |
| 50% | 86.8 | 0.0063 | 0.993 |

Table 6.18 Langmuir desorption parameters for Atta./Soil ratios in Hyamine

| Atta./Soil | $C_{s,max}$ | K_L | R^2 |
|------------|-------------|-------|-------|
| 20% | 43 | 0.478 | 0.914 |
| 30% | 81.32 | 0.073 | 0.981 |
| 40% | 40.24 | 0.525 | 0.887 |
| 50% | 57.84 | 0.103 | 0.972 |

Table 6.19 Freundlich desorption parameters for Kaolin/Soil ratios in SDS

| Kaolin/Soil | n | K_F | R² |
|--------------------|----------|----------------------|----------------------|
| 20% | 1.352 | 0.1032 | 0.841 |
| 30% | 1.191 | 0.0540 | 0.941 |
| 40% | 2.041 | 0.0528 | 0.867 |
| 50% | 1.857 | 0.3164 | 0.931 |

Table 6.20 Freundlich desorption parameters for Ca.Mon./Soil ratios in SDS

| Ca.Mon./Soil | n | K_F | R² |
|---------------------|----------|----------------------|----------------------|
| 20% | 1.823 | 0.2744 | No fitting |
| 30% | 0.246 | too small | 0.888 |
| 40% | 0.031 | too small | No fitting |
| 50% | | | |

Table 6.21 Freundlich desorption parameters for Atta./Soil ratios in SDS

| Atta./Soil | n | K_F | R² |
|-------------------|----------|----------------------|----------------------|
| 20% | 1.343 | 0.1632 | No fitting |
| 30% | 1.008 | 0.0612 | No fitting |
| 40% | 0.846 | 0.0260 | 0.907 |
| 50% | 1.04 | 0.0752 | No fitting |

Table 6.22 Freundlich desorption parameters for Kaolin/Soil ratios in Hyamine

| Kaolin/Soil | n | K_F | R² |
|--------------------|----------|----------------------|----------------------|
| 20% | 1.925 | 7.68 | 0.959 |
| 30% | 1.924 | 7.08 | 0.989 |
| 40% | 2.234 | 11.4 | 0.981 |
| 50% | 1.542 | 3.48 | 0.967 |

Table 6.23 Freundlich desorption parameters for Ca.Mon./Soil ratios in Hyamine

| Ca.Mon./Soil | n | K_F | R² |
|---------------------|----------|----------------------|----------------------|
| 20% | 1.964 | 6.12 | 0.949 |
| 30% | 1.842 | 4.40 | 0.986 |
| 40% | 1.453 | 1.70 | 0.957 |
| 50% | 1.45 | 1.288 | 0.985 |

Table 6.24 Freundlich desorption parameters for Atta.Soil ratios in Hyamine

| Atta./Soil | n | K_F | R² |
|-------------------|----------|----------------------|----------------------|
| 20% | 2.118 | 11.16 | 0.971 |
| 30% | 1.671 | 7.52 | 0.955 |
| 40% | 2.248 | 10.64 | 0.942 |
| 50% | 1.688 | 6.4 | 0.988 |

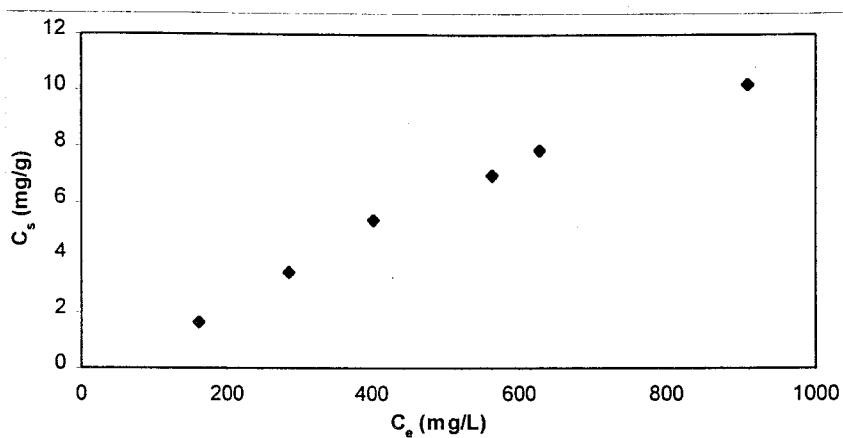


Figure 6.1 Adsorption data of SDS on %20 w/w Kaolin/Soil ratio

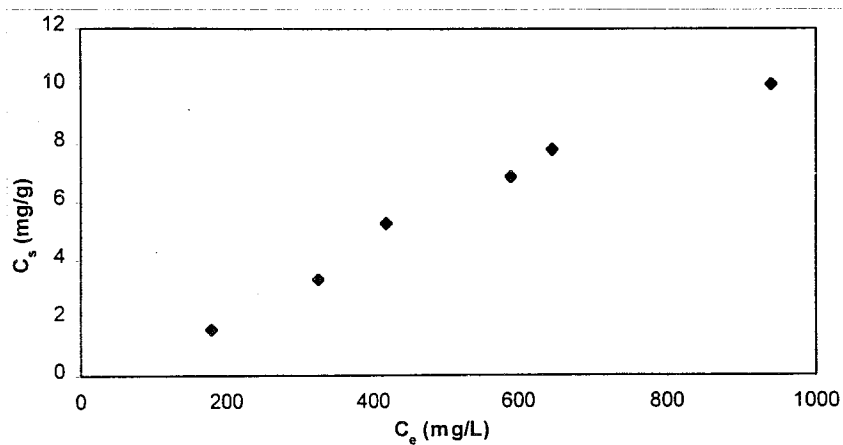


Figure 6.2 Adsorption data of SDS on %30 w/w Kaolin/Soil ratio

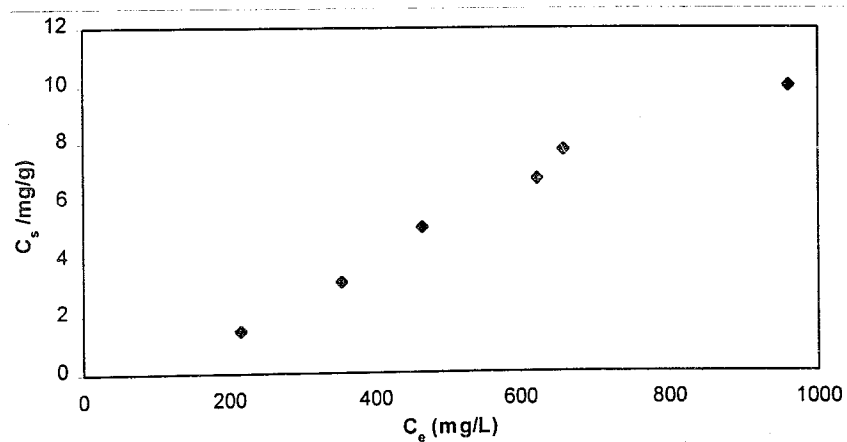


Figure 6.3 Adsorption data of SDS on %40 w/w Kaolin/Soil ratio

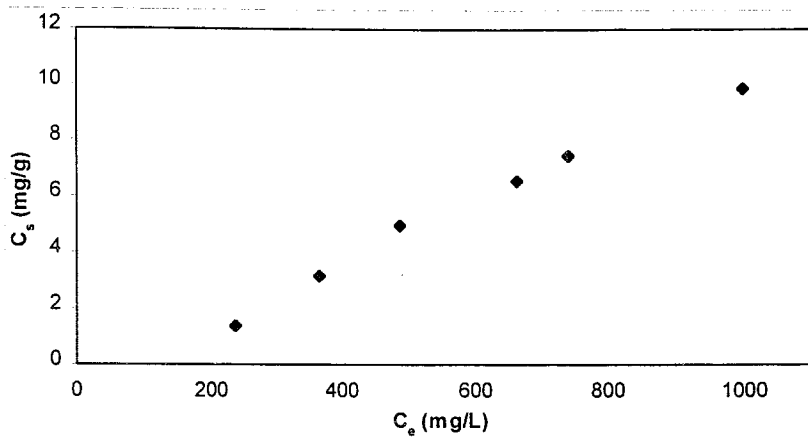


Figure 6.4 Adsorption data of SDS on %50 w/w Kaolin/Soil ratio

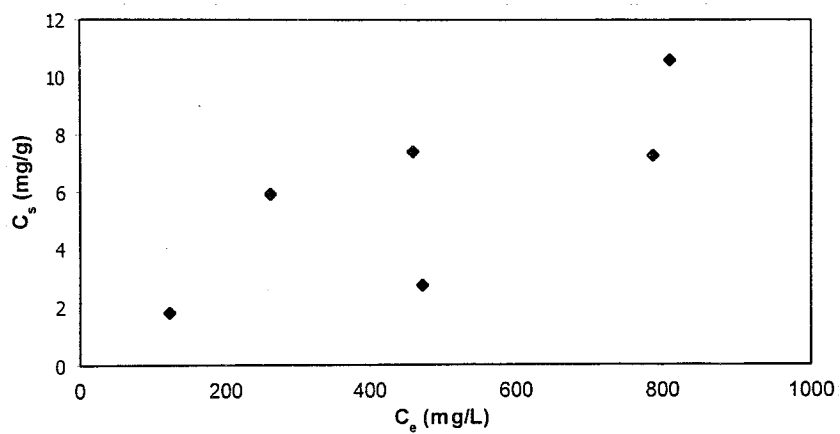


Figure 6.5 Adsorption data of SDS on %20 w/w Ca-Mon./Soil ratio

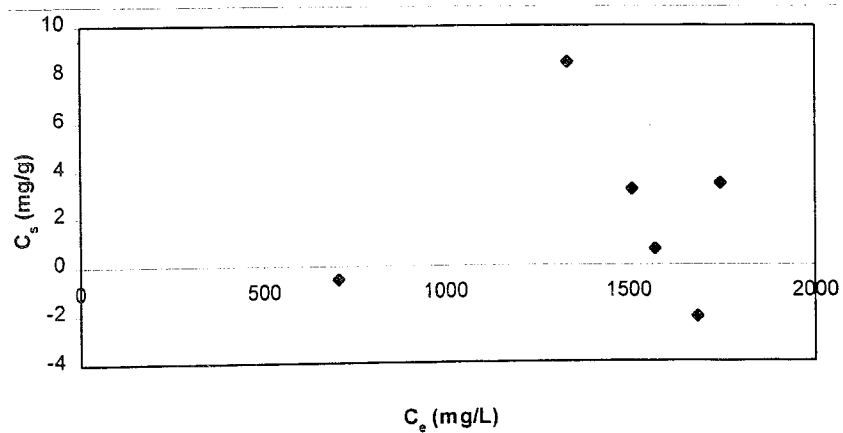


Figure 6.6 Adsorption data of SDS on %30 w/w Ca-Mon./Soil ratio

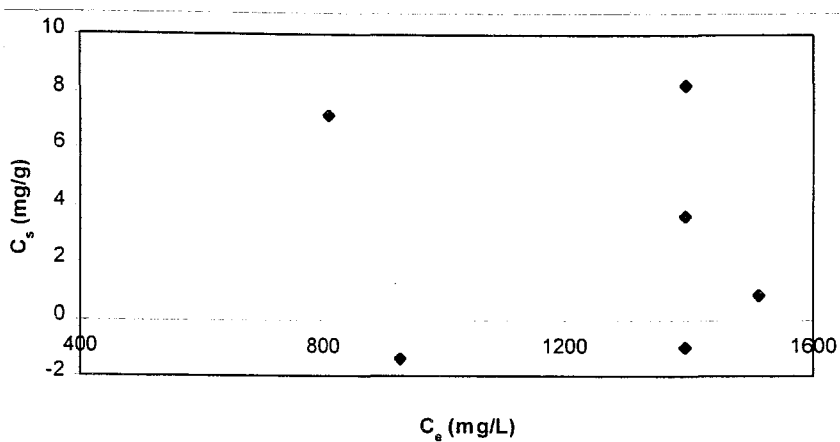


Figure 6.7 Adsorption data of SDS on %40 w/w Ca-Mon./Soil ratio

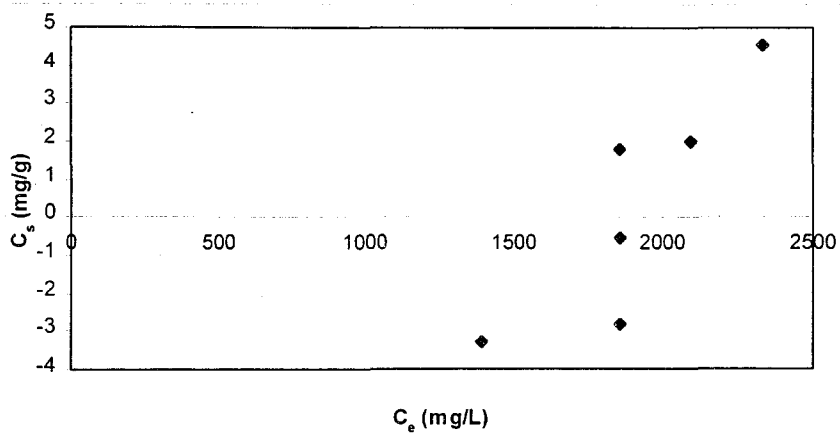


Figure 6.8 Adsorption data of SDS on %50 w/w Ca-Mon./Soil ratio

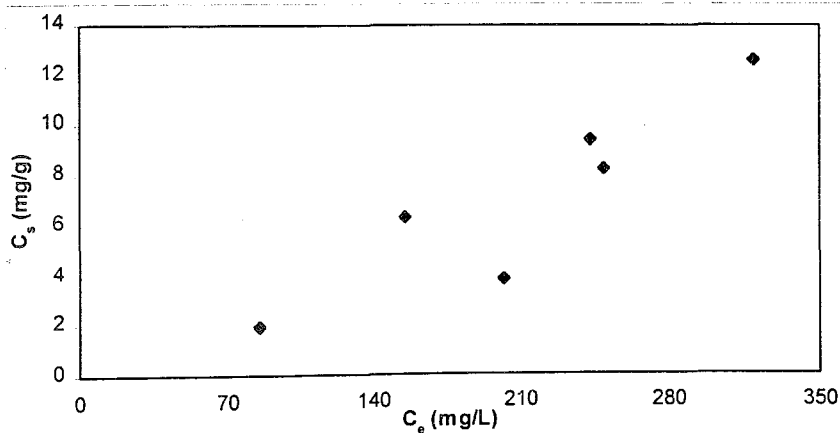


Figure 6.9 Adsorption data of SDS on %20 w/w Atta./Soil ratio

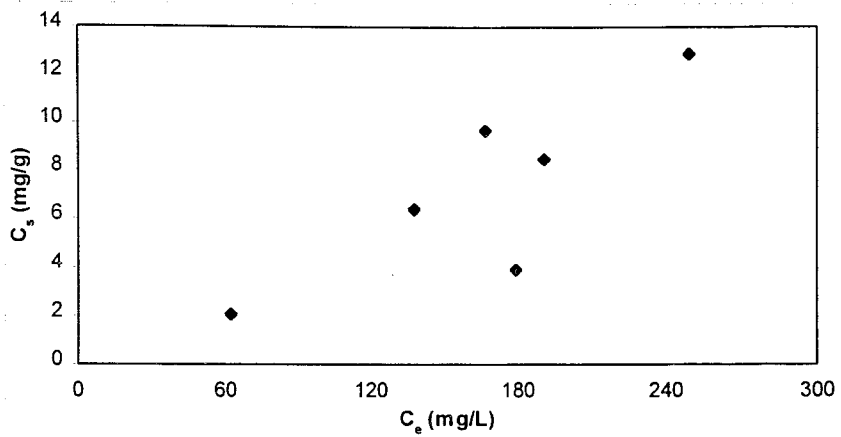


Figure 6.10 Adsorption data of SDS on %30 w/w Atta./Soil ratio

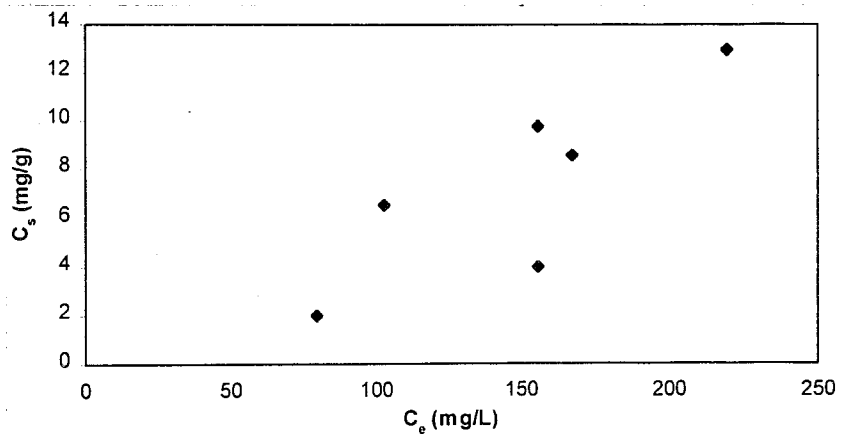


Figure 6.11 Adsorption data of SDS on %40 w/w Atta./Soil ratio

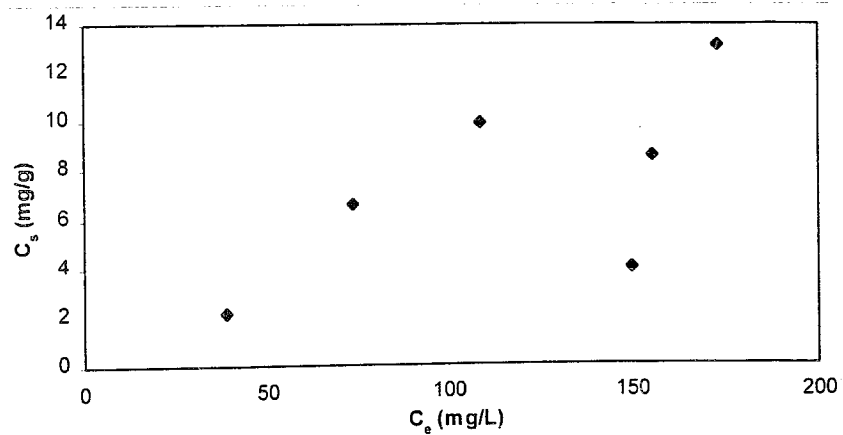


Figure 6.12 Adsorption data of SDS on %50 w/w Atta./Soil ratio

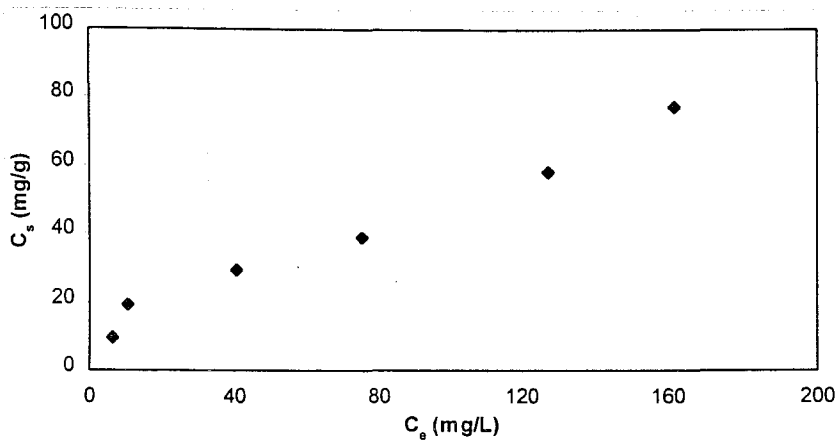


Figure 6.13 Adsorption data of Hyamine on %20 w/w Kaolin/Soil ratio

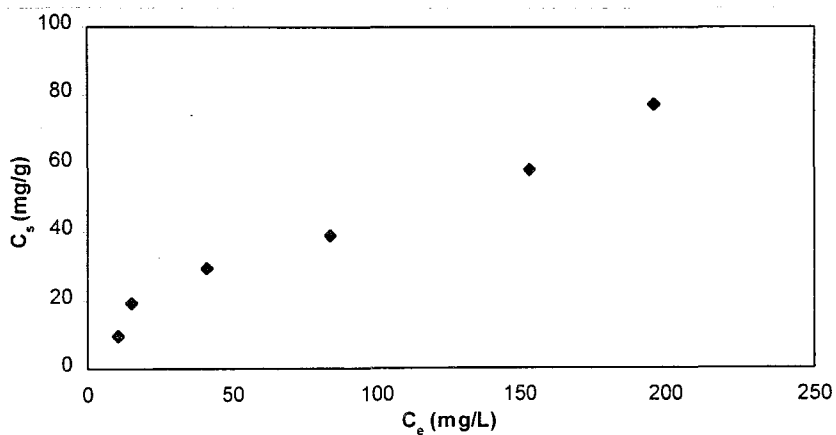


Figure 6.14 Adsorption data of Hyamine on %30 w/w Kaolin/Soil ratio

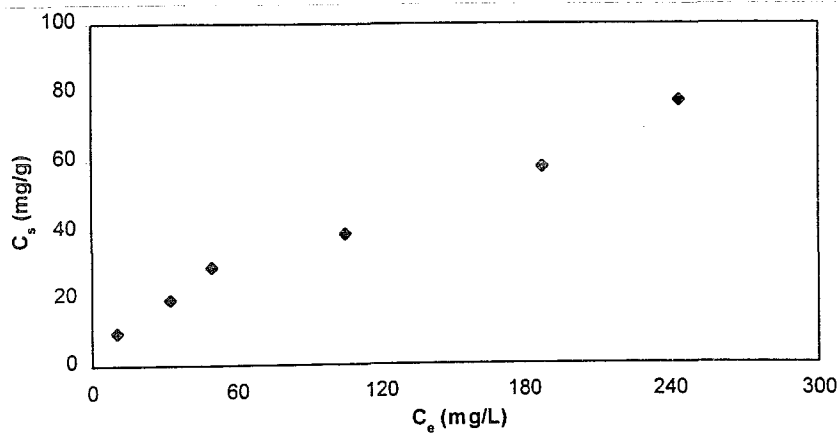


Figure 6.15 Adsorption data of Hyamine on %40 w/w Kaolin/Soil ratio

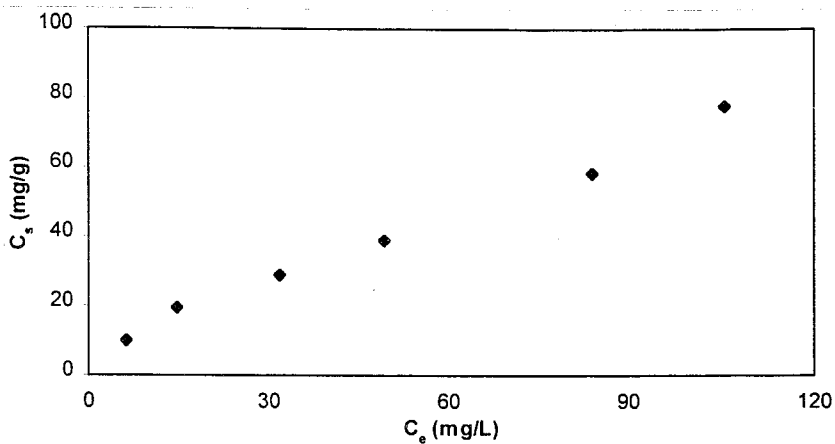


Figure 6.16 Adsorption data of Hyamine on %50 w/w Kaolin/Soil ratio

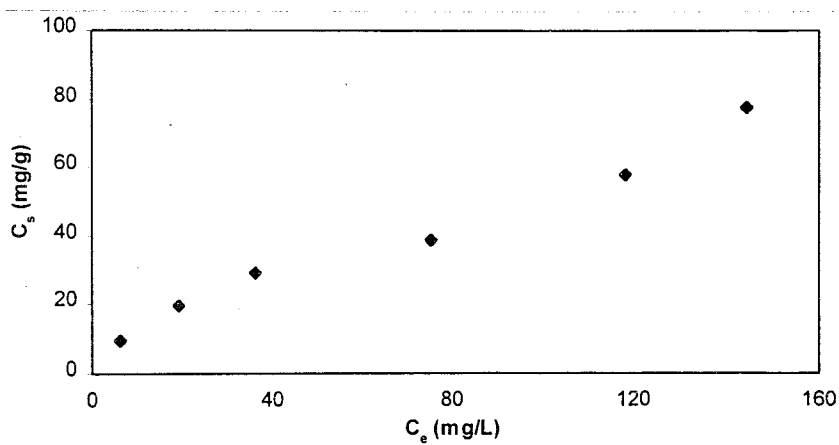


Figure 6.17 Adsorption data of Hyamine on %20 w/w Ca-Mon./Soil ratio

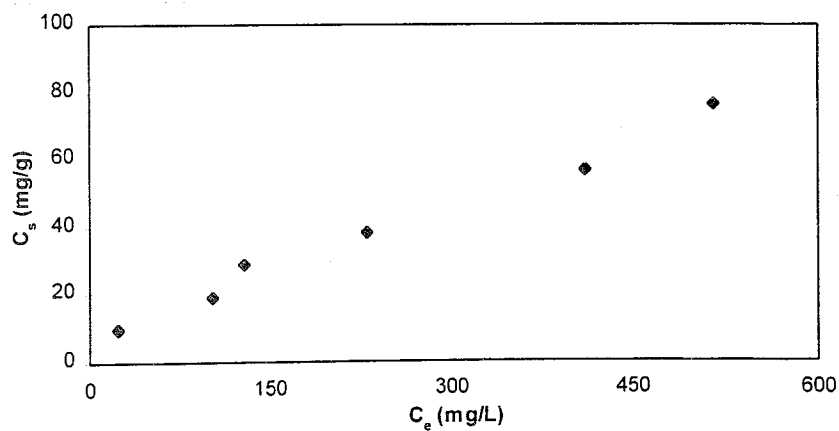


Figure 6.18 Adsorption data of Hyamine on %30 w/w Ca-Mon./Soil ratio

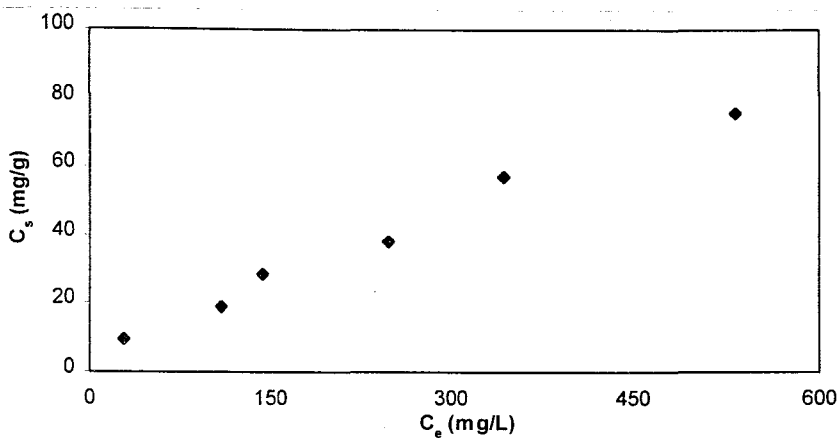


Figure 6.19 Adsorption data of Hyamine on %40 w/w Ca-Mon./Soil ratio

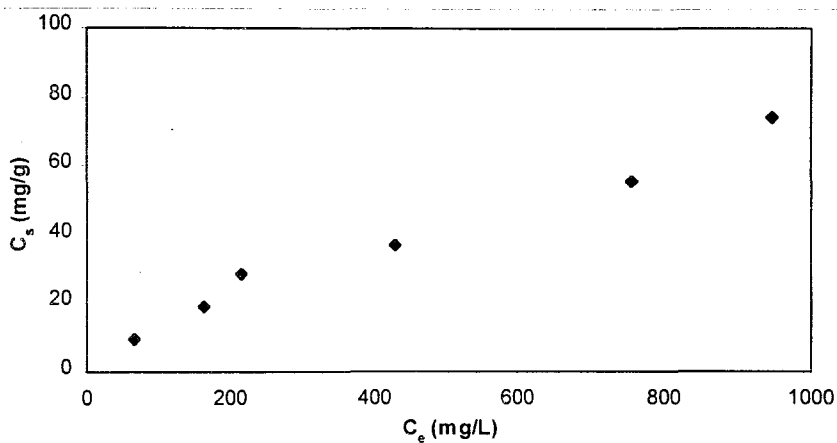


Figure 6.20 Adsorption data of Hyamine on %50 w/w Ca-Mon./Soil ratio

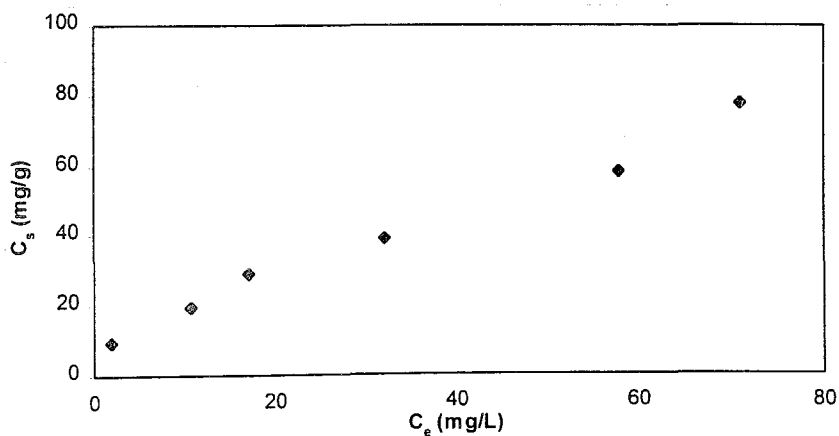


Figure 6.21 Adsorption data of Hyamine on %20 w/w Atta./Soil ratio

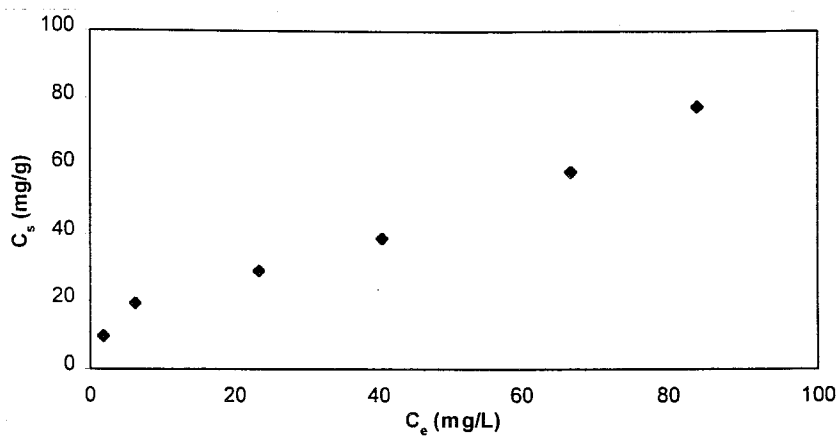


Figure 6.22 Adsorption data of Hyamine on %30 w/w Atta./Soil ratio

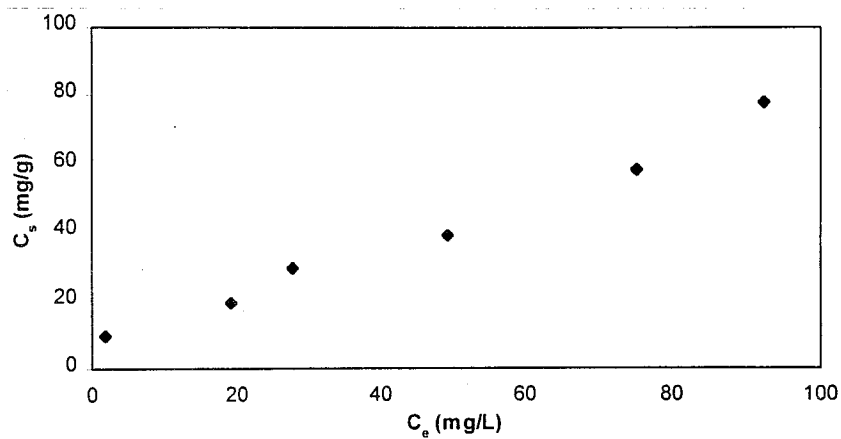


Figure 6.23 Adsorption data of Hyamine on %40 w/w Atta./Soil ratio

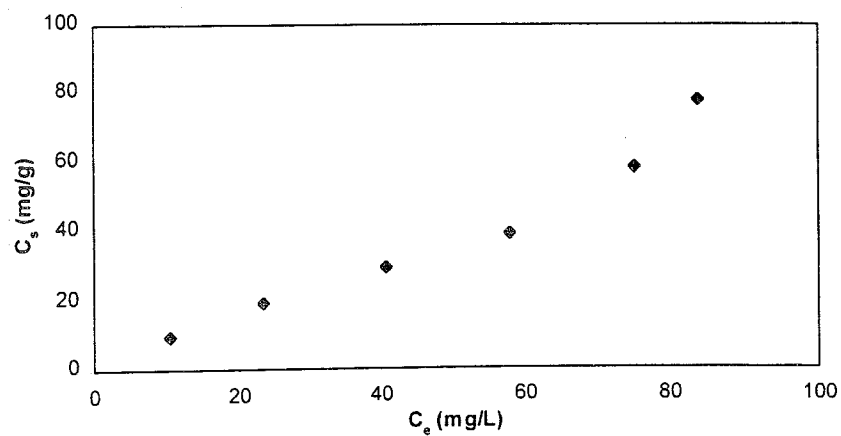


Figure 6.24 Adsorption data of Hyamine on %50 w/w Atta./Soil ratio

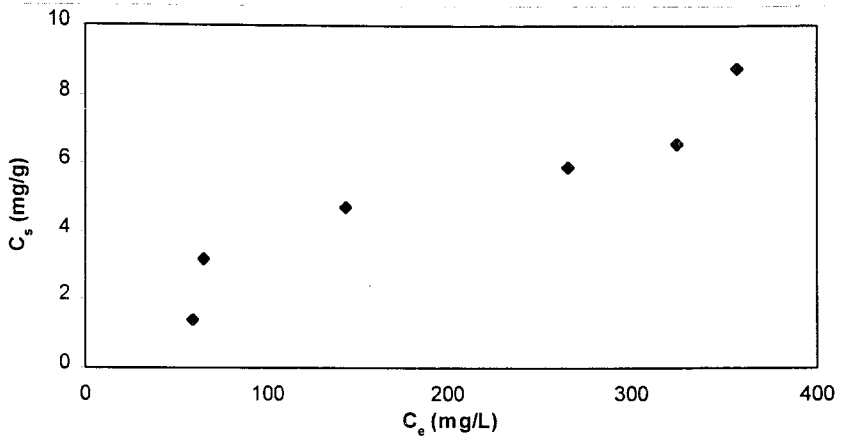


Figure 6.25 Desorption data of SDS on %20 w/w Kaolin/Soil ratio

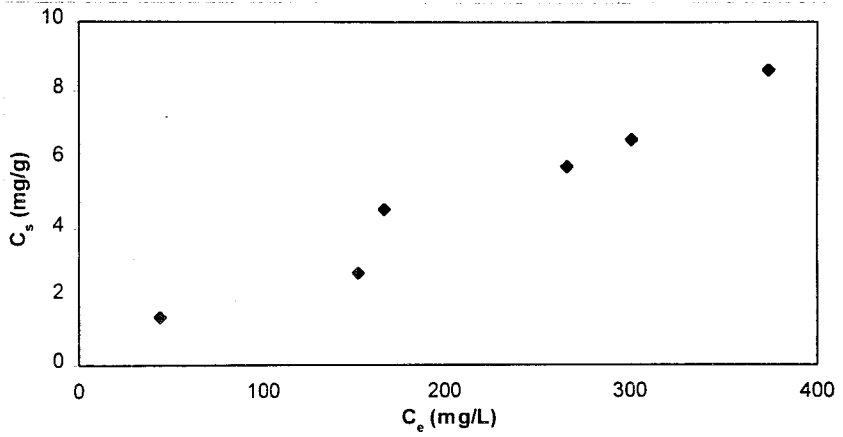


Figure 6.26 Desorption data of SDS on %30 w/w Kaolin/Soil ratio

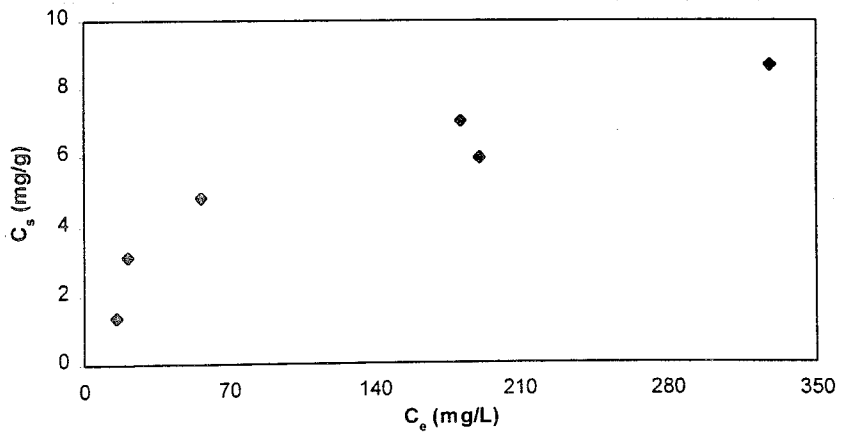


Figure 6.27 Desorption data of SDS on %40 w/w Kaolin/Soil ratio

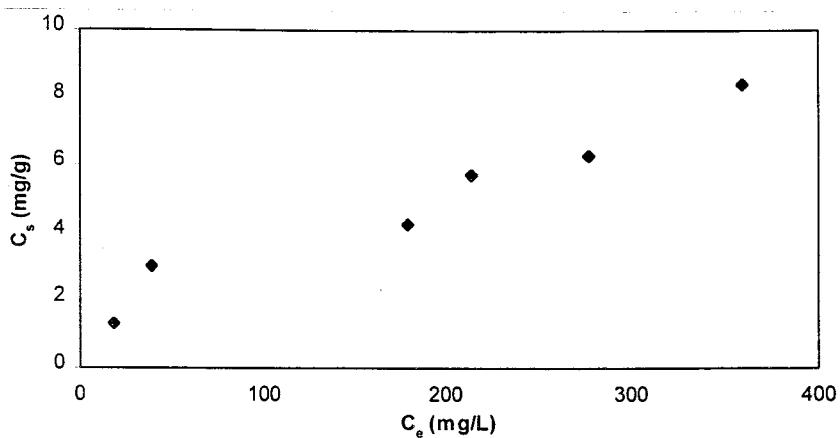


Figure 6.28 Desorption data of SDS on %50 w/w Kaolin/Soil ratio

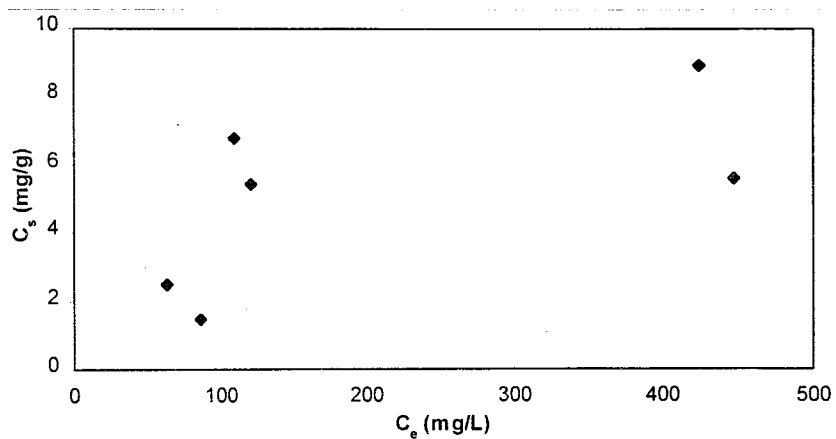


Figure 6.29 Desorption data of SDS on %20 w/w Ca-Mon./Soil ratio

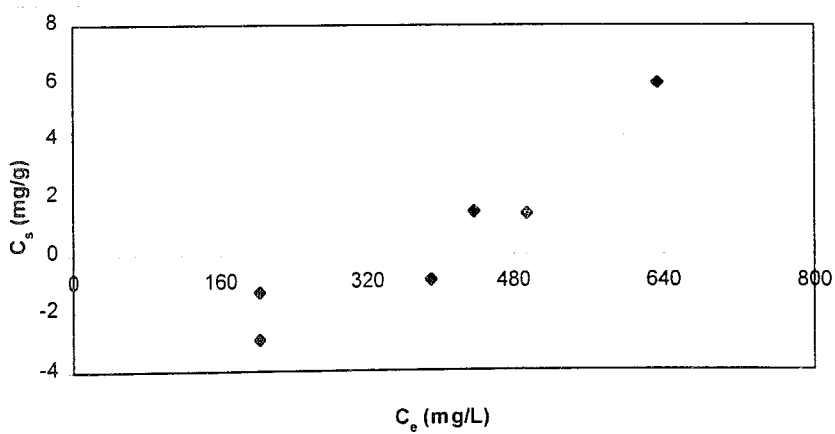


Figure 6.30 Desorption data of SDS on %30 w/w Ca-Mon./Soil ratio

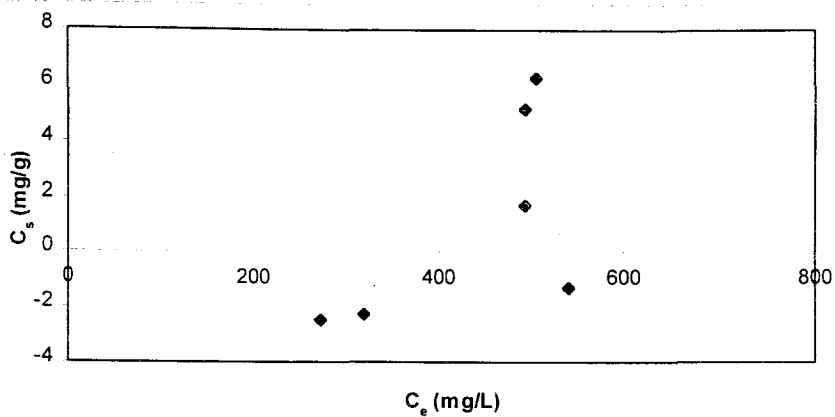


Figure 6.31 Desorption data of SDS on %40 w/w Ca-Mon./Soil ratio

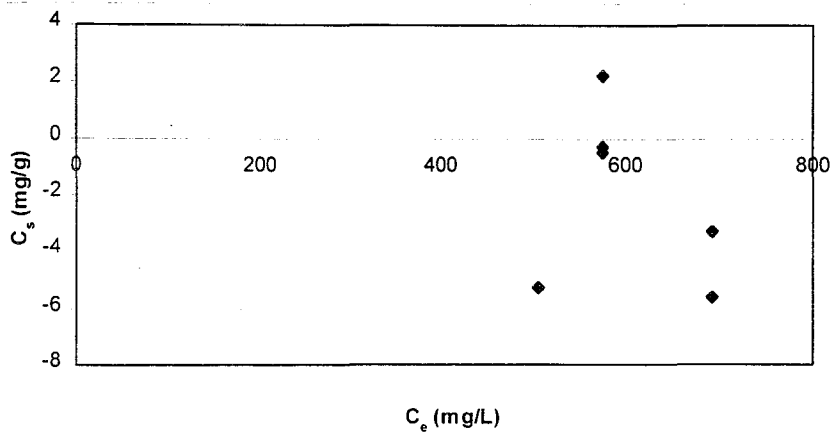


Figure 6.32 Desorption data of SDS on %50 w/w Ca-Mon./Soil ratio

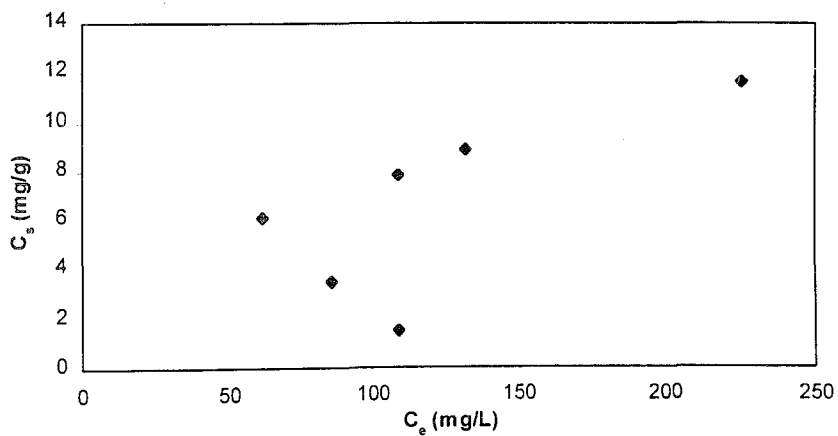


Figure 6.33 Desorption data of SDS on %20 w/w Atta./Soil ratio

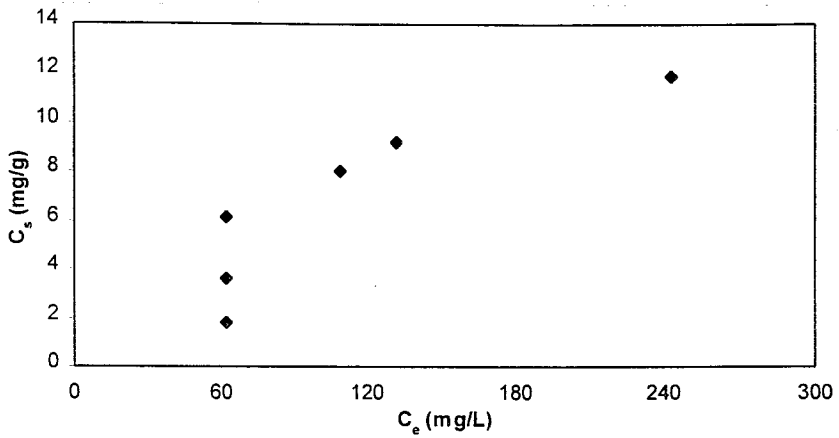


Figure 6.34 Desorption data of SDS on %30 w/w Atta./Soil ratio

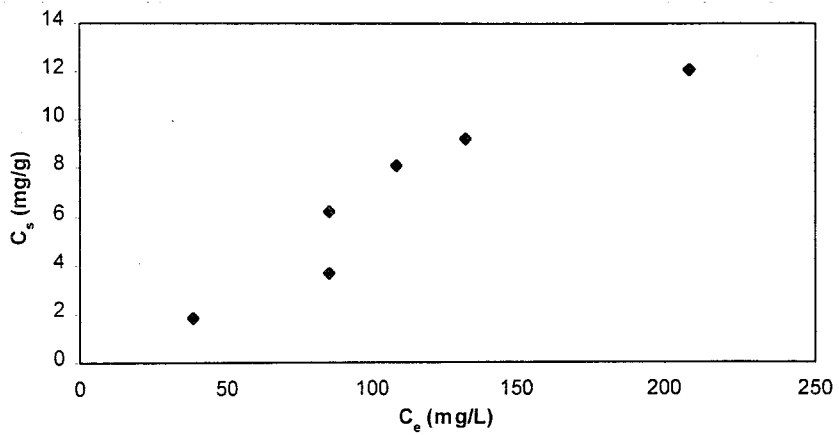


Figure 6.35 Desorption data of SDS on %40 w/w Atta./Soil ratio

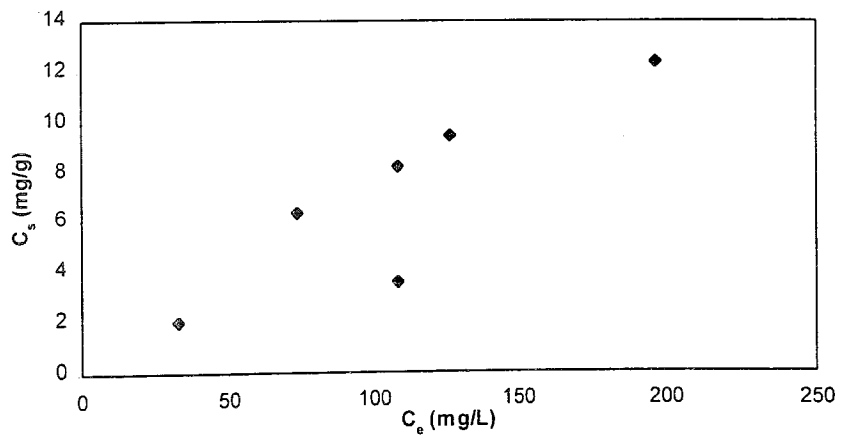


Figure 6.36 Desorption data of SDS on %50 w/w Atta./Soil ratio

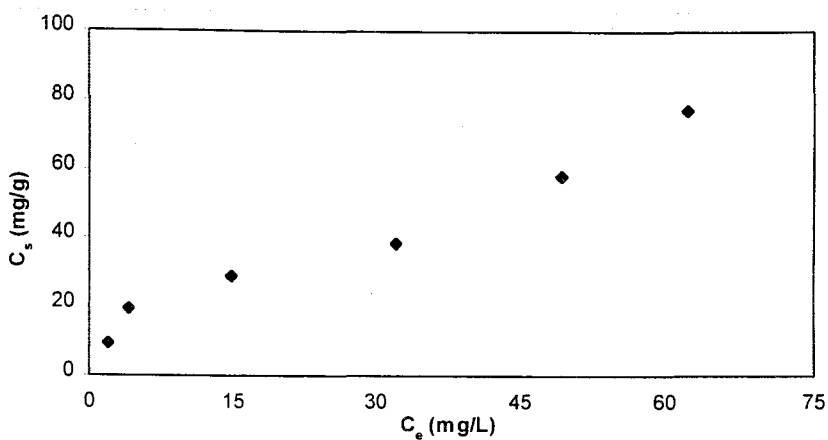


Figure 6.37 Desorption data of Hyamine on %20 w/w Kaolin/Soil ratio

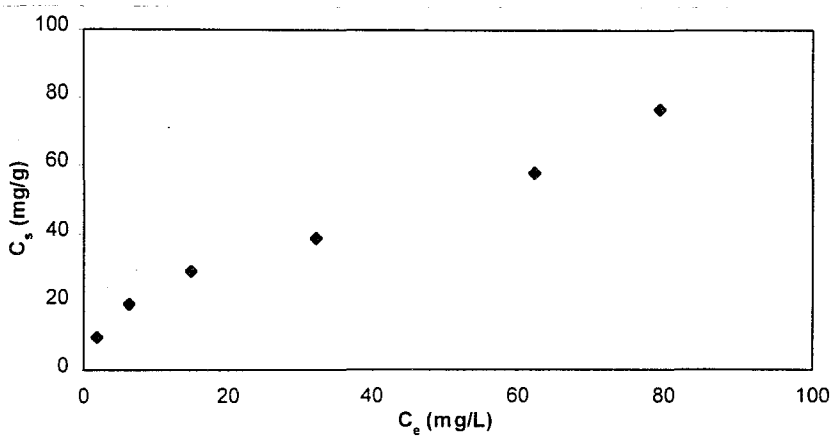


Figure 6.38 Desorption data of Hyamine on %30 w/w Kaolin/Soil ratio

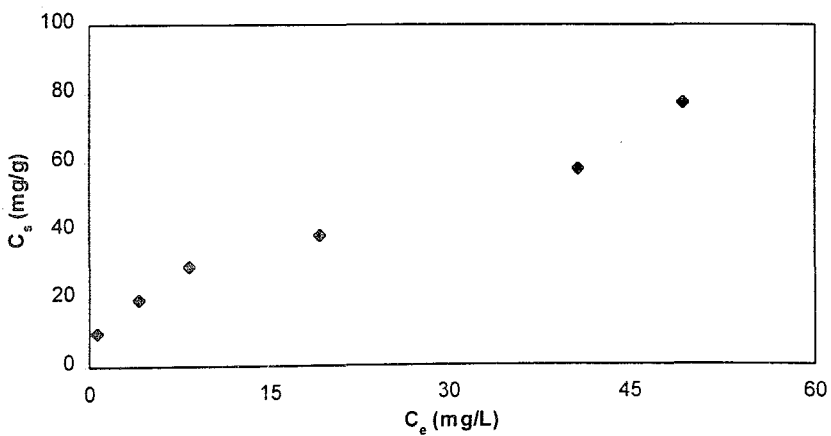


Figure 6.39 Desorption data of Hyamine on %40 w/w Kaolin/Soil ratio

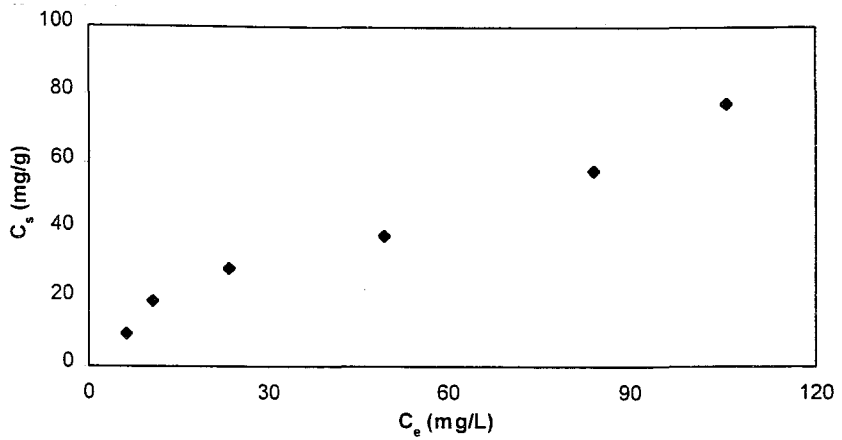


Figure 6.40 Desorption data of Hyamine on %50 w/w Kaolin/Soil ratio

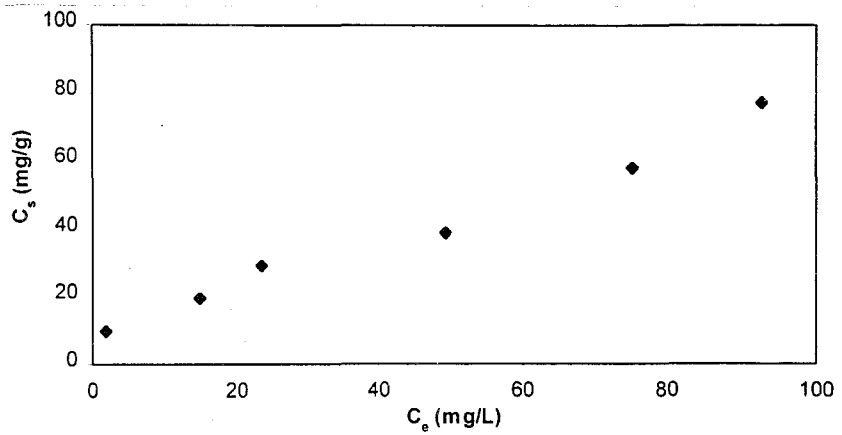


Figure 6.41 Desorption data of Hyamine on %20 w/w Ca-Mon./Soil ratio

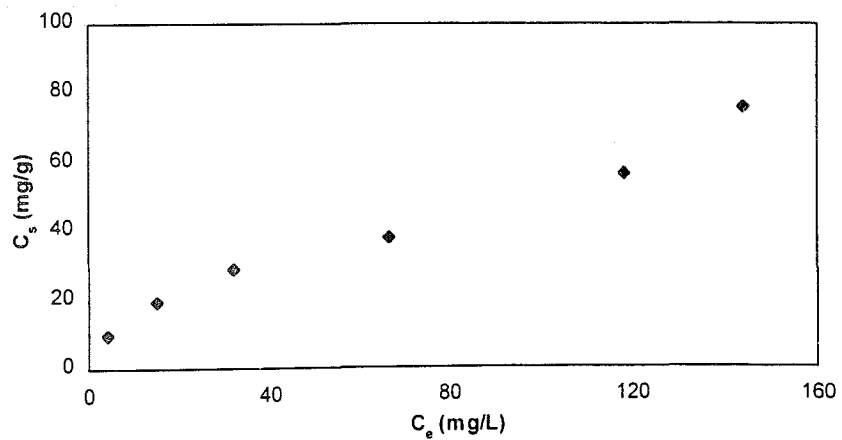


Figure 6.42 Desorption data of Hyamine on %30 w/w Ca-Mon./Soil ratio

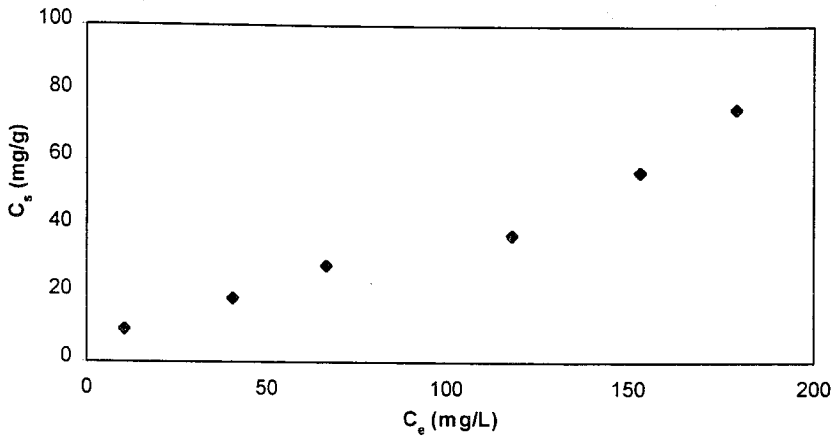


Figure 6.43 Desorption data of Hyamine on %40 w/w Ca-Mon./Soil ratio

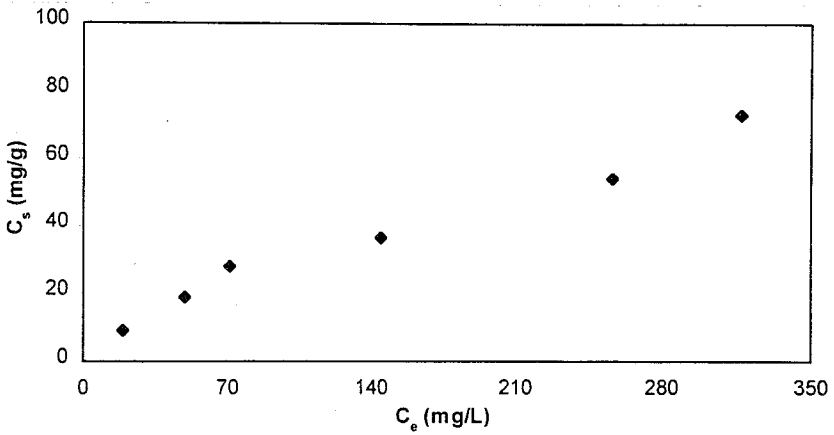


Figure 6.44 Desorption data of Hyamine on %50 w/w Ca-Mon./Soil ratio

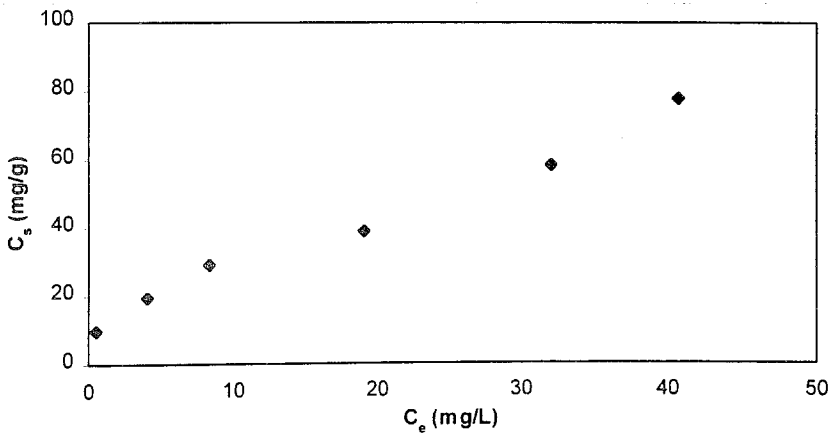


Figure 6.45 Desorption data of Hyamine on %20 w/w Atta./Soil ratio

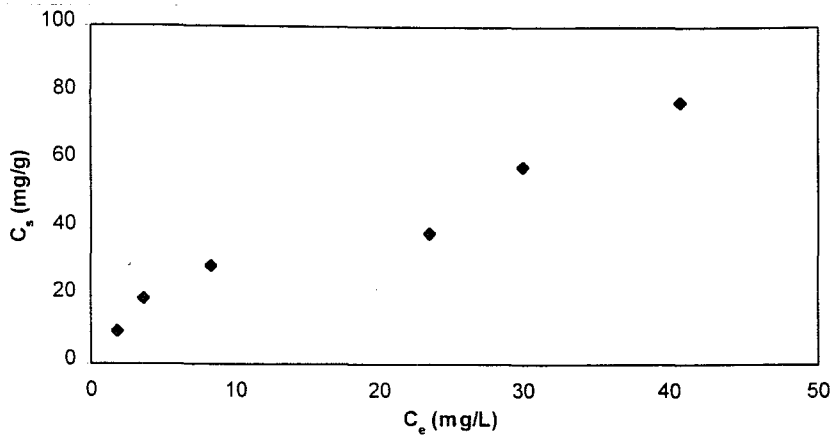


Figure 6.46 Desorption data of Hyamine on %30 w/w Atta./Soil ratio

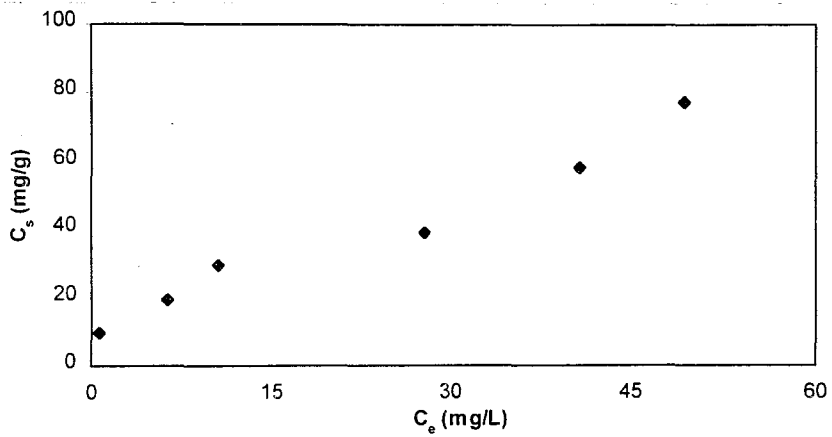


Figure 6.47 Desorption data of Hyamine on %40 w/w Atta./Soil ratio

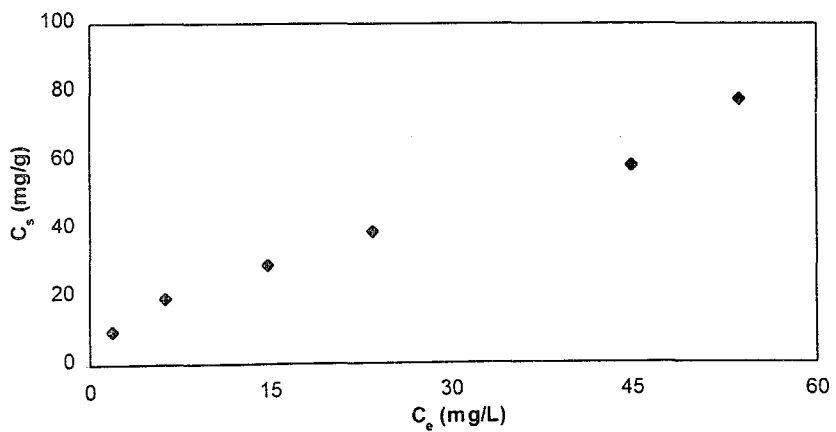


Figure 6.48 Desorption data of Hyamine on %50 w/w Atta./Soil ratio

It is observed that the sorption of sodium dodecyl sulfate (SDS) on the soil mixed with kaolin clay increased as the initial concentration of the surfactant is increased, but, on the other hand, the increase of the mixing ratio of kaolin with soil causes a quite small decrease in the sorbed surfactant concentration. It has been seen sharp decrease in the sorbed amount of surfactant when the mixing ratio of Ca.Mon/soil is augmented (especially %30 and %50 ratios). Concentration rise in each of the ratio brought about a sudden decline in the mass of sorbed surfactant compared to that of kaolin. The situation is different with the clay of Attapulgite. The augmentation of both the mixing ratio and the surfactant concentration also caused an increase in the sorbed surfactant concentration, contrary to the other two types of clay mentioned above.

It is known from the literature that SDS isotherms show the characteristic S-shaped curves on kaolin. This S-shaped curve has three different regions. In region 1, SDS sorption is low due to electrostatic repulsion between the anionic headgroup of the surfactant molecule and the kaoline surface. Any sorption which is likely to occur in this region results from interaction between the hydrophobic tail of SDS and the hydrophobic basal plane and/or by anion exchange to the small number of positively charged sites that exist. In the second region, it happens a sharp increase in the isotherm which shows increasing associations between SDS molecules at the surface. The sorption plateau which is observed in the region 3, is generally thought to correspond to either an increase in electrostatic repulsion between the anionic headgroups and/or the attainment of a constant surfactant monomer concentration in the aqueous phase. All these informations are totally agreeable with the results obtained from this research. A sorption plateau was obtained after the surfactant concentration was above critical micelle concentration is passed over.

The cationic surfactant hyamine gave different results compared to the anionic surfactant SDS when the soil, which was mixed with the three distinct clays, was placed in this surfactant solution. No change has been observed in the increasing mixing ratio of clay to soil composition in all of the three different clays. An increase in the concentration caused an increase in the sorbed amount of surfactant on the soil.

The desorption experiment results obtained according to the methods described in material and method section. C_i , C_e and C_s values are given in Tables A.25 – A.47 of Appendix A; C_i is the initial SDS and Hyamine 1622 concentration, which is taken from the difference of the initial and final concentration of the sorption experiment; C_e is the equilibrium desorbed concentration of the surfactants after the soil sample was re-equilibrated; C_s is the remaining sorbed concentration of the surfactants in soil per gram of soil. C_s was calculated from the difference between the initial C_i and the equilibrium C_e concentrations of the surfactants. C_e versus C_s plots are given in Figures 6.25 - 6.47.

The desorption experiments with SDS showed that there was no effect of the increasing amount of mixing ratio of kaolin clay to soil in the desorbed amount of surfactant, but as the concentration of the surfactant increased the desorbed amount also increased for the kaolin clay. In the case of the desorption of SDS from Ca.Mon/soil composition, it was seen that there was a decrease in the desorbed amount of surfactant when both the concentration in each mixing ratio and the ratio of clay to soil were decreased. The clay of attapulgite is different from the other two clay. The desorbed surfactant quantity augmented with the mixing ratio of clay to soil and with the increasing concentration in each mixing ratio.

The quantity of desorbed surfactant in the Hyamine solution increased with the increasing concentration of surfactant in solutions but remained almost same with the increasing mixing ratio in all of the three different clays.

When the ratios of the sorbed concentrations to the initial concentrations ($C_s:C_i$) of Hyamine for all ranges of all 3 different clay compared to those of SDS, it is that the ratios of Hyamine is bigger than the ratios of SDS indicating that the sorption capacity of Hyamine is a little better than that of SDS.

There is another important consequence is the sorption reversibilities of the surfactants. Even though the adsorption capacity of SDS is low compared to Hyamine, it shows a pretty good reversible behaviour. On the other hand, Hyamine is quite good in sorption but it is almost totally irreversible in desorption. This is probably due to the strong electrostatic attraction between the oppositely charged soil surface and the surfactant headgroup.

The anionic surfactants are sorbed due to the electrostatic repulsion between the (-) charges on soil surface and the molecule. The head-group is expected to sorb on a tail-on fashion on the surface. In this type of sorption, first sorption was low probably because of the electrostatic repulsion between the anionic head group of surfactant molecule and the negatively charged surface. In the first stages of the experiments sorption might be caused because of interactions between hydrophobic tails of anionic surfactant and the relatively hydrophobic soil surface. (Ko , et al. 1998).

As mentioned in section 4.2, adsorption isotherms can be classified according to their shapes. In 'C' type of behaviour, the sorption of solute increase almost linearly with concentration increase of the surfactant. In the 'S' type of behaviour, the adsorption of solute is low at low equilibrium concentrations. Then as initial concentration increases a rapid sorption takes place immediately. Finally although the initial concentration increase keep on rising, it is not observed any further sorption. The adsorption isotherms were expected to be 'S' type for Kaolin/Soil and Atta./Soil compositions in SDS. and 'L' type isotherm is suitable for Kaolin/Soil, Ca.Mon./Soil compositions in Hyamine. Atta./Soil mixture showed both 'S' type and 'L' type isotherm curves, while Ca.Mon./Soil mixture in SDS solution haven't showed any of the isotherm curves. The 'L' curve type is characterized by an initial slope which does not exhibit any significant increase with the concentration of the surfactant in the solution. 'H' type is characterized by a slope that indicates high affinity of soil solid phase for the adsorbate.

The desorption curves are almost totally different with those of the sorption ones. Kaolin/soil in SDS solution; and Ca.Mon./soil, attapulgite/soil in Hyamine show 'L' type whereas attapulgite/soil in SDS shows 'S' and kaoline/soil in Hyamine shows 'L' type.

The data from sorption and desorption experiments are fitted to Langmuir and Freundlich equations. The related parameters of the equations are listed in the starting section of adsorption in Tables 6.1 – 6.24. The stiffness of adsorption curve in Hyamine is bigger than that of SDS. This implies a rapid sorption behavior of the surfactant molecules to the surface of the soil. The fitting of data for Ca.Mon. in the SDS case is not good when it is compared to the sorption of SDS on the other two clays in SDS for Langmuir isotherms in sorption. On the contrary, the adaptation of data to the Langmuir equation for Hyamine for all kinds of clay is very good.

Ca.Mon. does not also behave well in fitting data to the Freundlich isotherm for SDS either. Kaolin is the best between the three types of clay. The desorption part of the fitting of data to these adsorption equation gave similar results .

7. CONCLUSION

In this study, the sorption and desorption behavior of an anionic (SDS) and a cationic (Hyamine 1622) surfactants on a soil which is mixed with three different clay at different mixing ratios were observed. Even though SDS shows the 'S' type of adsorption curves which indicate a low sorption of surfactant at the beginning and then a rapid increase in the sorption at low concentrations, the situation changes at higher concentrations and SDS exhibits the 'C' type of adsorption curve which indicates linearity, together with the 'L' type.

On the other hand, Hyamine shows same behaviour in the type of adsorption curves, which is 'L' type. At low C_1 , the adsorbed amount shows a linear increase with surfactant concentration. As the concentration of Hyamine 1622 in aqueous solution increases, there is relatively less sorption on the soil.

The anionic surfactants are sorbed due to the electrostatic repulsion between the (-) charges on soil surface and the molecule. The head-group is expected to sorb on a tail-on fashion on the surface. This is known as the 'Hydrophobic Bonding'.

The sorption of cationic surfactants might be due to the cation exchange between the head groups of the molecule and soil surface. The head-group is expected to sorb on a head-on fashion on the surface.

The sorption capacities for desorption of both surfactant were smaller than the sorption capacities for both surfactant types. The reason is that the sorption of surfactants was easier than their desorption. This result was similar for both cationic and anionic surfactants.

Hyamine 1622 gave the best results for both type of surfactants over all of the three clays. Among the three clays, kaoline is the one that brought about the finest outcome for the sorption experiments.

Langmuir is not a good isotherm to represent the data of Calcium-Montmorillonite/Soil mixture in SDS. The interaction between Calcium-Monmorillonite/Soil and SDS solution may be explained in terms of dissociation constant.

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APPENDIX A

Table A.1 Initial, equilibrium, and adsorbed concentration for SDS on 20% Kaolin/Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 3461 | 910 | 10.20 |
| 2596 | 629 | 7.87 |
| 2307 | 565 | 6.97 |
| 1730 | 401 | 5.32 |
| 1154 | 284 | 3.48 |
| 577 | 161 | 1.66 |

Table A.2 Initial, equilibrium, and adsorbed concentration for SDS on 30% Kaolin/Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 3461 | 940 | 10.08 |
| 2596 | 647 | 7.80 |
| 2307 | 588 | 6.88 |
| 1730 | 419 | 5.25 |
| 1154 | 325 | 3.31 |
| 577 | 179 | 1.59 |

Table A.3 Initial, equilibrium, and adsorbed concentration for SDS on 40% Kaolin/Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 3461 | 963 | 9.99 |
| 2596 | 658 | 7.75 |
| 2307 | 623 | 6.74 |
| 1730 | 465 | 5.06 |
| 1154 | 354 | 3.20 |
| 577 | 214 | 1.45 |

Table A.4 Initial, equilibrium, and adsorbed concentration for SDS on 50% Kaolin/Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 3461 | 998 | 9.85 |
| 2596 | 740 | 7.42 |
| 2307 | 664 | 6.57 |
| 1730 | 489 | 4.97 |
| 1154 | 366 | 3.15 |
| 577 | 237 | 1.36 |

Table A.5 Initial, equilibrium, and adsorbed concentration for SDS on 20% Ca.Mon./Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 3461 | 810 | 10.60 |
| 2596 | 787 | 7.23 |
| 2307 | 460 | 7.39 |
| 1730 | 261 | 5.88 |
| 1154 | 471 | 2.73 |
| 577 | 121 | 1.83 |

Table A.6 Initial, equilibrium, and adsorbed concentration for SDS on 30% Ca.Mon./Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 3461 | 1337 | 8.50 |
| 2596 | 1746 | 3.40 |
| 2307 | 1512 | 3.18 |
| 1730 | 1571 | 0.64 |
| 1154 | 1688 | -2.14 |
| 577 | 705 | -0.51 |

Table A.7 Initial, equilibrium, and adsorbed concentration for SDS on 40% Ca.Mon./Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 3461 | 1395 | 8.26 |
| 2596 | 810 | 7.14 |
| 2307 | 1395 | 3.65 |
| 1730 | 1512 | 0.87 |
| 1154 | 1395 | -0.97 |
| 577 | 927 | -1.40 |

Table A.8 Initial, equilibrium, and adsorbed concentration for SDS on 50% Ca.Mon./Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 3461 | 2331 | 4.52 |
| 2596 | 2097 | 1.99 |
| 2307 | 1863 | 1.78 |
| 1730 | 1863 | -0.53 |
| 1154 | 1863 | -2.84 |
| 577 | 1395 | -3.27 |

Table A.9 Initial, equilibrium, and adsorbed concentration for SDS on 20% Atta./Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 3461 | 319 | 12.57 |
| 2596 | 243 | 9.41 |
| 2307 | 249 | 8.23 |
| 1730 | 156 | 6.30 |
| 1154 | 202 | 3.80 |
| 577 | 85 | 1.97 |

Table A.10 Initial, equilibrium, and adsorbed concentration for SDS on 30% Atta./Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 3461 | 249 | 12.85 |
| 2596 | 167 | 9.71 |
| 2307 | 191 | 8.47 |
| 1730 | 138 | 6.37 |
| 1154 | 179 | 3.90 |
| 577 | 62 | 2.06 |

Table A.11 Initial, equilibrium, and adsorbed concentration for SDS on 40% Atta./Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 3461 | 220 | 12.96 |
| 2596 | 156 | 9.76 |
| 2307 | 167 | 8.56 |
| 1730 | 103 | 6.51 |
| 1154 | 156 | 3.99 |
| 577 | 80 | 1.99 |

Table A.12 Initial, equilibrium, and adsorbed concentration for SDS on 50% Atta./Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 3461 | 173 | 13.15 |
| 2596 | 109 | 9.95 |
| 2307 | 156 | 8.61 |
| 1730 | 74 | 6.63 |
| 1154 | 150 | 4.02 |
| 577 | 39 | 2.15 |

Table A.13 Initial, equilibrium, and adsorbed concentration for Hyamine on 20% Kaolin/Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 19520 | 162 | 77.43 |
| 14640 | 127 | 58.05 |
| 9760 | 75 | 38.74 |
| 7320 | 41 | 29.12 |
| 4880 | 11 | 19.48 |
| 2440 | 6 | 9.74 |

Table A.14 Initial, equilibrium, and adsorbed concentration for Hyamine on 30% Kaolin/Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 19520 | 196 | 77.30 |
| 14640 | 153 | 57.95 |
| 9760 | 84 | 38.70 |
| 7320 | 41 | 29.12 |
| 4880 | 15 | 19.46 |
| 2440 | 11 | 9.72 |

Table A.15 Initial, equilibrium, and adsorbed concentration for Hyamine on 40% Kaolin/Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 19520 | 244 | 77.11 |
| 14640 | 188 | 57.81 |
| 9760 | 106 | 38.62 |
| 7320 | 49 | 29.08 |
| 4880 | 32 | 19.39 |
| 2440 | 11 | 9.72 |

Table A.16 Initial, equilibrium, and adsorbed concentration for Hyamine on 50% Kaolin/Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 19520 | 106 | 77.66 |
| 14640 | 84 | 58.22 |
| 9760 | 49 | 38.84 |
| 7320 | 32 | 29.15 |
| 4880 | 15 | 19.46 |
| 2440 | 6 | 9.74 |

Table A.17 Initial, equilibrium, and adsorbed concentration for Hyamine on 20% Ca.Mon./Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 19520 | 144 | 77.50 |
| 14640 | 118 | 58.09 |
| 9760 | 75 | 38.74 |
| 7320 | 36 | 29.13 |
| 4880 | 19 | 19.44 |
| 2440 | 6 | 9.74 |

Table A.18 Initial, equilibrium, and adsorbed concentration for Hyamine on 30% Ca.Mon./Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 19520 | 516 | 76.02 |
| 14640 | 412 | 56.91 |
| 9760 | 231 | 38.12 |
| 7320 | 127 | 28.77 |
| 4880 | 101 | 19.12 |
| 2440 | 23 | 9.67 |

Table A.19 Initial, equilibrium, and adsorbed concentration for Hyamine on 40% Ca.Mon./Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 19520 | 533 | 75.95 |
| 14640 | 343 | 57.19 |
| 9760 | 248 | 38.05 |
| 7320 | 144 | 28.70 |
| 4880 | 110 | 19.08 |
| 2440 | 28 | 9.65 |

Table A.20 Initial, equilibrium, and adsorbed concentration for Hyamine on 50% Ca.Mon./Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 19520 | 948 | 74.29 |
| 14640 | 758 | 55.53 |
| 9760 | 429 | 37.32 |
| 7320 | 214 | 28.43 |
| 4880 | 162 | 18.87 |
| 2440 | 67 | 9.49 |

Table A.21 Initial, equilibrium, and adsorbed concentration for Hyamine on 20% Atta./Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 19520 | 71 | 77.80 |
| 14640 | 58 | 58.33 |
| 9760 | 32 | 38.91 |
| 7320 | 17 | 29.21 |
| 4880 | 11 | 19.48 |
| 2440 | 2 | 9.75 |

Table A.22 Initial, equilibrium, and adsorbed concentration for Hyamine on 30% Atta./Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 19520 | 84 | 77.74 |
| 14640 | 67 | 58.29 |
| 9760 | 41 | 38.88 |
| 7320 | 23 | 29.19 |
| 4880 | 6 | 19.50 |
| 2440 | 2 | 9.75 |

Table A.23 Initial, equilibrium, and adsorbed concentration for Hyamine on 40% Atta./Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 19520 | 93 | 77.71 |
| 14640 | 75 | 58.26 |
| 9760 | 49 | 38.84 |
| 7320 | 28 | 29.17 |
| 4880 | 19 | 19.44 |
| 2440 | 2 | 9.75 |

Table A.24 Initial, equilibrium, and adsorbed concentration for Hyamine on 50% Atta./Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 19520 | 84 | 77.74 |
| 14640 | 75 | 58.26 |
| 9760 | 58 | 38.81 |
| 7320 | 41 | 29.12 |
| 4880 | 23 | 19.43 |
| 2440 | 11 | 9.72 |

Table A.25 Initial, equilibrium, and desorbed concentration for SDS on 20% Kaolin/Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 2551 | 357 | 8.77 |
| 1966 | 325 | 6.56 |
| 1742 | 267 | 5.90 |
| 1329 | 144 | 4.74 |
| 869 | 65 | 3.22 |
| 415 | 59 | 1.42 |

Table A.26 Initial, equilibrium, and desorbed concentration for SDS on 30% Kaolin/Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 2520 | 375 | 8.58 |
| 1949 | 302 | 6.59 |
| 1719 | 267 | 5.81 |
| 1312 | 167 | 4.58 |
| 828 | 153 | 2.70 |
| 398 | 44 | 1.41 |

Table A.27 Initial, equilibrium, and desorbed concentration for SDS on 40% Kaolin/Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 2498 | 328 | 8.68 |
| 1937 | 182 | 7.02 |
| 1684 | 191 | 5.97 |
| 1265 | 56 | 4.83 |
| 799 | 21 | 3.11 |
| 363 | 15 | 1.39 |

Table A.28 Initial, equilibrium, and desorbed concentration for SDS on 50% Kaolin/Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 2463 | 360 | 8.41 |
| 1855 | 278 | 6.31 |
| 1643 | 214 | 5.72 |
| 1242 | 179 | 4.25 |
| 788 | 39 | 3.00 |
| 339 | 18 | 1.28 |

Table A.29 Initial, equilibrium, and desorbed concentration for SDS on 20% Ca.Mon./Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 2650 | 425 | 8.90 |
| 1808 | 109 | 6.80 |
| 1848 | 448 | 5.60 |
| 1470 | 121 | 5.40 |
| 682 | 62 | 2.48 |
| 456 | 85 | 1.48 |

Table A.30 Initial, equilibrium, and desorbed concentration for SDS on 30% Ca.Mon./Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 2124 | 635 | 5.96 |
| 850 | 495 | 1.42 |
| 795 | 436 | 1.44 |
| 160 | 389 | -0.92 |
| -534 | 202 | -2.95 |
| -128 | 202 | -1.32 |

Table A.31 Initial, equilibrium, and desorbed concentration for SDS on 40% Ca.Mon./Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 2066 | 506 | 6.24 |
| 1785 | 495 | 5.16 |
| 912 | 495 | 1.67 |
| 218 | 542 | -1.29 |
| -242 | 319 | -2.24 |
| -351 | 273 | -2.49 |

Table A.32 Initial, equilibrium, and desorbed concentration for SDS on 50% Ca.Mon./Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 1130 | 577 | 2.21 |
| 499 | 577 | -0.31 |
| 444 | 577 | -0.53 |
| -133 | 694 | -3.30 |
| -709 | 694 | -5.61 |
| -818 | 506 | -5.30 |

Table A.33 Initial, equilibrium, and desorbed concentration for SDS on 20% Atta./Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 3141 | 226 | 11.66 |
| 2352 | 132 | 8.88 |
| 2058 | 109 | 7.80 |
| 1575 | 62 | 6.05 |
| 951 | 85 | 3.46 |
| 491 | 109 | 1.53 |

Table A.34 Initial, equilibrium, and desorbed concentration for SDS on 30% Atta./Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 3212 | 243 | 11.87 |
| 2428 | 132 | 9.18 |
| 2117 | 109 | 8.03 |
| 1592 | 62 | 6.12 |
| 975 | 62 | 3.65 |
| 515 | 62 | 1.81 |

Table A.35 Initial, equilibrium, and desorbed concentration for SDS on 40% Atta./Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 3241 | 208 | 12.13 |
| 2440 | 132 | 9.23 |
| 2140 | 109 | 8.12 |
| 1627 | 85 | 6.17 |
| 998 | 85 | 3.65 |
| 497 | 39 | 1.83 |

Table A.36 Initial, equilibrium, and desorbed concentration for SDS on 50% Atta./Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 3288 | 197 | 12.36 |
| 2487 | 126 | 9.44 |
| 2152 | 109 | 8.17 |
| 1657 | 74 | 6.33 |
| 1004 | 109 | 3.58 |
| 538 | 33 | 2.02 |

Table A.37 Initial, equilibrium, and desorbed concentration for Hyamine on 20% Kaolin/Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 19358 | 62 | 77.18 |
| 14513 | 49 | 57.85 |
| 9685 | 32 | 38.61 |
| 7279 | 15 | 29.06 |
| 4869 | 4 | 19.46 |
| 2434 | 2 | 9.73 |

Table A.38 Initial, equilibrium, and desorbed concentration for Hyamine on 30% Kaolin/Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 19324 | 80 | 76.98 |
| 14487 | 62 | 57.70 |
| 9676 | 32 | 38.58 |
| 7279 | 15 | 29.06 |
| 4865 | 6 | 19.44 |
| 2429 | 2 | 9.71 |

Table A.39 Initial, equilibrium, and desorbed concentration for Hyamine on 40% Kaolin/Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 19276 | 49 | 76.91 |
| 14452 | 41 | 57.65 |
| 9654 | 19 | 38.54 |
| 7271 | 8 | 29.05 |
| 4857 | 4 | 19.41 |
| 2425 | 1 | 9.70 |

Table A.40 Initial, equilibrium, and desorbed concentration for Hyamine on 50% Kaolin/Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 19414 | 106 | 77.24 |
| 14556 | 84 | 57.89 |
| 9711 | 49 | 38.64 |
| 7297 | 23 | 29.09 |
| 4869 | 11 | 19.44 |
| 2434 | 6 | 9.71 |

Table A.41 Initial, equilibrium, and desorbed concentration for Hyamine on 20% Ca.Mon./Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 19376 | 93 | 77.13 |
| 14522 | 75 | 57.78 |
| 9685 | 49 | 38.54 |
| 7284 | 23 | 29.04 |
| 4872 | 15 | 19.43 |
| 2434 | 2 | 9.73 |

Table A.42 Initial, equilibrium, and desorbed concentration for Hyamine on 30% Ca.Mon./Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 19004 | 144 | 75.44 |
| 14228 | 118 | 56.44 |
| 9529 | 67 | 37.85 |
| 7193 | 32 | 28.64 |
| 4839 | 15 | 19.30 |
| 2417 | 4 | 9.65 |

Table A.43 Initial, equilibrium, and desorbed concentration for Hyamine on 40% Ca.Mon./Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 18987 | 179 | 75.23 |
| 14254 | 153 | 56.40 |
| 9512 | 118 | 37.57 |
| 7176 | 67 | 28.44 |
| 4818 | 41 | 19.11 |
| 2412 | 11 | 9.61 |

Table A.44 Initial, equilibrium, and desorbed concentration for Hyamine on 50% Ca.Mon./Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 18572 | 317 | 73.02 |
| 13882 | 257 | 54.50 |
| 9331 | 144 | 36.74 |
| 7107 | 71 | 28.14 |
| 4787 | 49 | 18.95 |
| 2373 | 19 | 9.42 |

Table A.45 Initial, equilibrium, and desorbed concentration for Hyamine on 20% Atta./Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 19449 | 41 | 77.63 |
| 14582 | 32 | 58.20 |
| 9728 | 19 | 38.83 |
| 7303 | 8 | 29.18 |
| 4839 | 4 | 19.34 |
| 2399 | 1 | 9.59 |

Table A.46 Initial, equilibrium, and desorbed concentration for Hyamine on 30% Atta./Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 19453 | 41 | 77.65 |
| 14591 | 30 | 58.24 |
| 9732 | 23 | 38.83 |
| 7305 | 8 | 29.19 |
| 4818 | 4 | 19.26 |
| 2399 | 2 | 9.59 |

Table A.47 Initial, equilibrium, and desorbed concentration for Hyamine on 40% Atta./Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 19449 | 49 | 77.60 |
| 14586 | 41 | 58.18 |
| 9732 | 28 | 38.82 |
| 7305 | 11 | 29.18 |
| 4818 | 6 | 19.25 |
| 2399 | 1 | 9.59 |

Table A.48 Initial, equilibrium, and desorbed concentration for Hyamine on 50% Atta./Soil ratio

| C_i (mg/L) | C_e (mg/L) | C_s (mg/g) |
|--------------|--------------|--------------|
| 19462 | 54 | 77.63 |
| 14595 | 45 | 58.20 |
| 9737 | 23 | 38.85 |
| 7305 | 15 | 29.16 |
| 4874 | 6 | 19.47 |
| 2399 | 2 | 9.59 |

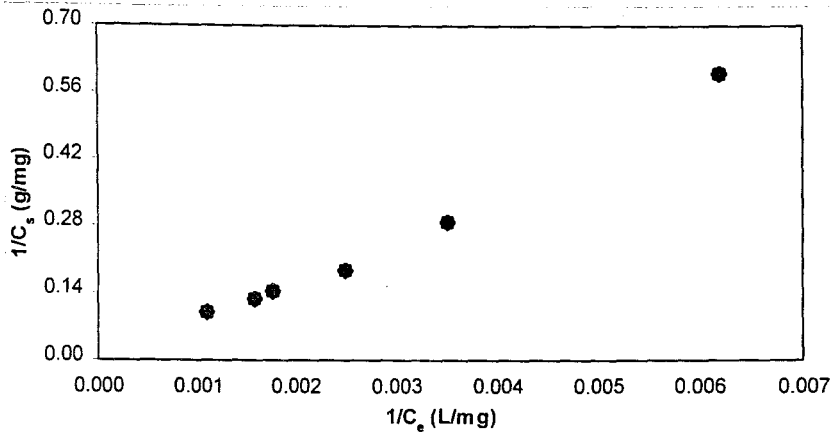


Figure A.1 Langmuir adsorption isotherm of SDS on %20 w/w Kaolin/Soil ratio

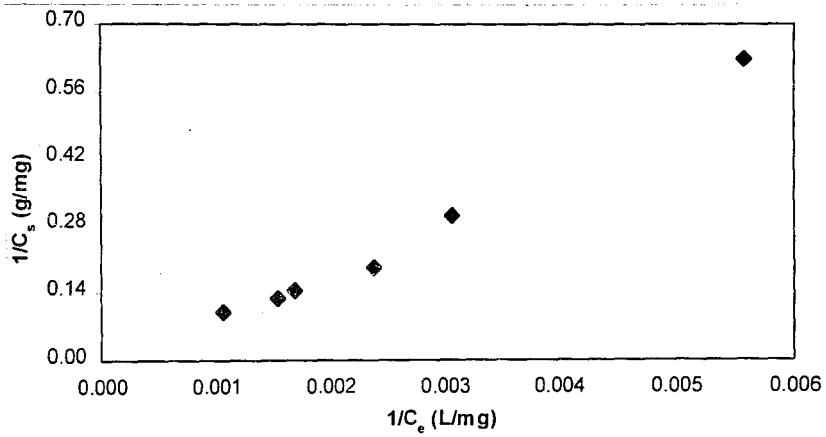


Figure A.2 Langmuir adsorption isotherm of SDS on %30 w/w Kaolin/Soil ratio

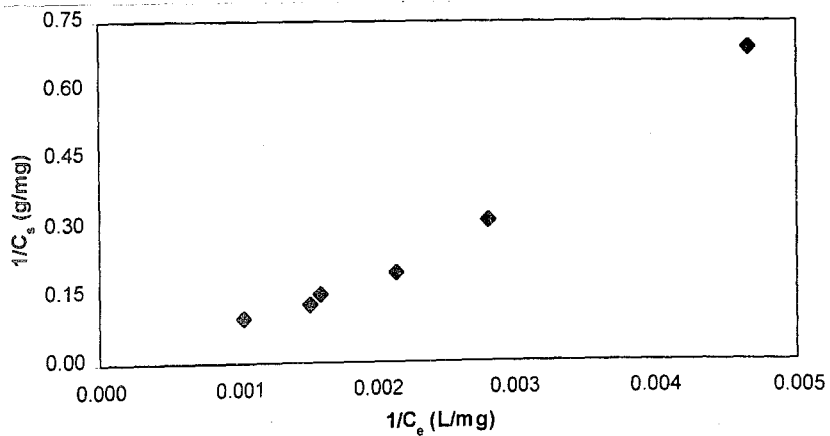


Figure A.3 Langmuir adsorption isotherm of SDS on %40 w/w Kaolin/Soil ratio

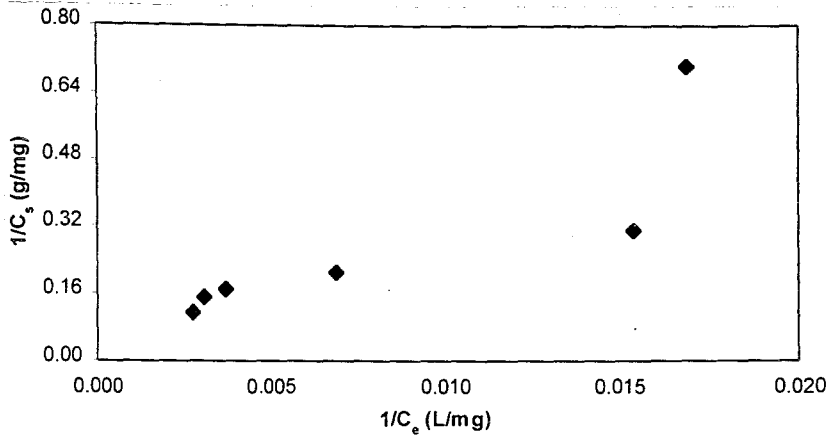


Figure A.4 Langmuir adsorption isotherm of SDS on %50 w/w Kaolin/Soil ratio

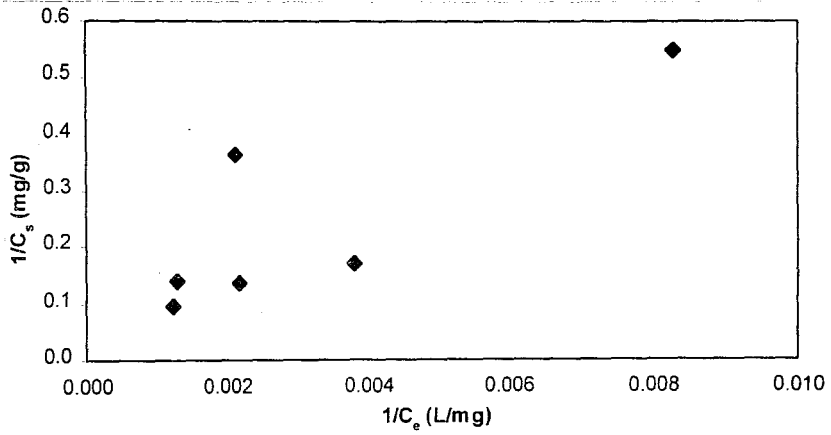


Figure A.5 Langmuir adsorption isotherm of SDS on %20 w/w Ca-Mon./Soil ratio

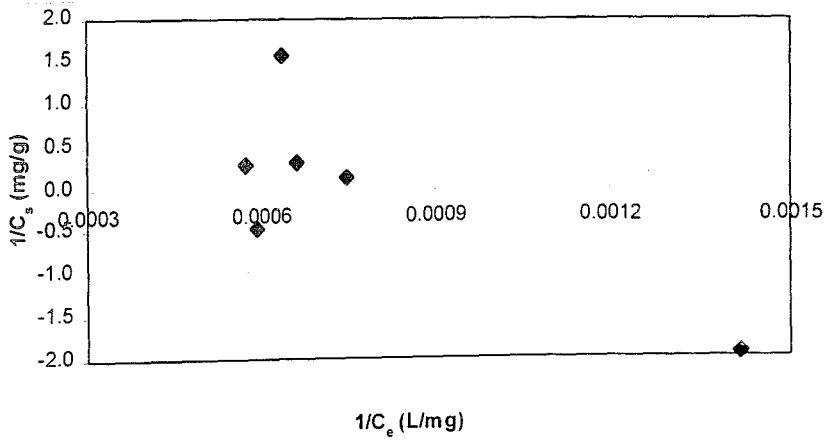


Figure A.6 Langmuir adsorption isotherm of SDS on %30 w/w Ca-Mon./Soil ratio

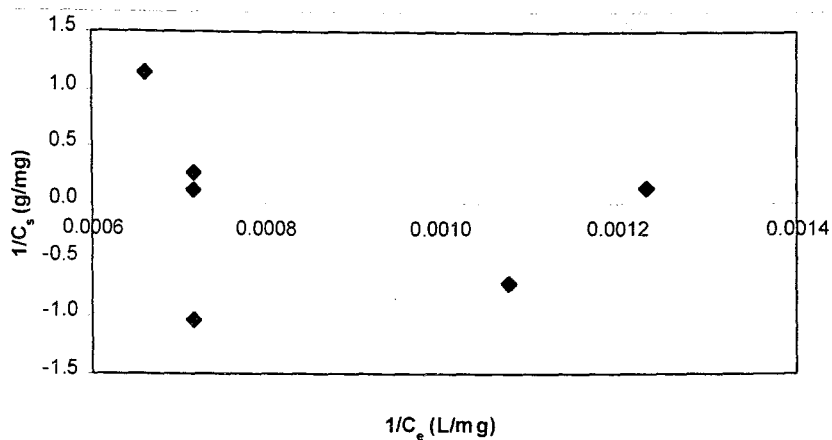


Figure A.7 Langmuir adsorption isotherm of SDS on %40 w/w Ca-Mon./Soil ratio

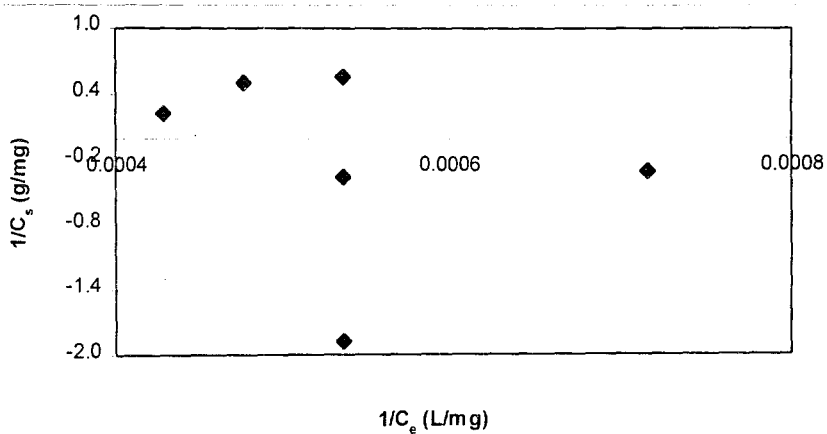


Figure A.8 Langmuir adsorption isotherm of SDS on %50 w/w Ca-Mon./Soil ratio

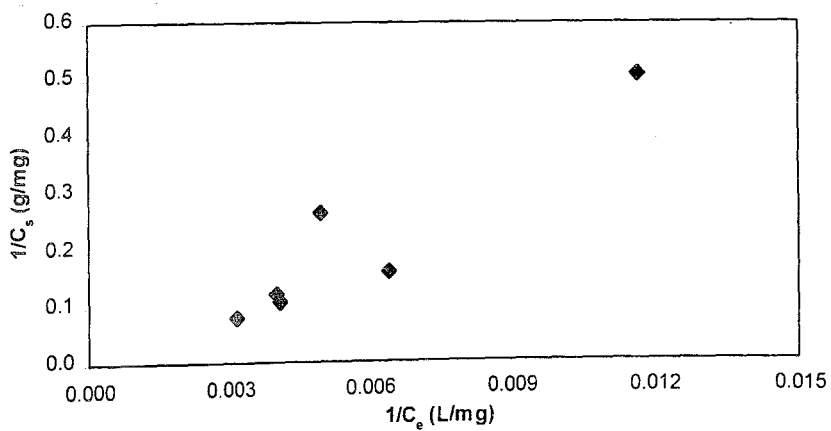


Figure A.9 Langmuir adsorption isotherm of SDS on %20 w/w Atta./Soil ratio

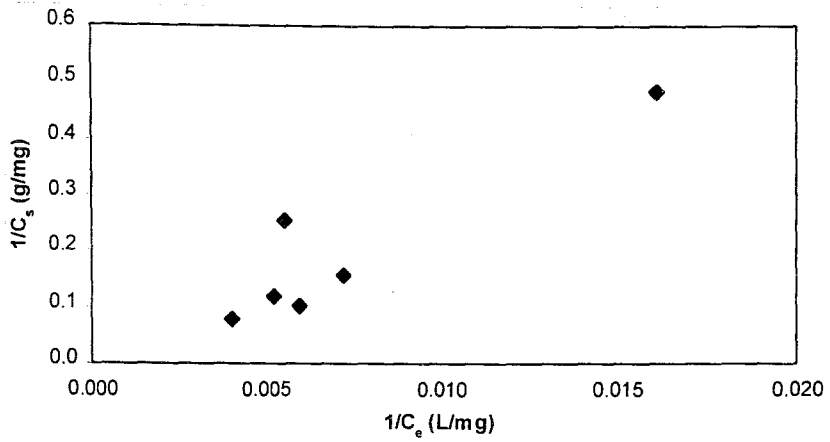


Figure A.10 Langmuir adsorption isotherm of SDS on %30 w/w Atta./Soil ratio

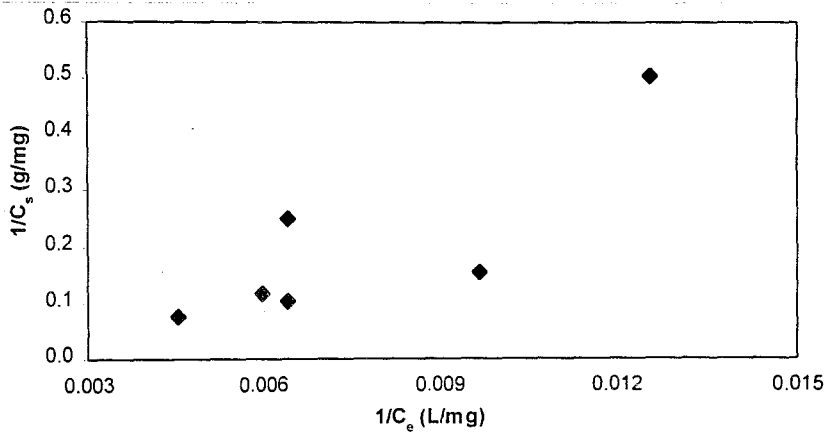


Figure A.11 Langmuir adsorption isotherm of SDS on %40 w/w Atta./Soil ratio

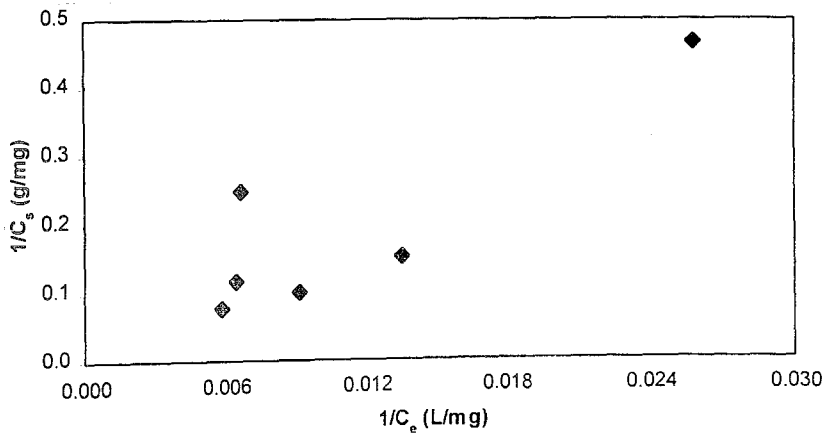


Figure A.12 Langmuir adsorption isotherm of SDS on %50 w/w Atta./Soil ratio

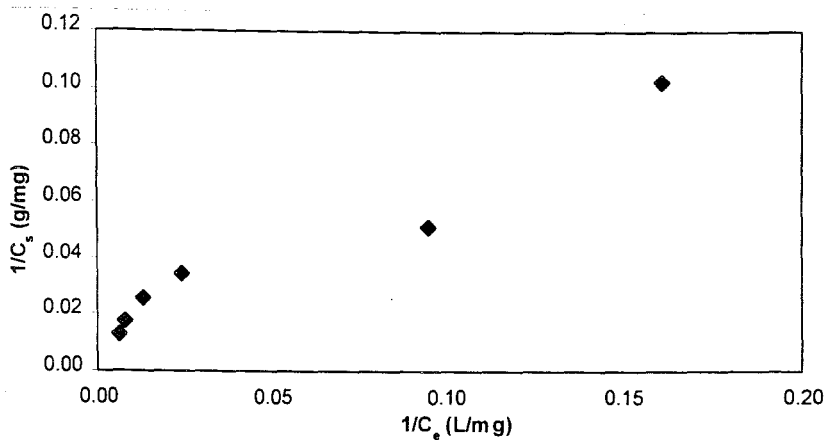


Figure A.13 Langmuir adsorption isotherm of Hyamine on %20 w/w Kaolin/Soil ratio

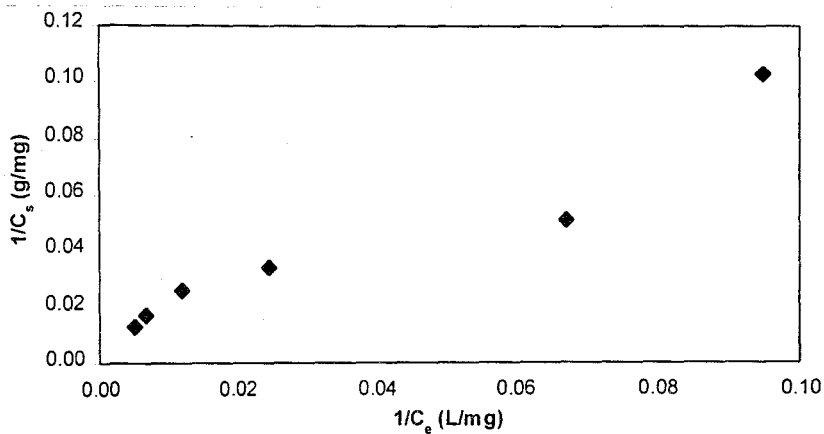


Figure A.14 Langmuir adsorption isotherm of Hyamine on %30 w/w Kaolin/Soil ratio

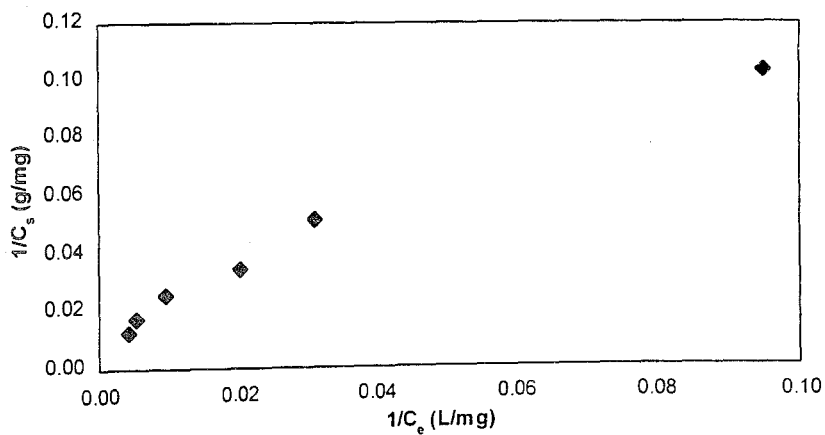


Figure A.15 Langmuir adsorption isotherm of Hyamine on %40 w/w Kaolin/Soil ratio

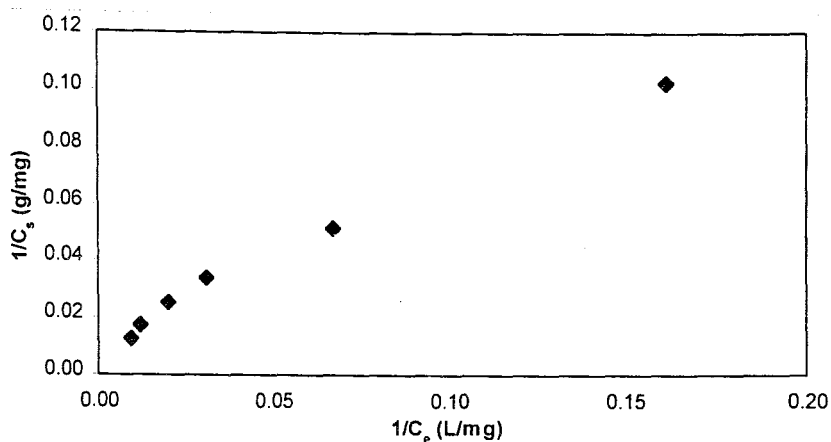


Figure A.16 Langmuir adsorption isotherm of Hyamine on %50 w/w Kaolin/Soil ratio

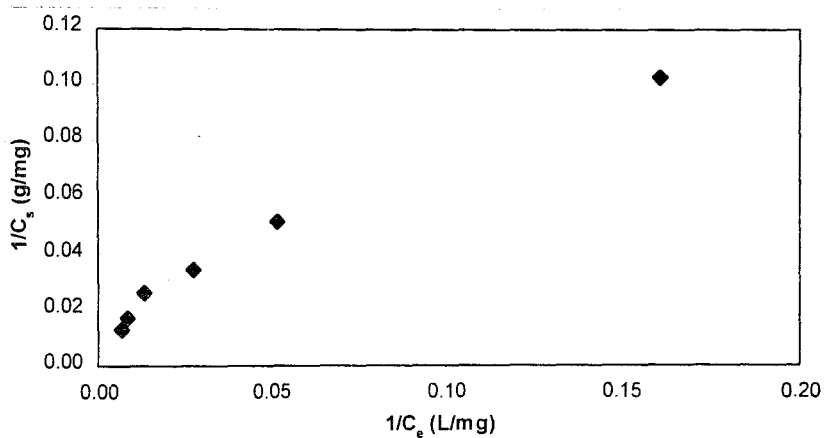


Figure A.17 Langmuir adsorption isotherm of Hyamine on %20 w/w Ca-Mon./Soil ratio

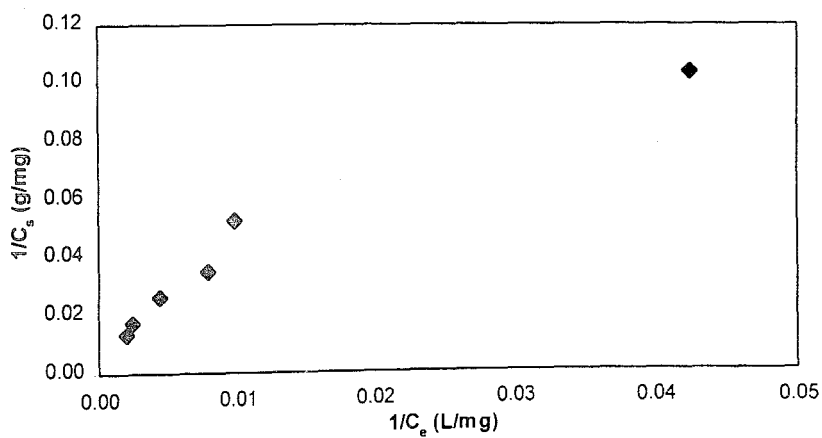


Figure A.18 Langmuir adsorption isotherm of Hyamine on %30 w/w Ca-Mon./Soil ratio

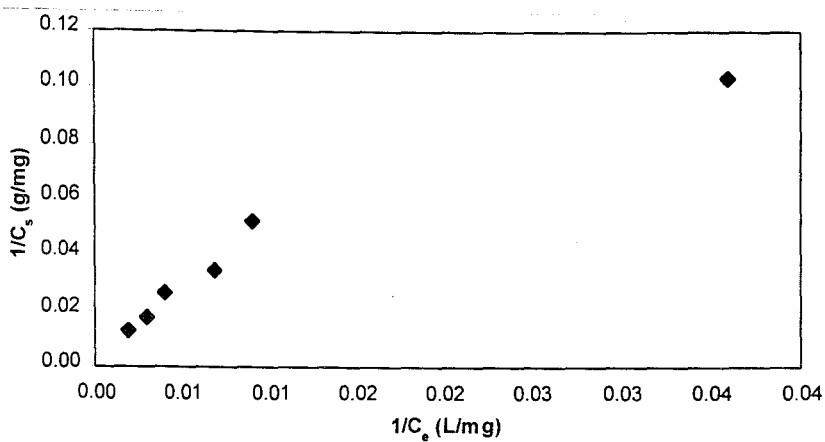


Figure A.19 Langmuir adsorption isotherm of Hyamine on %40 w/w Ca-Mon./Soil ratio

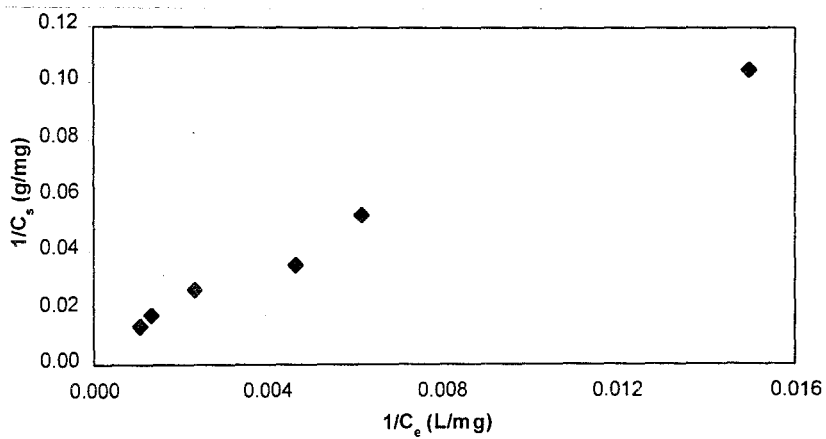


Figure A.20 Langmuir adsorption isotherm of Hyamine on %50 w/w Ca-Mon./Soil ratio

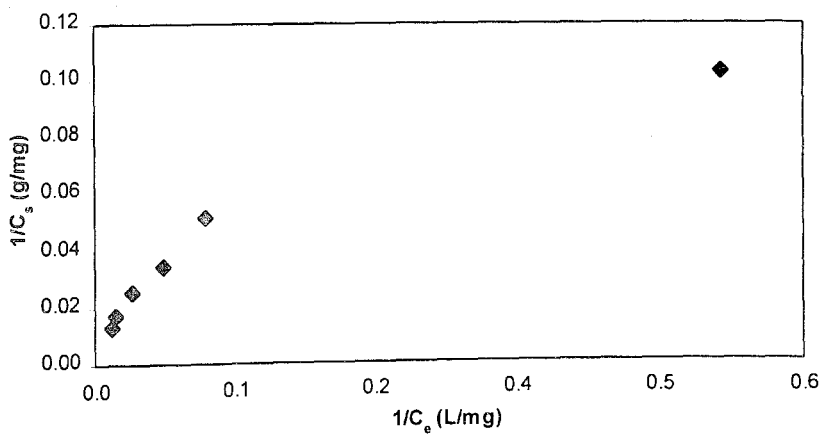


Figure A.21 Langmuir adsorption isotherm of Hyamine on %20 w/w Atta./Soil ratio

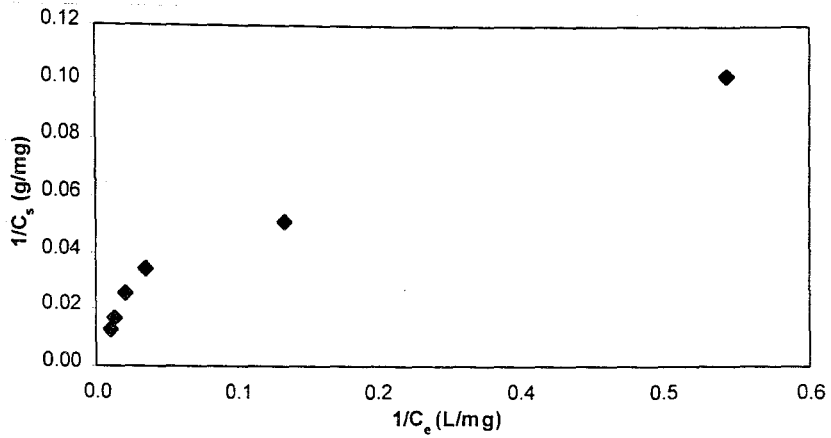


Figure A.22 Langmuir adsorption isotherm of Hyamine on %30 w/w Atta./Soil ratio

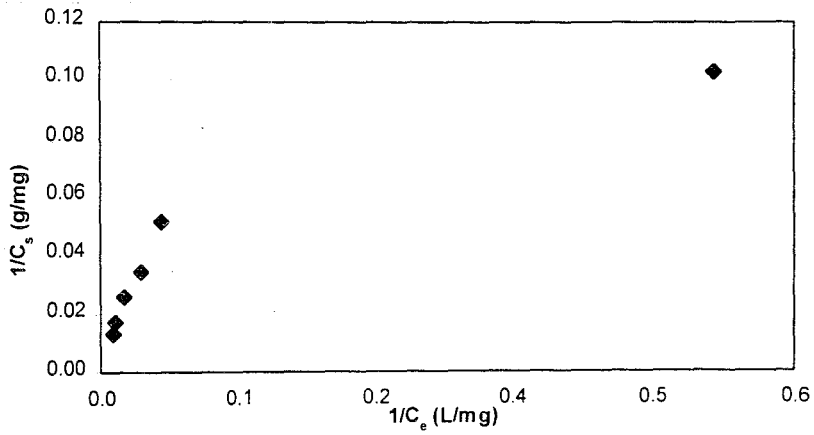


Figure A.23 Langmuir adsorption isotherm of Hyamine on %40 w/w Atta./Soil ratio

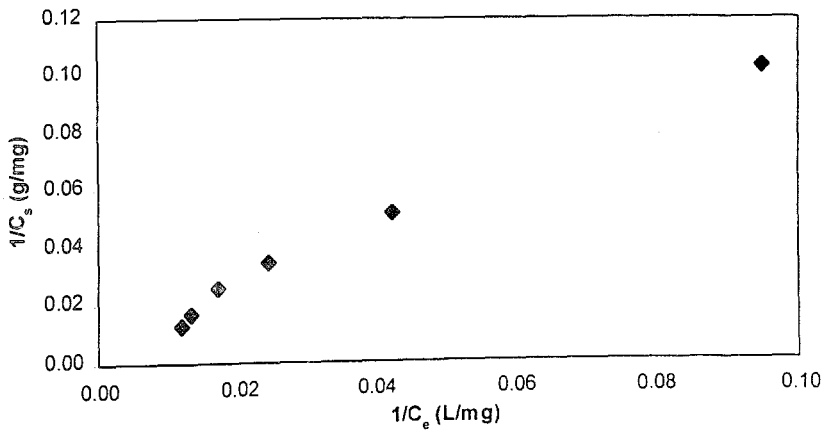


Figure A.24 Langmuir adsorption isotherm of Hyamine on %50 w/w Atta./Soil ratio

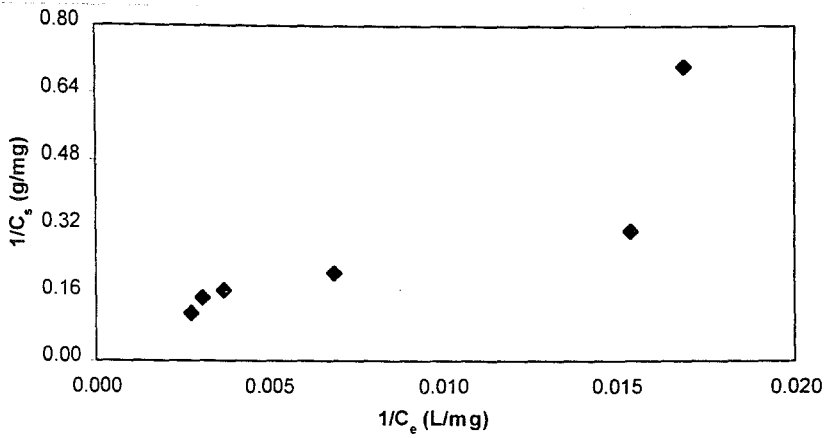


Figure A.25 Langmuir desorption isotherm of SDS on %20 w/w Kaolin/Soil ratio

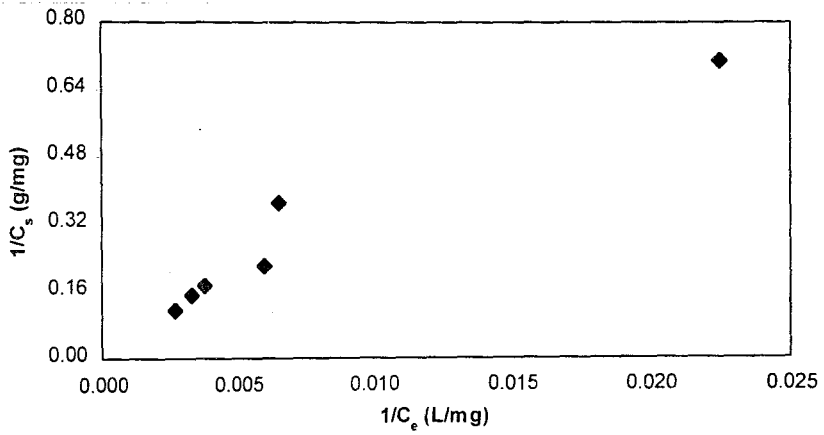


Figure A.26 Langmuir desorption isotherm of SDS on %30 w/w Kaolin/Soil ratio

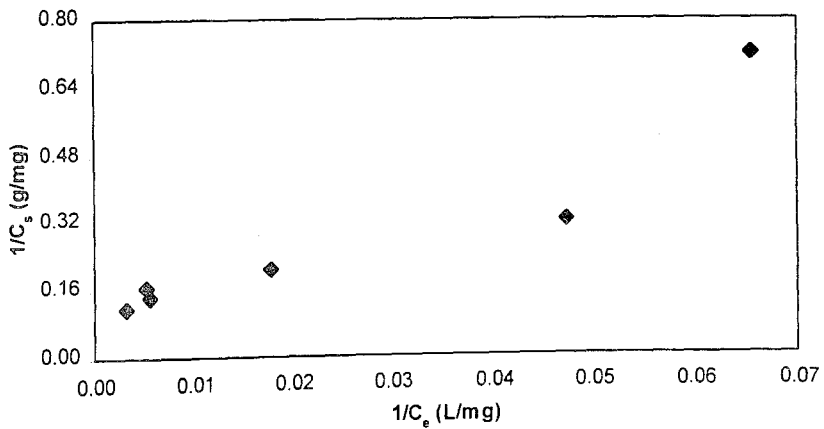


Figure A.27 Langmuir desorption isotherm of SDS on %40 w/w Kaolin/Soil ratio

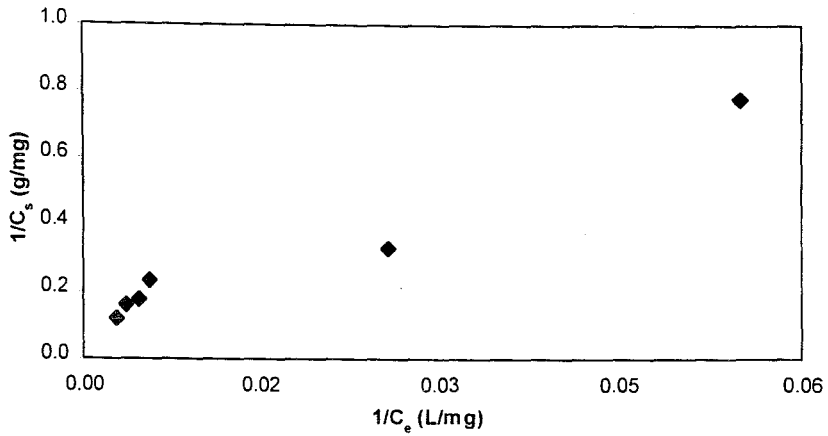


Figure A.28 Langmuir desorption isotherm of SDS on %50 w/w Kaolin/Soil ratio

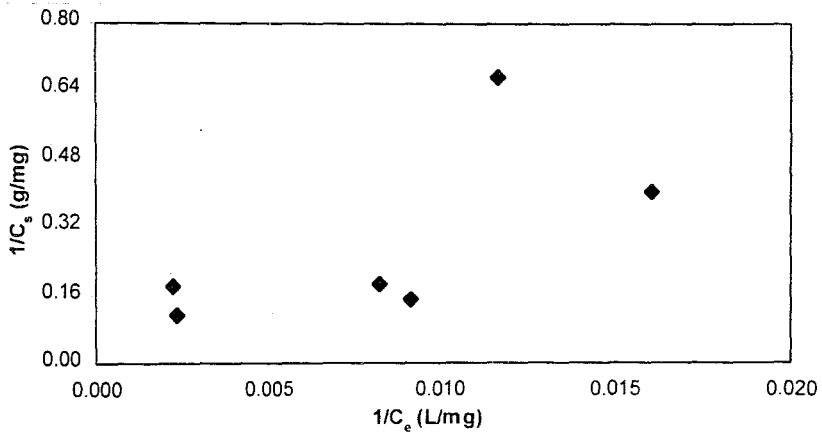


Figure A.29 Langmuir desorption isotherm of SDS on %20 w/w Ca-Mon./Soil ratio

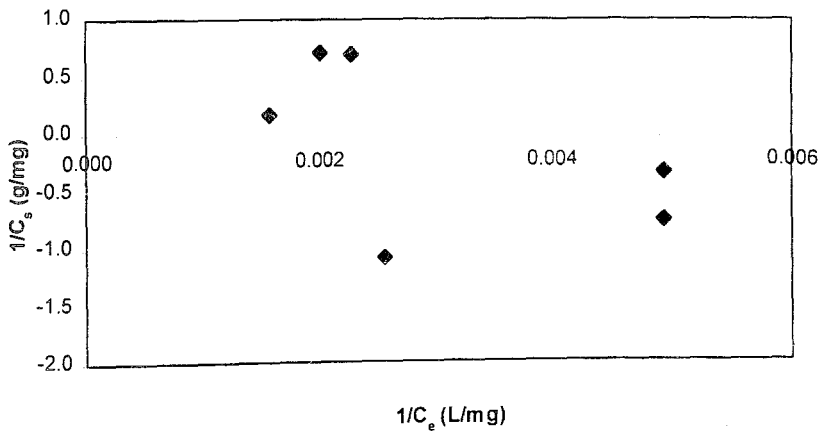


Figure A.30 Langmuir desorption isotherm of SDS on %30 w/w Ca-Mon./Soil ratio

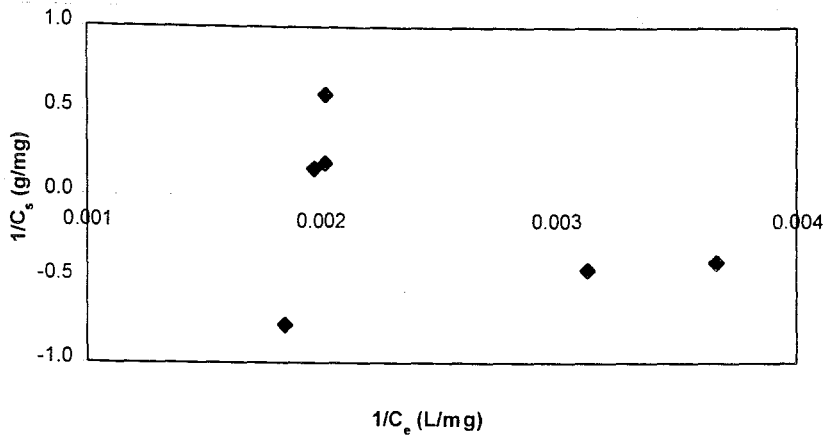


Figure A.31 Langmuir desorption isotherm of SDS on %40 w/w Ca-Mon./Soil ratio

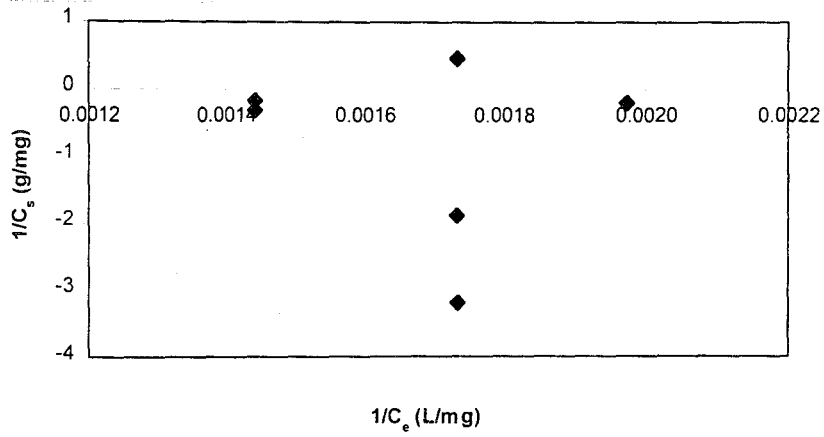


Figure A.32 Langmuir desorption isotherm of SDS on %50 w/w Ca-Mon./Soil ratio

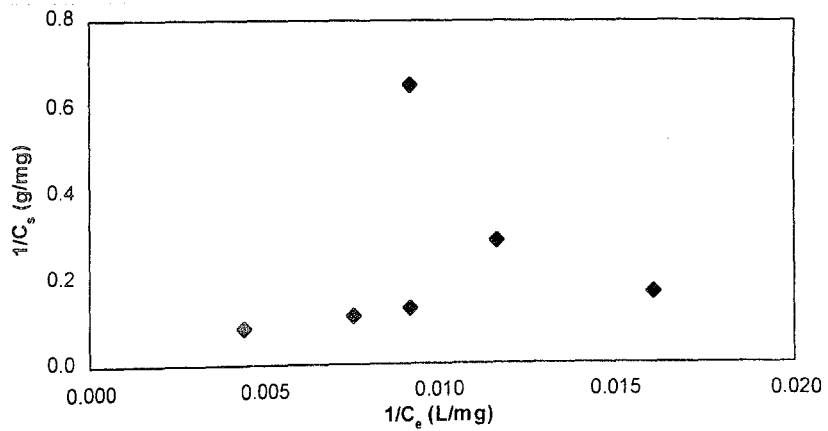


Figure A.33 Langmuir desorption isotherm of SDS on %20 w/w Atta./Soil ratio

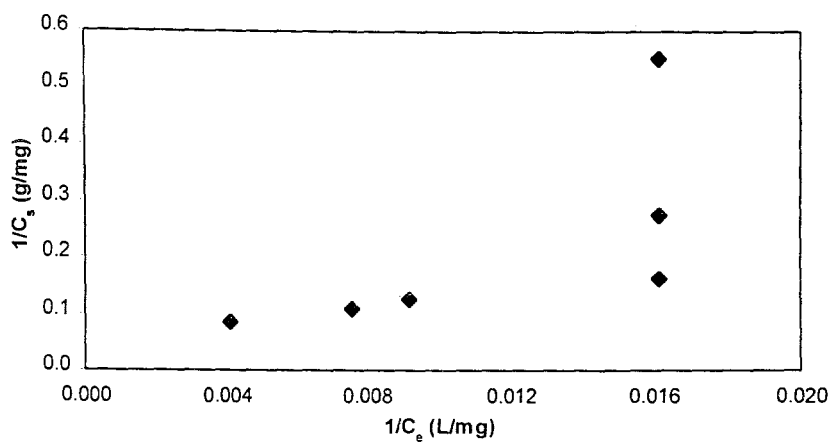


Figure A.34 Langmuir desorption isotherm of SDS on %30 w/w Atta./Soil ratio

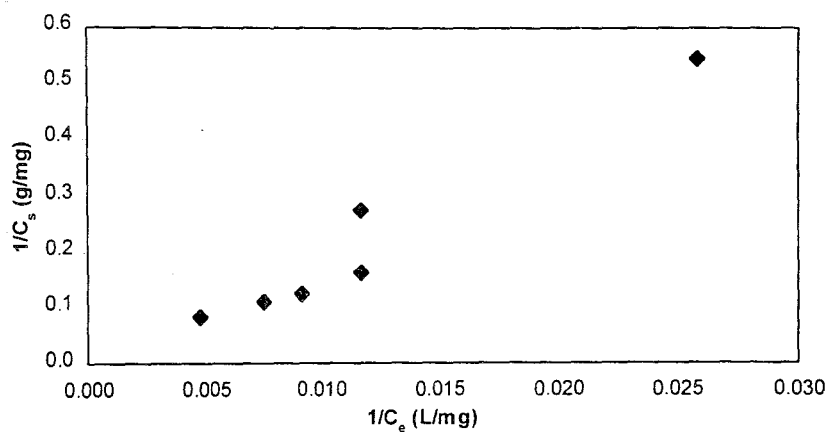


Figure A.35 Langmuir desorption isotherm of SDS on %40 w/w Atta./Soil ratio

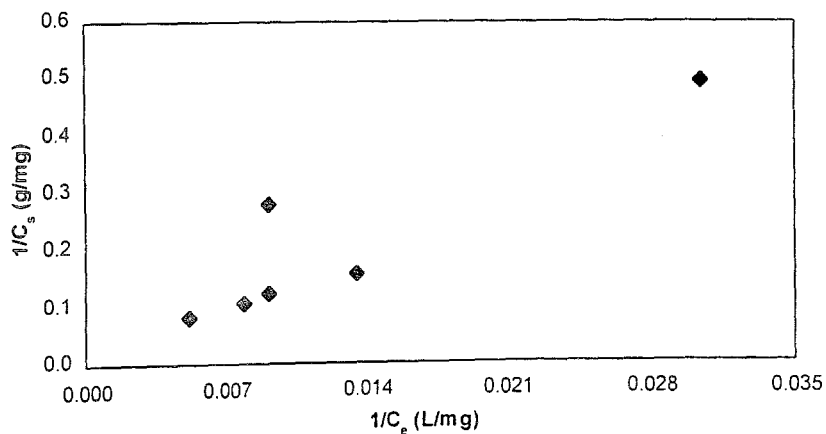


Figure A.36 Langmuir desorption isotherm of SDS on %50 w/w Atta./Soil ratio

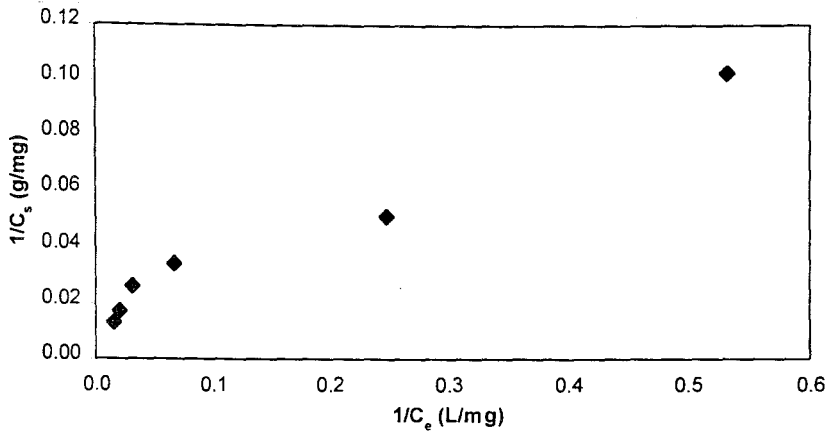


Figure A.37 Langmuir desorption isotherm of Hyamine on %20 w/w Kaolin/Soil ratio

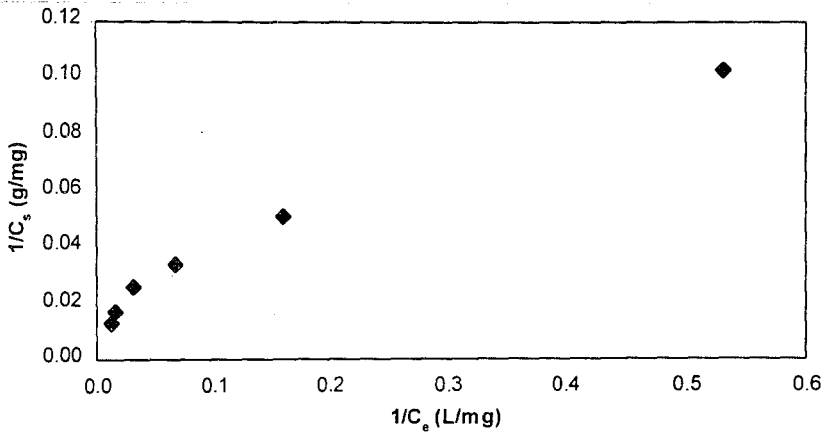


Figure A.38 Langmuir desorption isotherm of Hyamine on %30 w/w Kaolin/Soil ratio

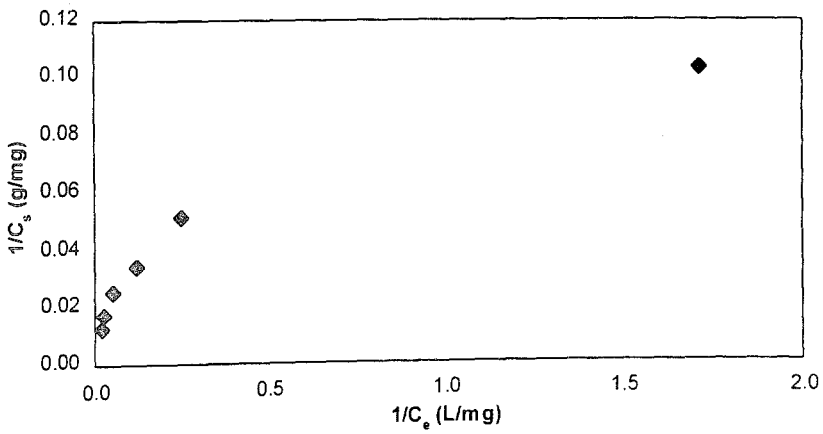


Figure A.39 Langmuir desorption isotherm of Hyamine on %40 w/w Kaolin/Soil ratio

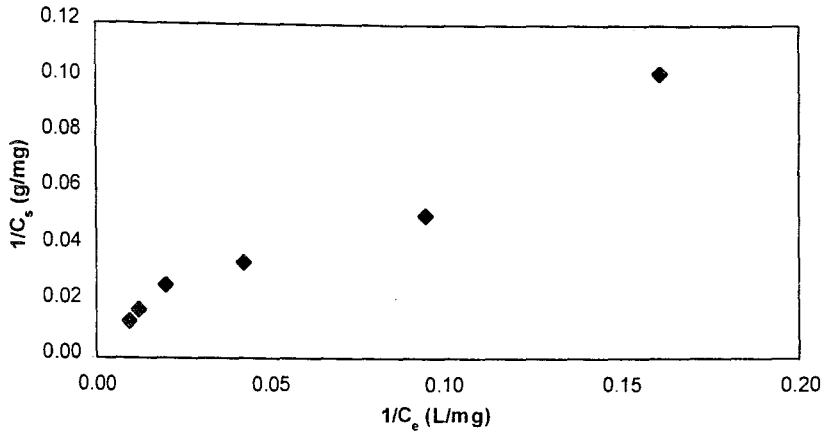


Figure A.40 Langmuir desorption isotherm of Hyamine on %50 w/w Kaolin/Soil ratio

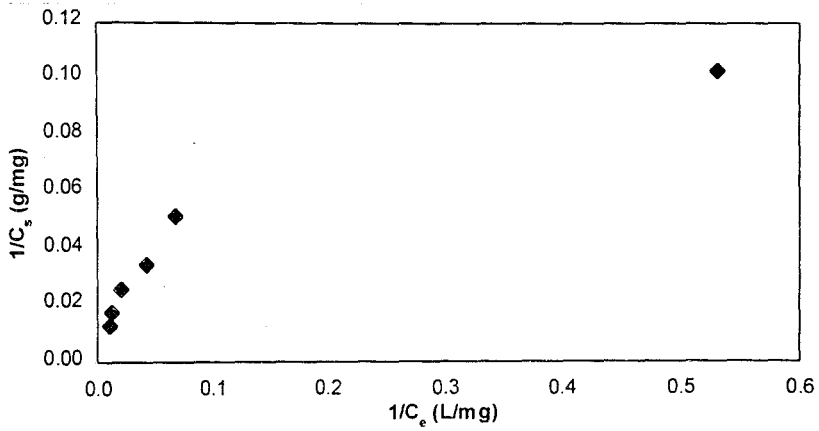


Figure A.41 Langmuir desorption isotherm of Hyamine on %20 w/w Ca-Mon./Soil ratio

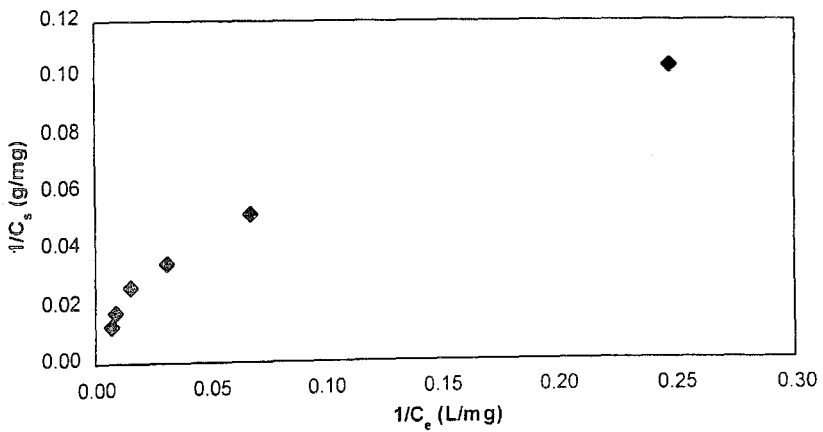


Figure A.42 Langmuir desorption isotherm of Hyamine on %30 w/w Ca-Mon./Soil ratio

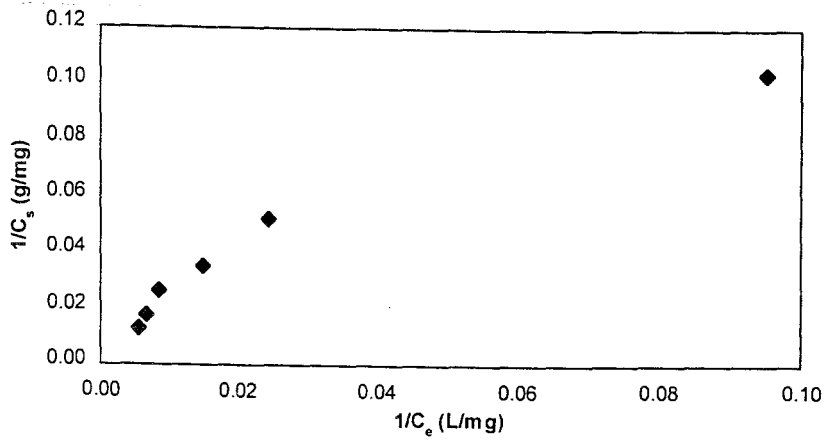


Figure A.43 Langmuir desorption isotherm of Hyamine on %40 w/w Ca-Mon./Soil ratio

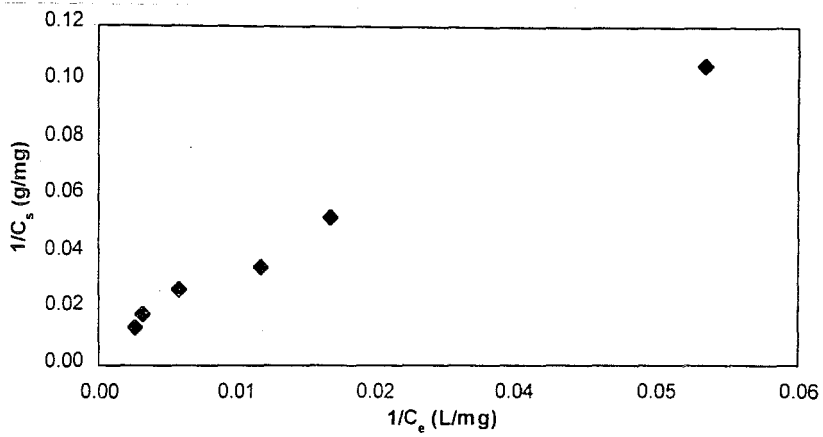


Figure A.44 Langmuir desorption isotherm of Hyamine on %50 w/w Ca-Mon./Soil ratio

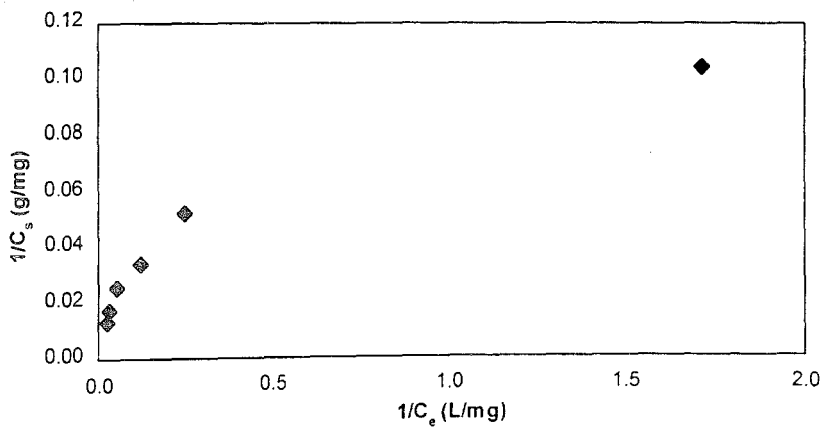


Figure A.45 Langmuir desorption isotherm of Hyamine on %20 w/w Atta./Soil ratio

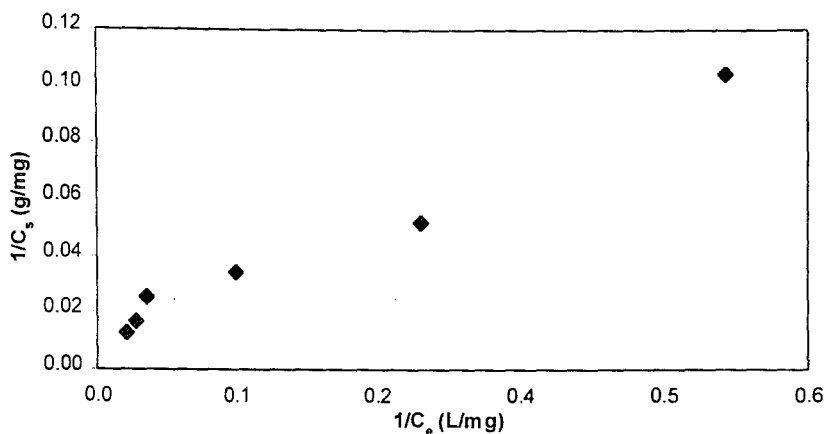


Figure A.46 Langmuir desorption isotherm of Hyamine on %30 w/w Atta./Soil ratio

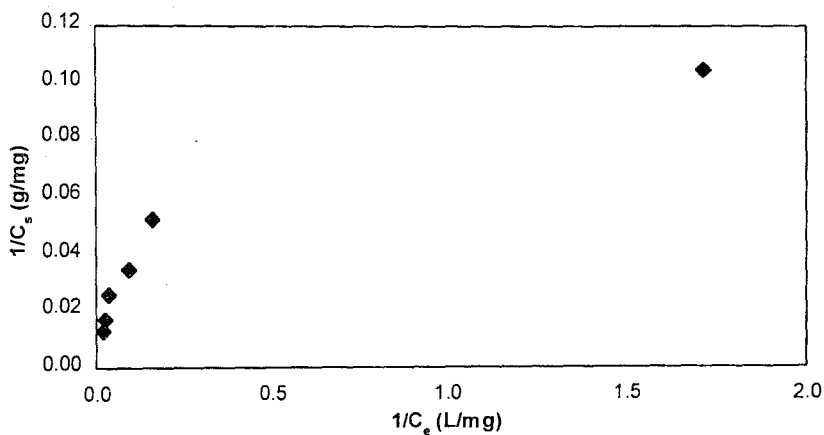


Figure A.47 Langmuir desorption isotherm of Hyamine on %40 w/w Atta./Soil ratio

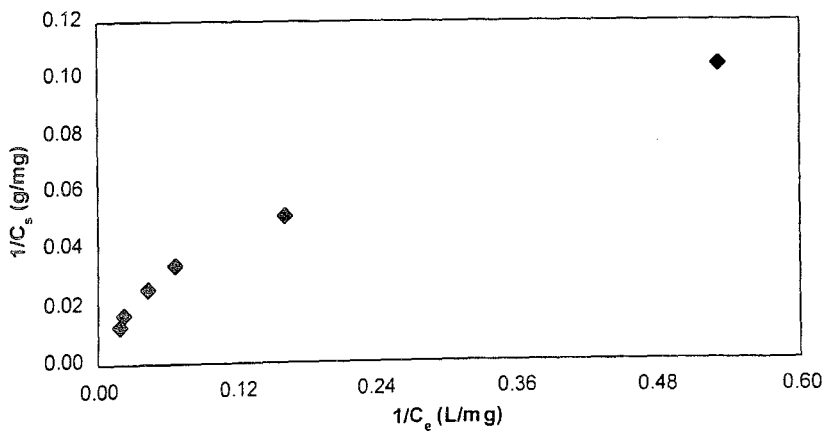


Figure A.48 Langmuir desorption isotherm of Hyamine on %50 w/w Atta./Soil ratio

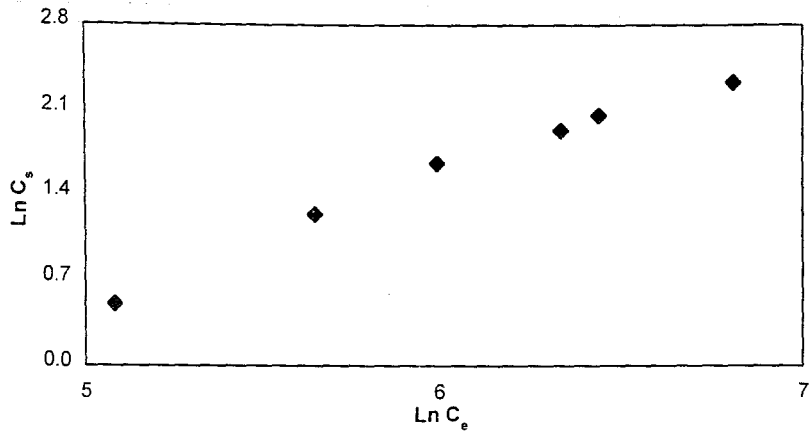


Figure A.49 Freundlich adsorption isotherm of SDS on %20 w/w Kaolin/Soil ratio

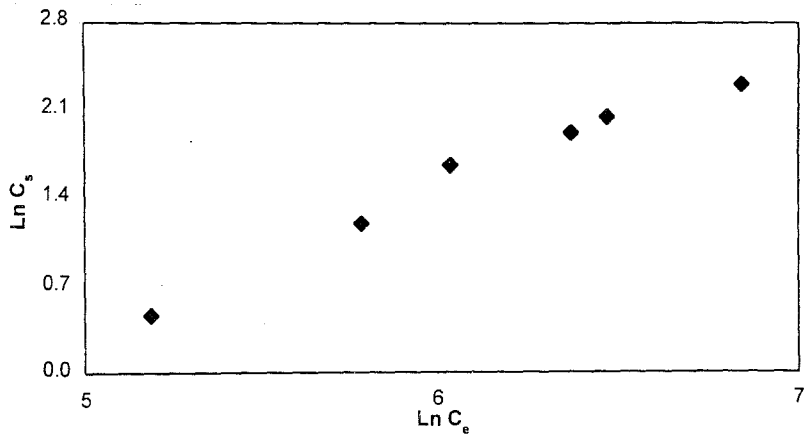


Figure A.50 Freundlich adsorption isotherm of SDS on %30 w/w Kaolin/Soil ratio

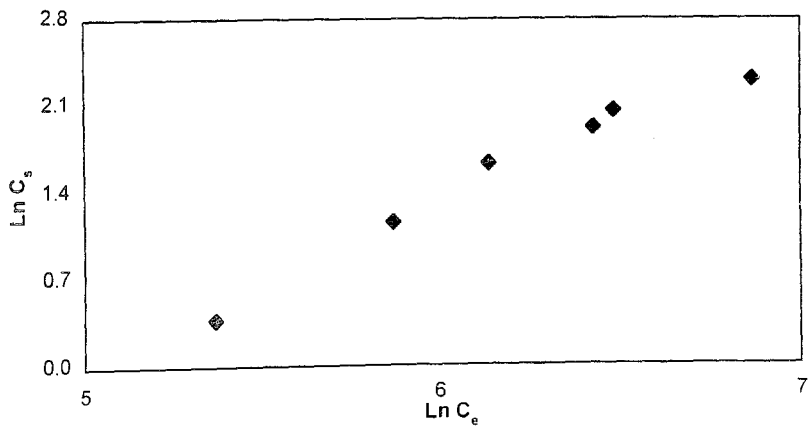


Figure A.51 Freundlich adsorption isotherm of SDS on %40 w/w Kaolin/Soil ratio

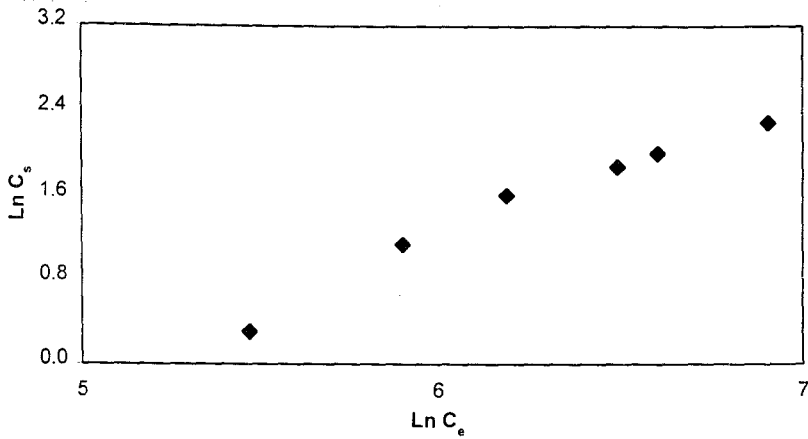


Figure A.52 Freundlich adsorption isotherm of SDS on %50 w/w Kaolin/Soil ratio

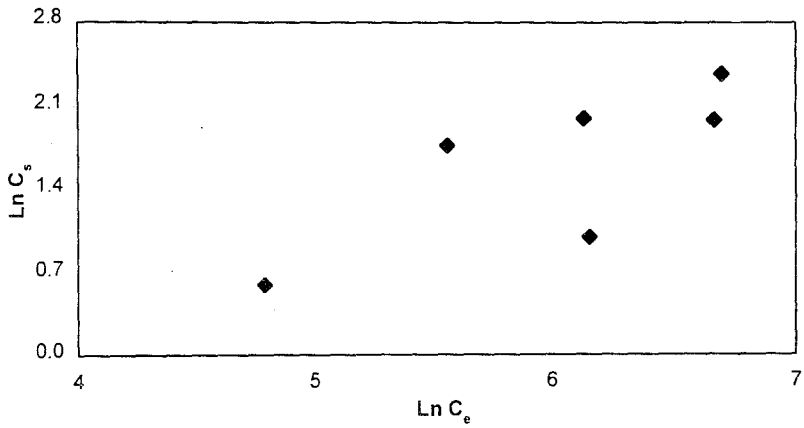


Figure A.53 Freundlich adsorption isotherm of SDS on %20 w/w Ca-Mon./Soil ratio

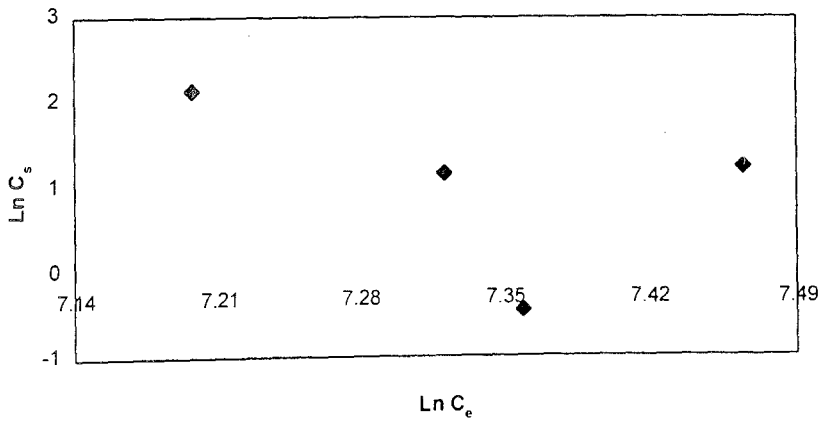


Figure A.54 Freundlich adsorption isotherm of SDS on %30 w/w Ca-Mon./Soil ratio

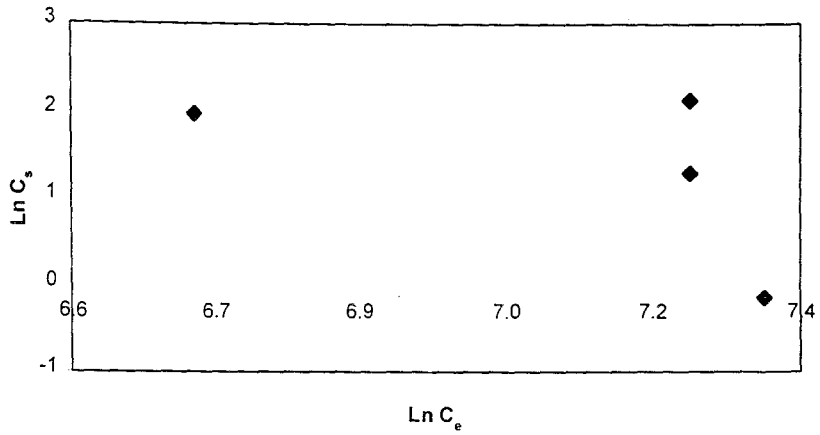


Figure A.55 Freundlich adsorption isotherm of SDS on %40 w/w Ca-Mon./Soil ratio

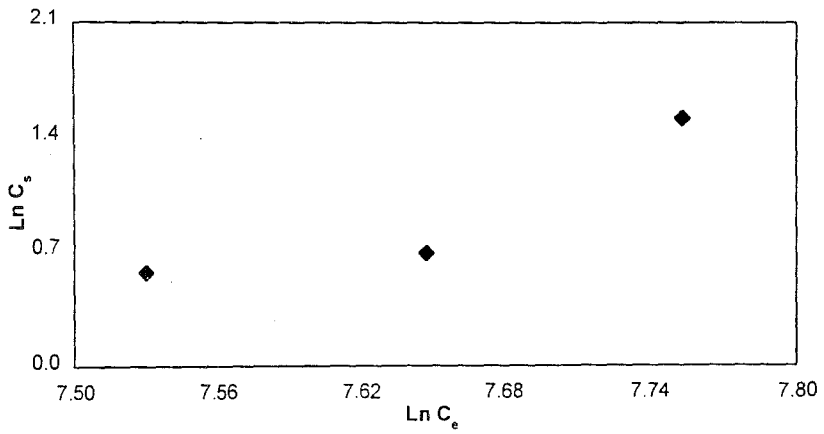


Figure A.56 Freundlich adsorption isotherm of SDS on %50 w/w Ca-Mon./Soil ratio

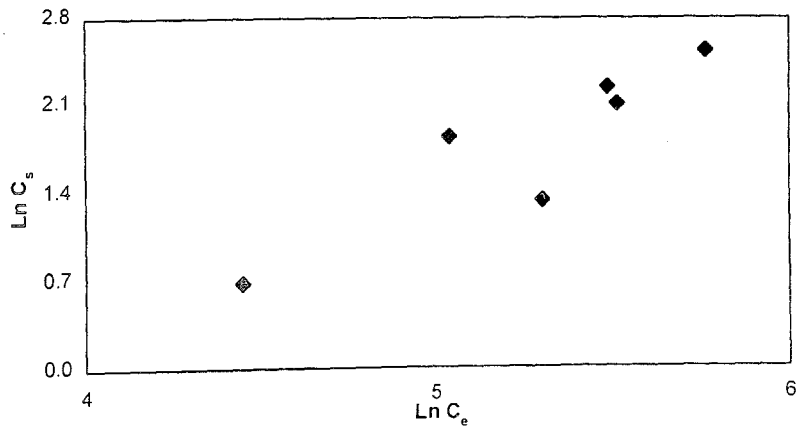


Figure A.57 Freundlich adsorption isotherm of SDS on %20 w/w Atta./Soil ratio

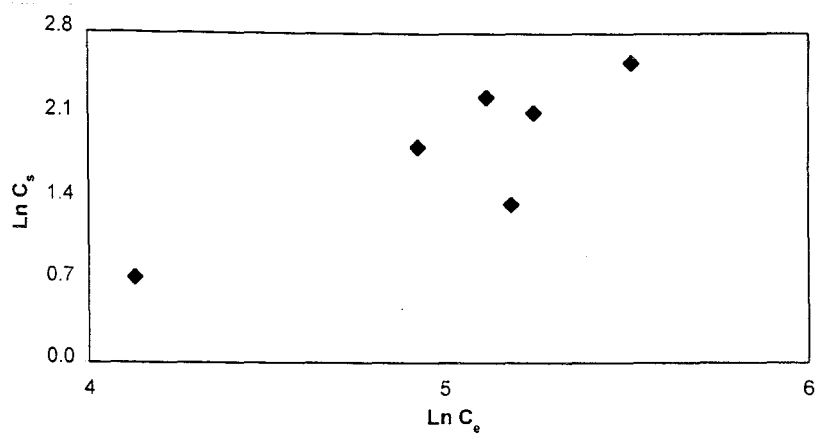


Figure A.58 Freundlich adsorption isotherm of SDS on %30 w/w Atta./Soil ratio

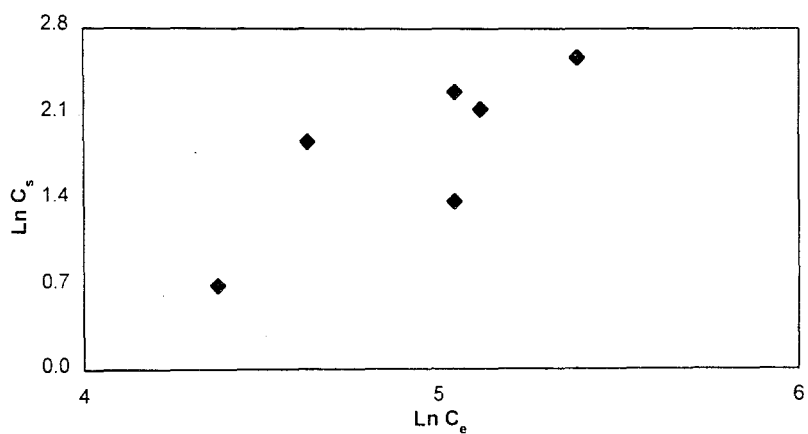


Figure A.59 Freundlich adsorption isotherm of SDS on %40 w/w Atta./Soil ratio

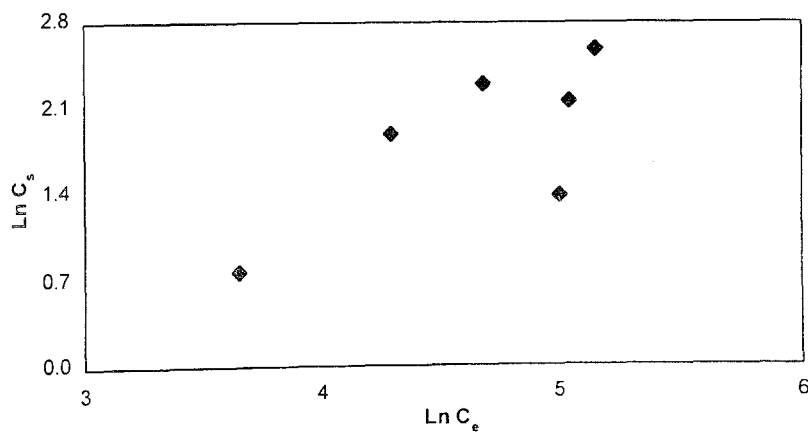


Figure A.60 Freundlich adsorption isotherm of SDS on %50 w/w Atta./Soil ratio

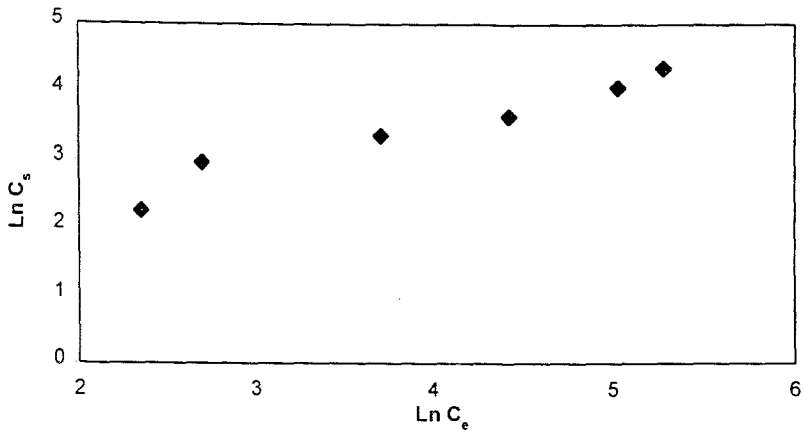


Figure A.61 Freundlich adsorption isotherm of Hyamine on %20 w/w Kaoline/Soil ratio

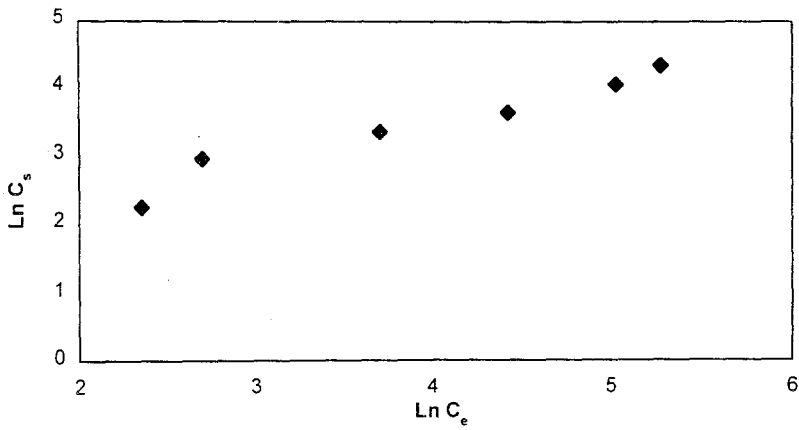


Figure A.62 Freundlich adsorption isotherm of Hyamine on %30 w/w Kaoline/Soil ratio

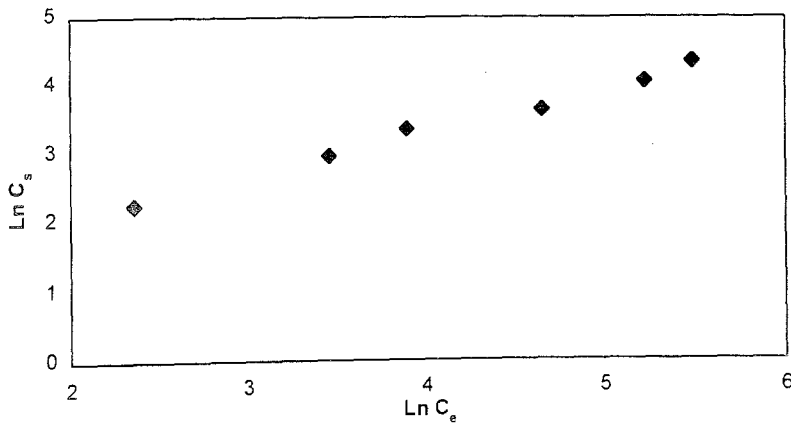


Figure A.63 Freundlich adsorption isotherm of Hyamine on %40 w/w Kaoline/Soil ratio

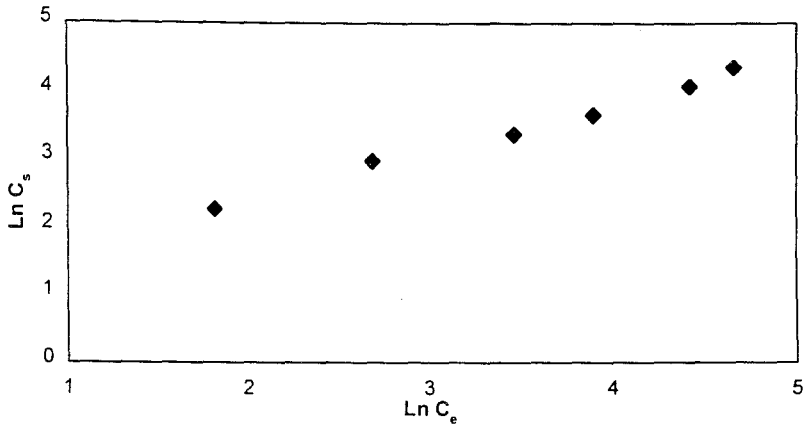


Figure A.64 Freundlich adsorption isotherm of Hyamine on %50 w/w Kaoline/Soil ratio

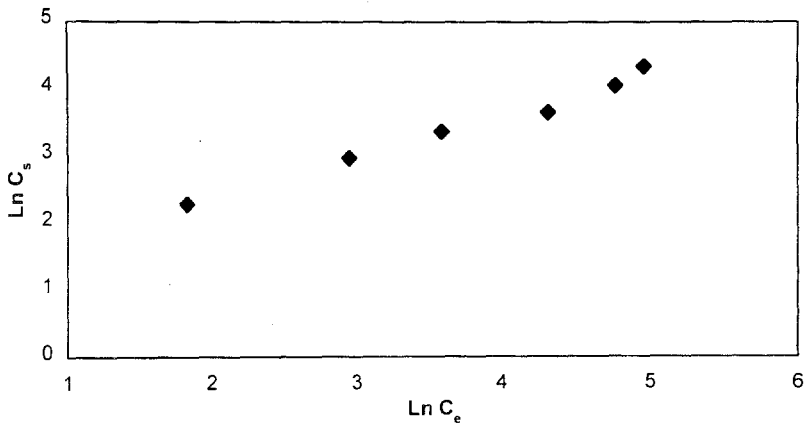


Figure A.65 Freundlich adsorption isotherm of Hyamine on %20 w/w Ca-Mon./Soil ratio

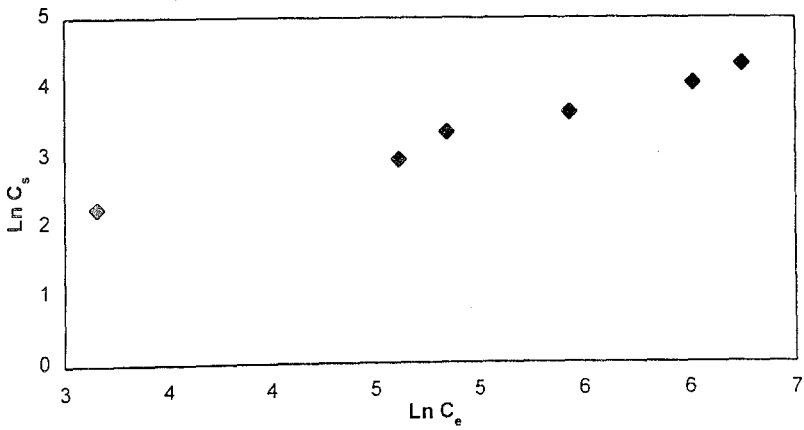


Figure A.66 Freundlich adsorption isotherm of Hyamine on %30 w/w Ca-Mon./Soil ratio

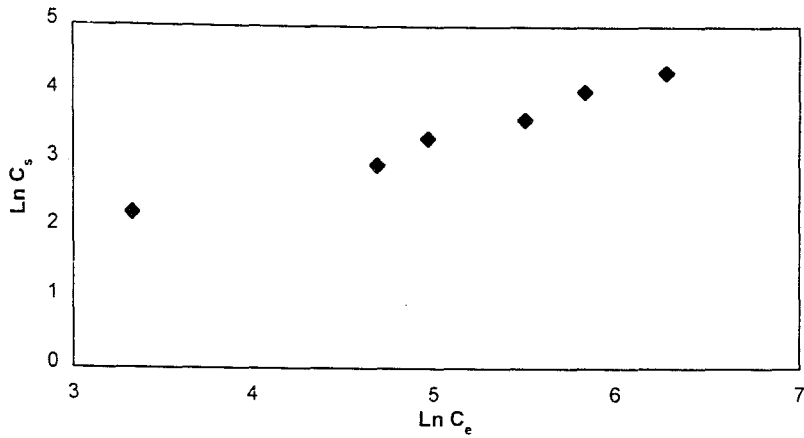


Figure A.67 Freundlich adsorption isotherm of Hyamine on %40 w/w Ca-Mon./Soil ratio

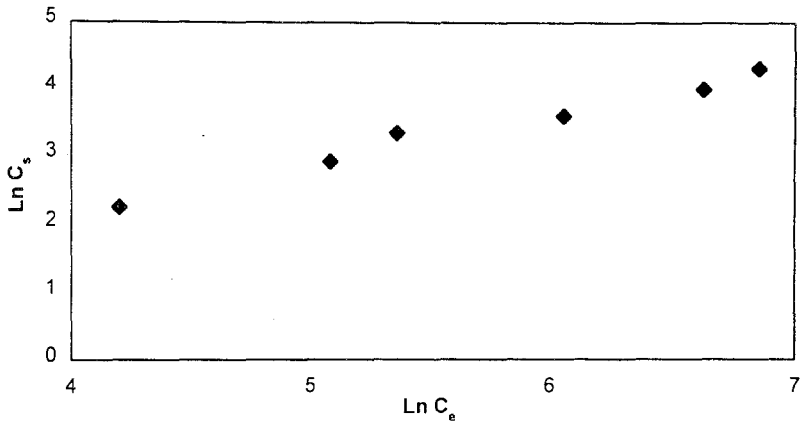


Figure A.68 Freundlich adsorption isotherm of Hyamine on %50 w/w Ca-Mon./Soil ratio

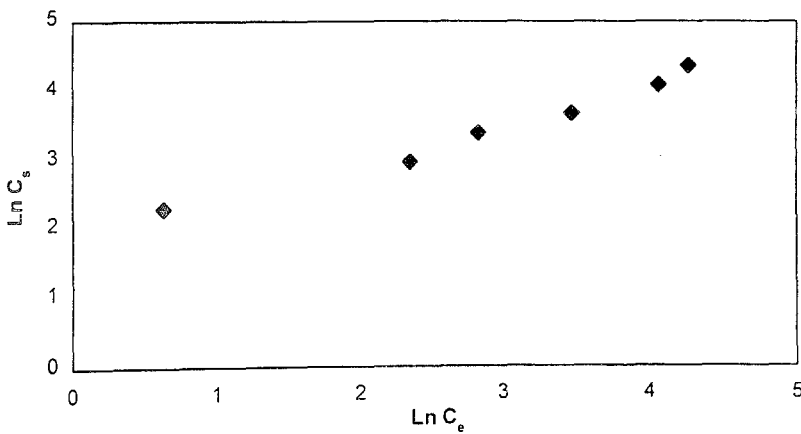


Figure A.69 Freundlich adsorption isotherm of Hyamine on %20 w/w Atta./Soil ratio

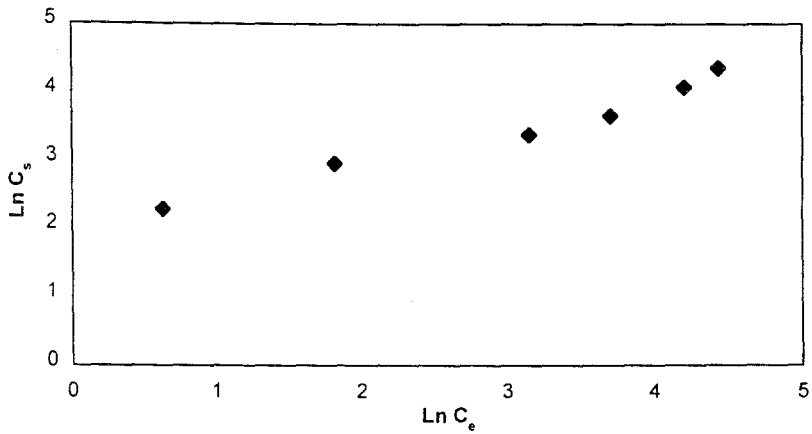


Figure A.70 Freundlich adsorption isotherm of Hyamine on %30 w/w Atta./Soil ratio

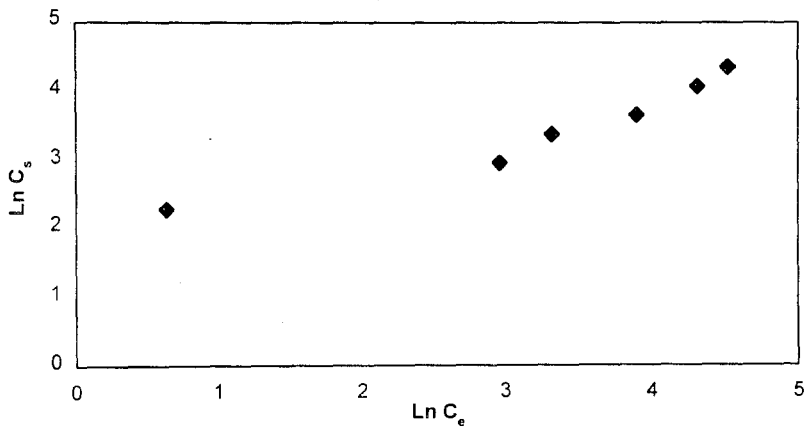


Figure A.71 Freundlich adsorption isotherm of Hyamine on %40 w/w Atta./Soil ratio

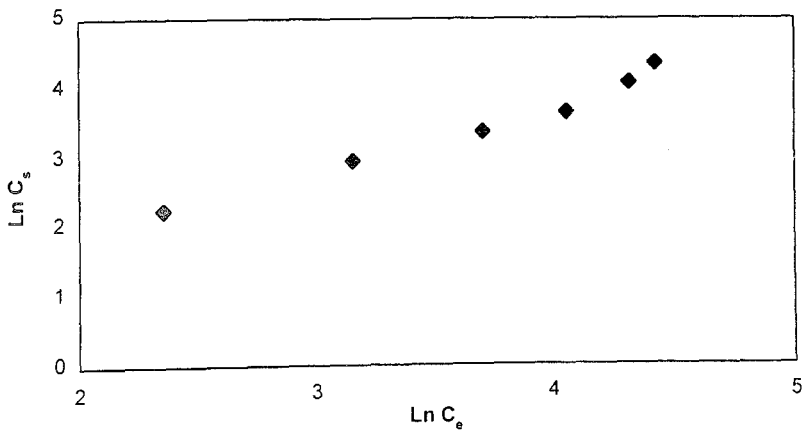


Figure A.72 Freundlich adsorption isotherm of Hyamine on %50 w/w Atta./Soil ratio

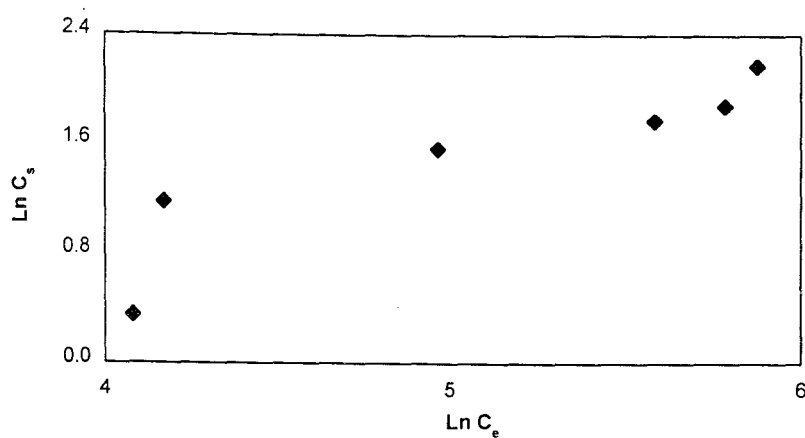


Figure A.73 Freundlich desorption isotherm of SDS on %20 w/w Kaolin/Soil ratio

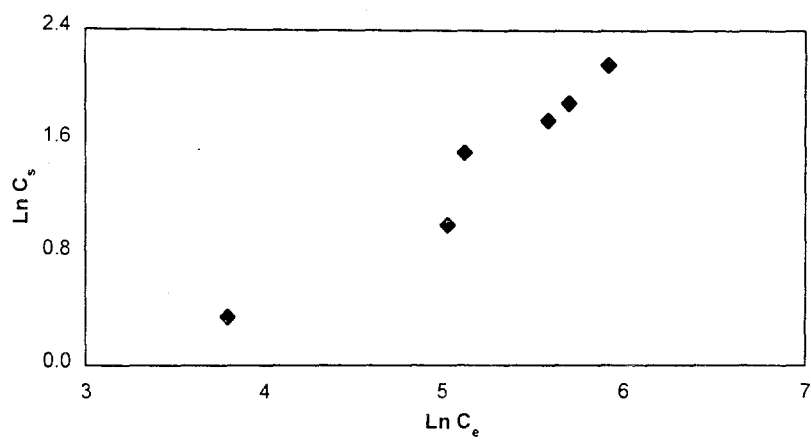


Figure A.74 Freundlich desorption isotherm of SDS on %30 w/w Kaolin/Soil ratio

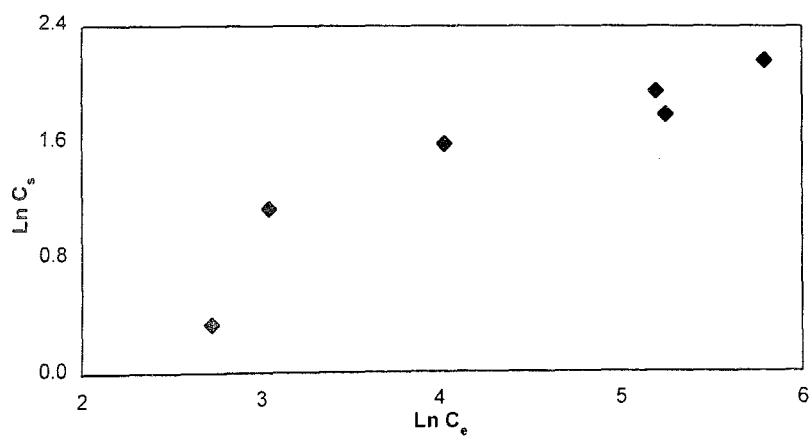


Figure A.75 Freundlich desorption isotherm of SDS on %40 w/w Kaolin/Soil ratio

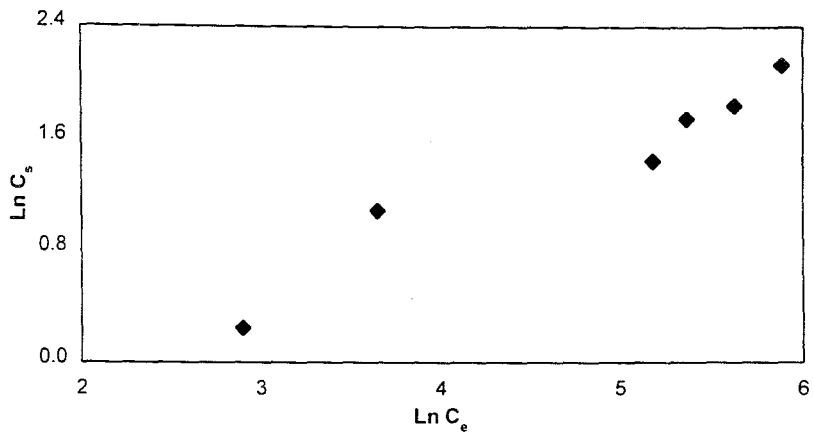


Figure A.76 Freundlich desorption isotherm of SDS on %50 w/w Kaolin/Soil ratio

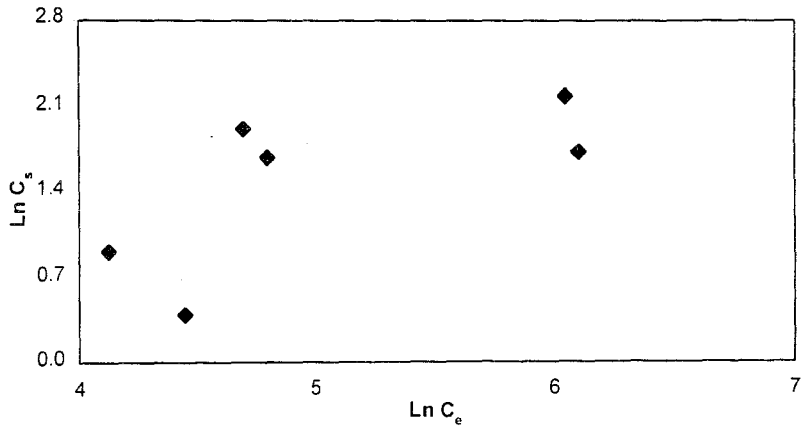


Figure A.77 Freundlich desorption isotherm of SDS on %20 w/w Ca-Mon./Soil ratio

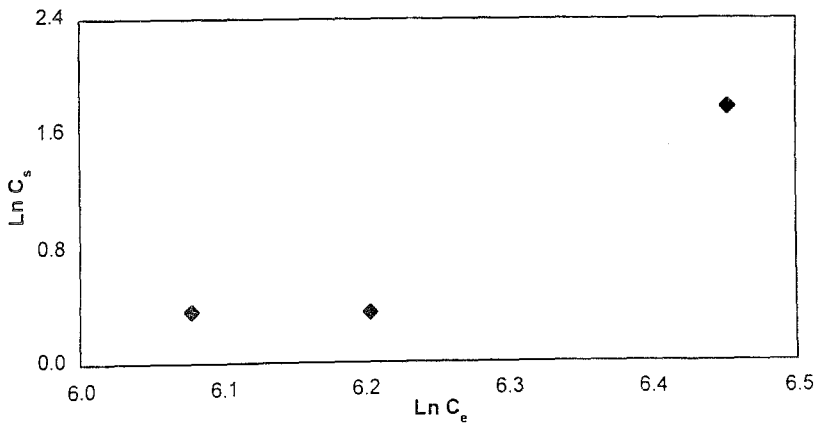


Figure A.78 Freundlich desorption isotherm of SDS on %30 w/w Ca-Mon./Soil ratio

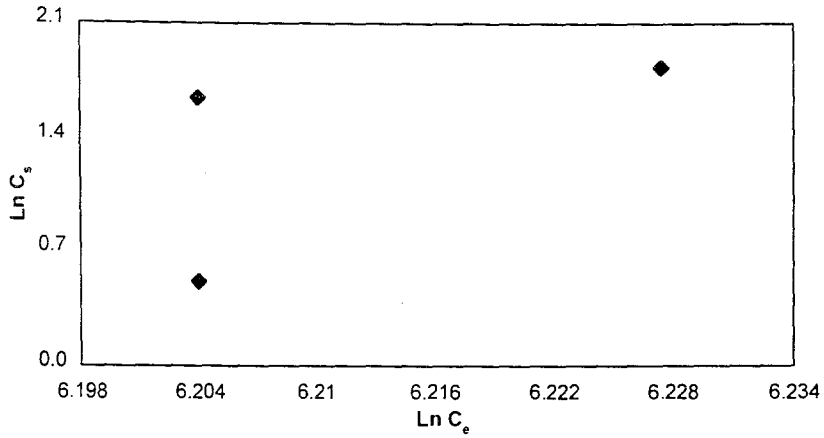


Figure A.79 Freundlich desorption isotherm of SDS on %40 w/w Ca-Mon./Soil ratio

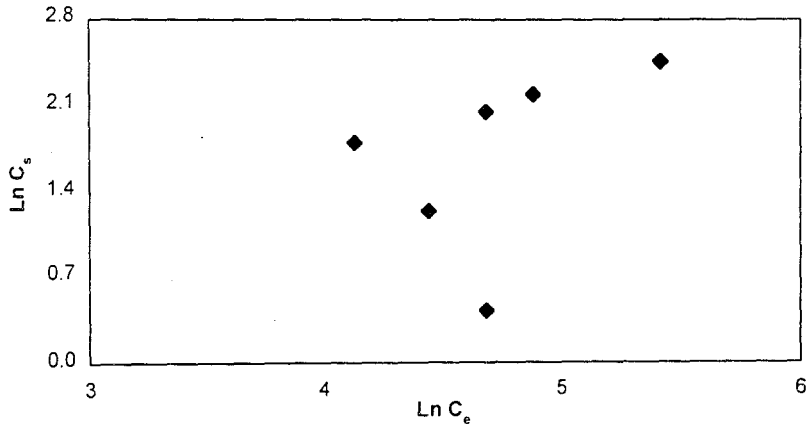


Figure A.80 Freundlich desorption isotherm of SDS on %20 w/w Atta./Soil ratio

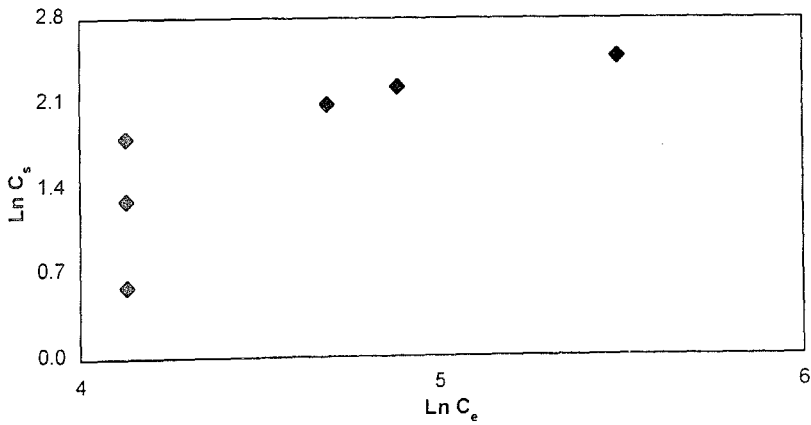


Figure A.81 Freundlich desorption isotherm of SDS on %30 w/w Atta./Soil ratio

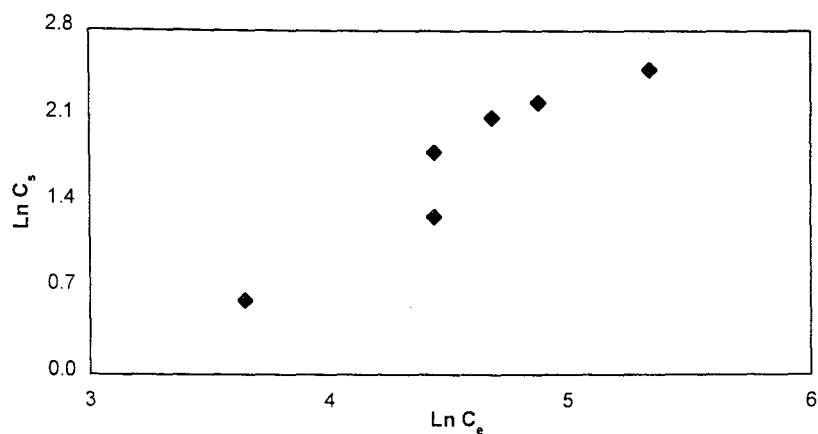


Figure A.82 Freundlich desorption isotherm of SDS on %40 w/w Atta./Soil ratio

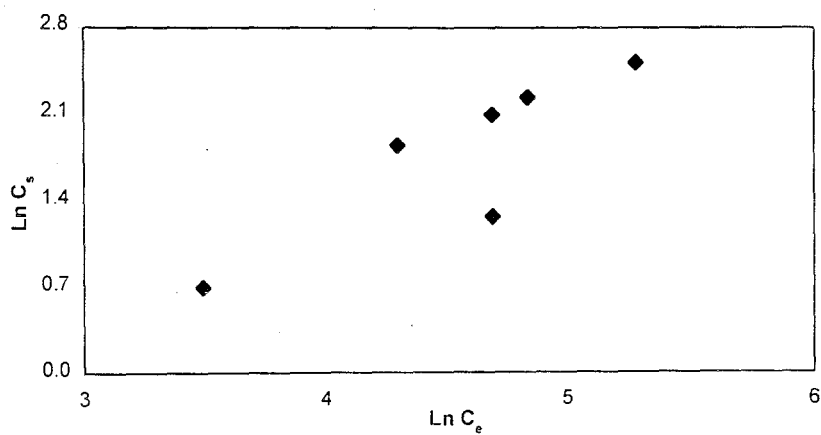


Figure A.83 Freundlich desorption isotherm of SDS on %50 w/w Atta./Soil ratio

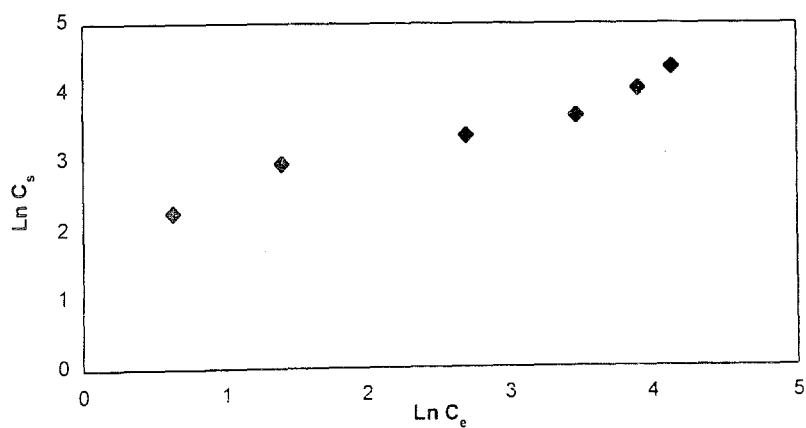


Figure A.84 Freundlich desorption isotherm of Hyamine on %20 w/w Kaoline/Soil ratio

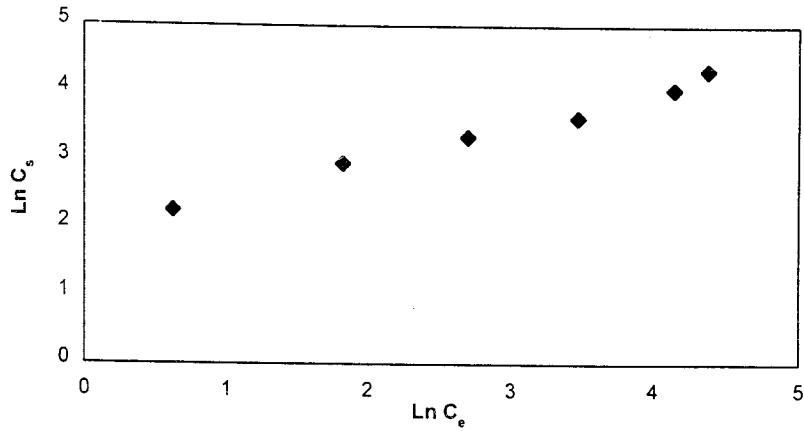


Figure A.85 Freundlich desorption isotherm of Hyamine on %30 w/w Kaoline/Soil ratio

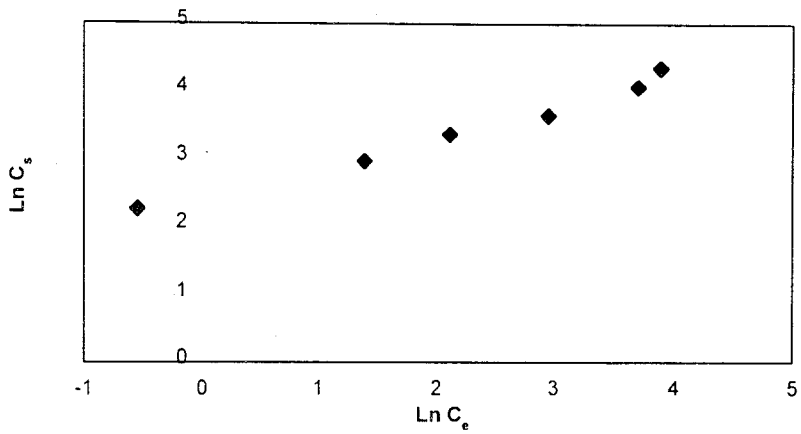


Figure A.86 Freundlich desorption isotherm of Hyamine on %40 w/w Kaoline/Soil ratio

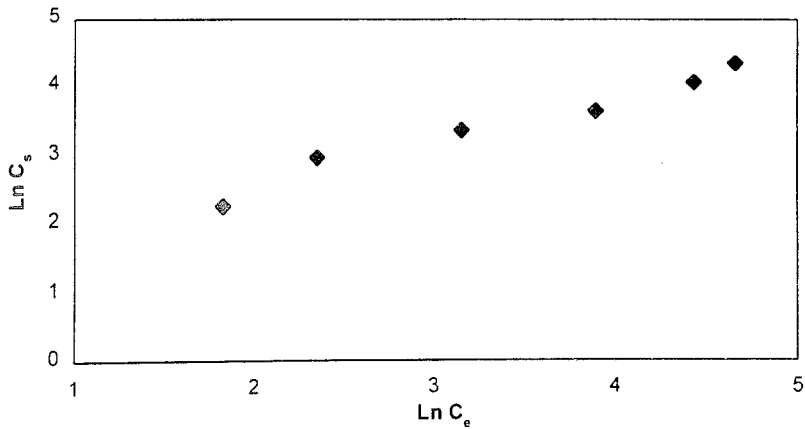


Figure A.87 Freundlich desorption isotherm of Hyamine on %50 w/w Kaoline/Soil ratio

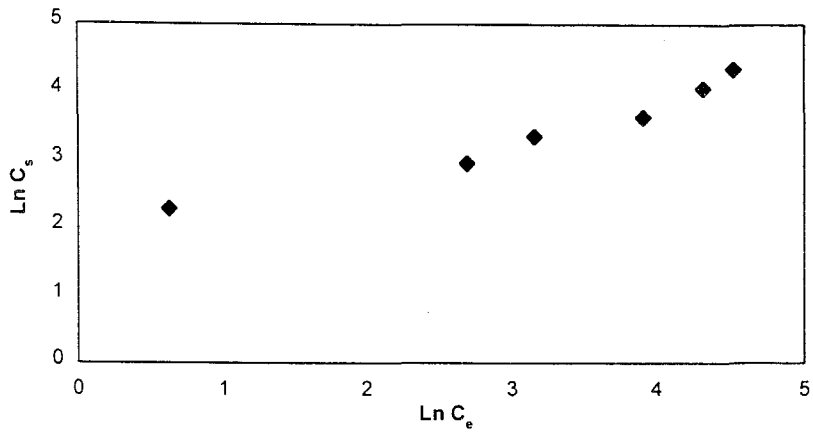


Figure A.88 Freundlich desorption isotherm of Hyamine on %20 w/w Ca-Mon./Soil ratio

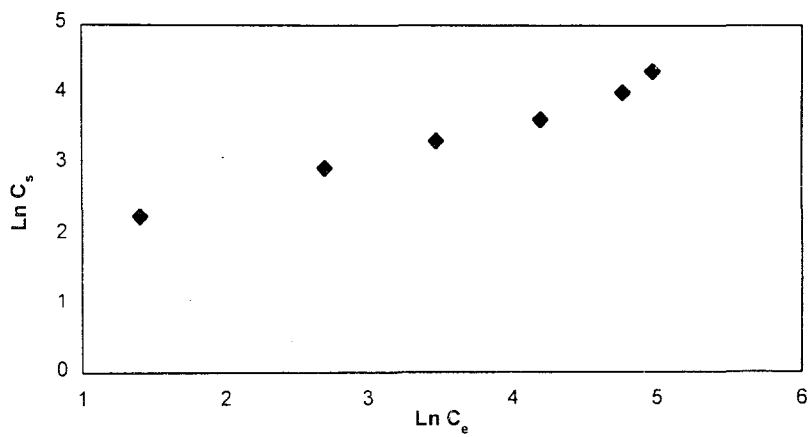


Figure A.89 Freundlich desorption isotherm of Hyamine on %30 w/w Ca-Mon./Soil ratio

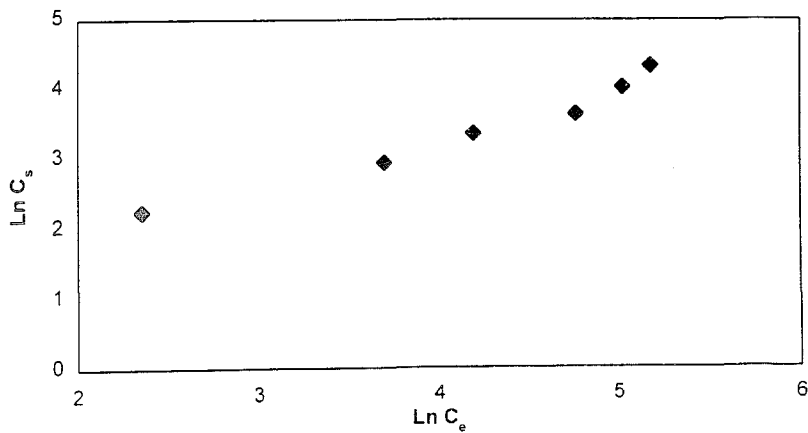


Figure A.90 Freundlich desorption isotherm of Hyamine on %40 w/w Ca-Mon./Soil ratio

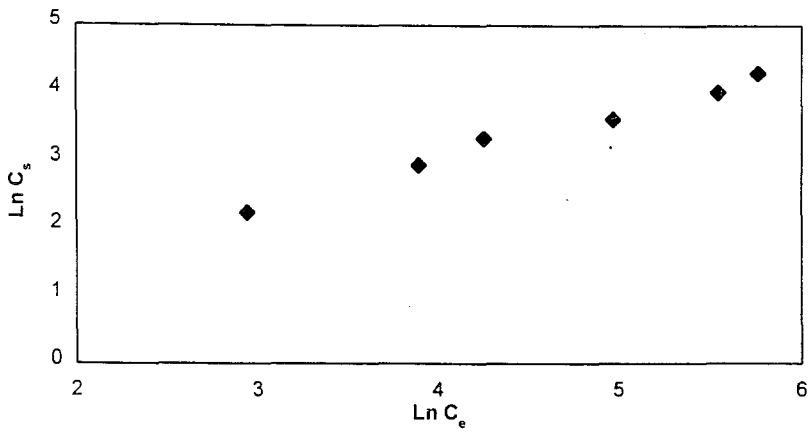


Figure A.91 Freundlich desorption isotherm of Hyamine on %50 w/w Ca-Mon./Soil ratio

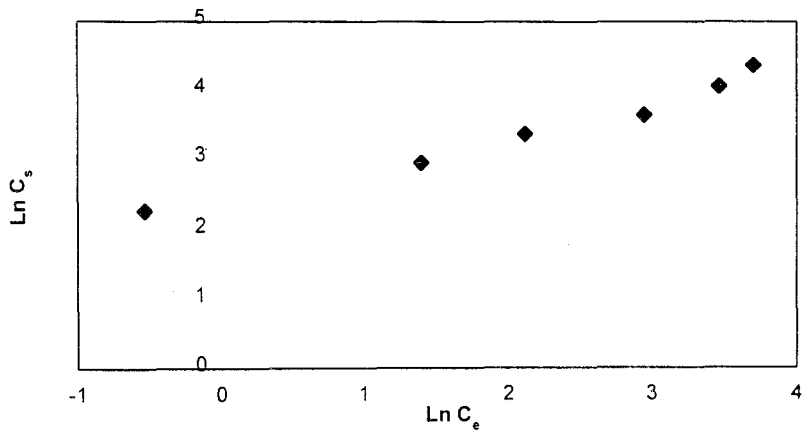


Figure A.92 Freundlich desorption isotherm of Hyamine on %20 w/w Atta./Soil ratio

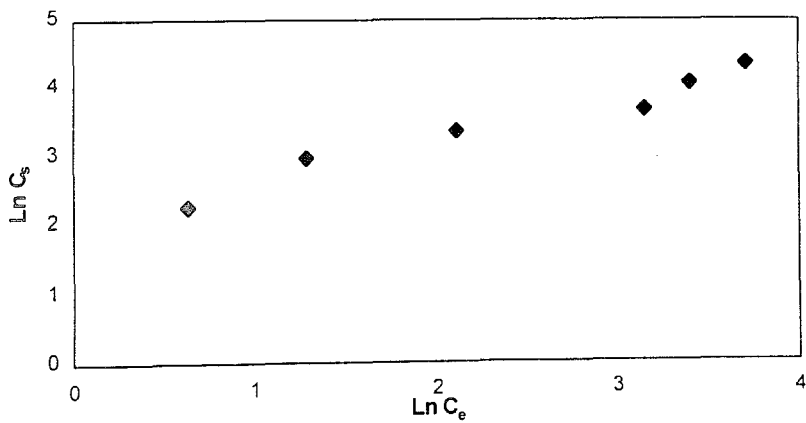


Figure A.93 Freundlich desorption isotherm of Hyamine on %30 w/w Atta./Soil ratio

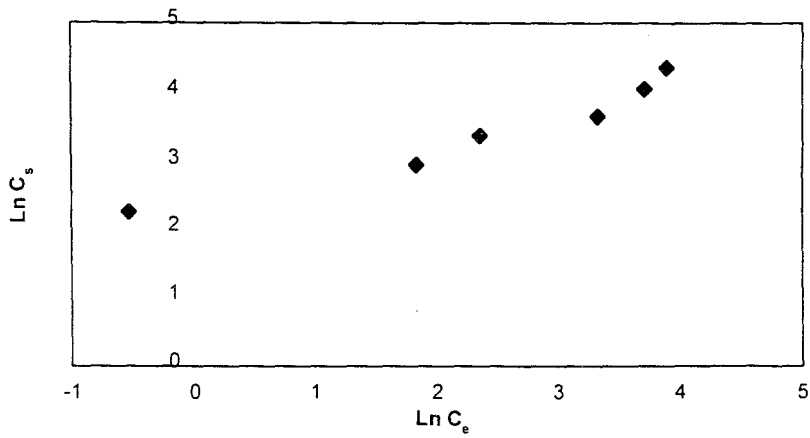


Figure A.94 Freundlich desorption isotherm of Hyamine on %40 w/w Atta./Soil ratio

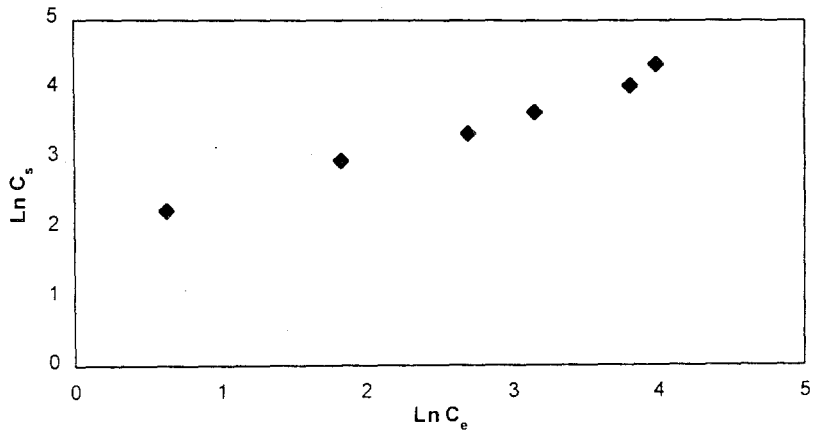


Figure A.95 Freundlich desorption isotherm of Hyamine on %50 w/w Atta./Soil ratio

APPENDIX B**Kaolin**

Cation Exchange Capacity : 2.0 meq/100 g

Surface Area : 10.05 +/- 0.02 m²/g

Chemical Composition :

| Chemical Composition | % |
|--------------------------------|----------|
| SiO ₂ | 44.2 |
| Al ₂ O ₃ | 39.7 |
| TiO ₂ | 1.39 |
| Fe ₂ O ₃ | 0.13 |
| FeO | 0.08 |
| MnO | 0.002 |
| MgO | 0.03 |
| Na ₂ O | 0.013 |
| K ₂ O | 0.05 |
| F | 0.013 |
| P ₂ O ₅ | 0.034 |

Calcium-Montmorillonite

Cation Exchange Capacity : 84.4 meq/100 g

Surface Area : 83.79 +/- 0.22 m²/g

Chemical Composition :

| Chemical Composition | % |
|--------------------------------|----------|
| SiO ₂ | 70.1 |
| Al ₂ O ₃ | 16 |
| TiO ₂ | 0.22 |
| Fe ₂ O ₃ | 0.65 |
| FeO | 0.15 |
| MnO | 0.009 |
| MgO | 3.69 |
| CaO | 1.59 |
| Na ₂ O | 0.27 |
| K ₂ O | 0.078 |
| F | 0.084 |
| P ₂ O ₅ | 0.026 |
| S | 0.04 |

Attapulgite

Cation Exchange Capacity : 19.5 meq/100 g

Surface Area : 136.35 +/- 0.31 m²/g

Chemical Composition :

| Chemical Composition | % |
|--------------------------------|-------|
| SiO ₂ | 60.9 |
| Al ₂ O ₃ | 10.4 |
| TiO ₂ | 0.49 |
| Fe ₂ O ₃ | 2.98 |
| FeO | 0.40 |
| MnO | 0.058 |
| MgO | 10.2 |
| CaO | 1.98 |
| Na ₂ O | 0.058 |
| K ₂ O | 0.80 |
| F | 0.542 |
| P ₂ O ₅ | 0.80 |
| S | 0.11 |