IMPORTANCE OF SURFACTANT ADSORPTION IN SOIL & GROUND WATER REMEDIATION

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF

Bachelor of Technology
in
Chemical Engineering

By

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DHARMENDRA KUMAR MISHRA (Roll No. - 10300031)

Department of Chemical Engineering
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CERTIFICATE

This is to certify that the thesis entitled, “**IMPORTANCE OF SURFACTANT ADSORPTION IN SOIL & GROUND WATER REMEDIATION** ” submitted by Sri Sankalp Tripathi & Dharmendra Kumar Mishra in partial fulfillments for the requirements for the award of Bachelor of Technology Degree in Chemical Engineering at National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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CHAPTER 1

GENERAL INTRODUCTION

1.1 INTRODUCTION TO SURFACTANT

The term surfactant is derived from the words surface active agent. Surfactants provide remarkable benefits in many textile wet processes. A surface active chemical is one which tends to accumulate at a surface or interface. An interface is the area of contact between two substances. Where the interface is between two substances not in the same phase, the interface is usually called a surface.

Surface active agents interfere with the ability of the molecules of a substance to interact with one another and, thereby, lower the surface tension of the substance. Surfactants used in industrial applications usually cause a dramatic decrease in surface tension when used at low concentration. The surface tension of a liquid is an internal pressure caused by the attraction of molecules below the surface for those at the surface of a liquid. This molecular attraction creates an inward pull, or internal pressure, which tends to restrict the tendency of the liquid to flow and form a large interface with another substance. The surface tension (or inter-facial tension if the interface is not a surface) determines the tendency for surfaces to establish contact with one another. Therefore, surface tension is responsible for the shape of a droplet of liquid. If the surface tension is high, the molecules in the liquid are greatly attracted to one another and not so much to the surrounding air. If the droplet of water is in contact with a solid such as a fabric, its shape will also be affected by the surface tension at the solid/liquid interface. If the surface tension in the liquid is lower, the droplet forms a more ellipsoidal shape.

Chemically, surfactants are amphipathic molecules. That is, they have two distinctly different characteristics, polar and non polar, in different parts of the same molecule. Therefore a surfactant molecule has both hydrophilic (water-loving) and hydrophobic (water-hating) characteristics. Symbolically, a surfactant molecule can be represented as having a polar “head” and a non polar “tail” as shown below

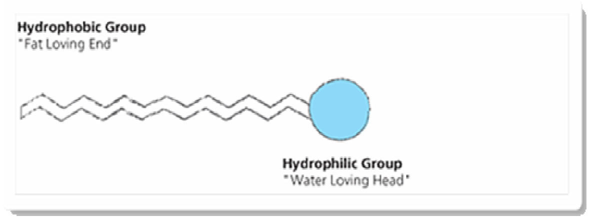
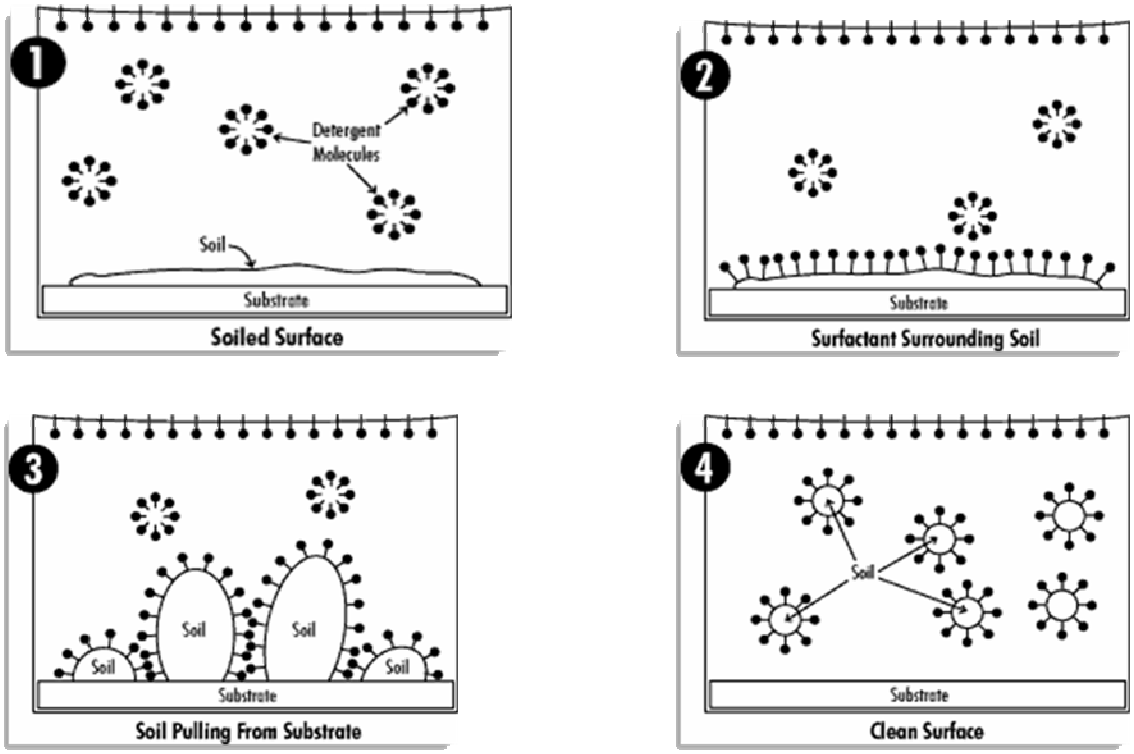


Fig 1.1 Representation of surfactant molecule

The hydrophobic group in a surfactant for use in aqueous medium is usually a hydrocarbon chain but may be a fluorocarbon or siloxane chain of appropriate length. The hydrophilic group is polar and may be either ionic or nonionic. The surfactant lines up at the interface as diagrammed below in Fig1.2.The hydrophobic end of the molecule gets away from the water and the hydrophilic end stays next to the water. When dirt or grease is present (hydrophobic in nature) the surfactants surround it until it is dislodged from the boundary. Notice in Fig 1.2(4) that the dirt molecules are actually suspended in solution. Micelles consist of hydrophobic interior regions where hydrophobic tails interact with one another. These hydrophobic regions are surrounded by the hydrophilic regions where the heads of the surfactant molecules interact with water. At very low concentration in water, surfactant molecules are unassociated. At higher concentration of surfactant in water, micelles forms. The concentration at which micelle form is called the critical micelle concentration (CMC). The surface tension of water undergoes a precipitous decrease, and the detergency of the mixture increases dramatically at the CMC.



Soiled Surface

Surfactant Surrounding Soil

Soil Pulling From Substrate

Clean Surface

Fig. 1.2 Cleansing action of surfactants on soiled surface

1.1.1 Types of surfactants

There is a broad range of different surfactant types, each with unique properties and characteristics Depending on the type of the charge of the head, a surfactant belongs to the anionic, cationic, non-ionic or amphoteric / zwitterionic family.

- ***Anionic Surfactant***

These are dissociated in water in an amphiphilic anion and a cation which is in general an alkaline metal (Na^+, K^+) or a quaternary ammonium. They are the most commonly used surfactants. Anionic surfactants account for about 50 % of the world production. In solution, the head is negatively charged. This is the most widely used type of surfactant for laundering, dishwashing liquids and shampoos because of its excellent cleaning properties and. The surfactant is particularly good at keeping the dirt away from fabrics, and removing residues of fabric softener from fabrics. Anionic surfactants are particularly effective at oily soil cleaning and oil/clay soil suspension. Still, they can react in the wash water with the positively charged water hardness ions (calcium and magnesium), which can lead to partial deactivation. The more calcium and magnesium molecules in the water, the more the anionic surfactant system suffers from deactivation. To prevent this, the anionic surfactants need help from other ingredients such as builders (Ca/Mg sequestrants) and more detergent should be dosed in hard water. The most commonly used anionic surfactants are alkyl sulfates, alkyl ethoxylate sulfates and soaps.

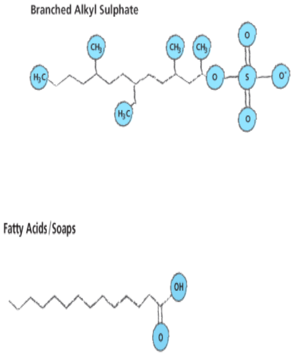


Fig.1.3 Types of Anionic surfactant

- ***Cationic surfactants***

These are dissociated in water into an amphiphilic cation and an anion, most often of halogen type. A very large proportion of this class corresponds to nitrogen compounds such as fatty amine salts and quaternary ammoniums, with one or several long chain of the alkyl type, often coming from natural fatty acids. These surfactants are in general more expensive than anionics, because of the high pressure hydrogenation reaction to be carried out during their synthesis. As a consequence, they are only used in two cases in which there is no cheaper substitute, i.e. (1) as bactericide, (2) as positively charged substance which is able to adsorb on negatively charged substrates to produce antistatic and hydrophobant effect, often of great commercial importance such as in corrosion inhibition.

In solution, the head is positively charged. There are 3 different categories of cationic each with their specific application:

In fabric softeners and in detergents with built-in fabric softener, cationic surfactants provide softness. Their main use in laundry products is in rinse added fabric softeners, such as esterquats, one of the most widely used cationic surfactants in rinse added fabric softeners. An example of cationic surfactants is the esterquat

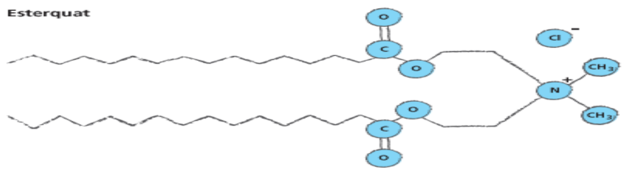


Fig 1.4. Esterquat (cationic surfactant)

In laundry detergents, cationic surfactants (positive charge) improve the packing of anionic surfactant molecules (negative charge) at the stain/water interface. This helps to reduce the dirt /water interfacial tension in a very efficient way, leading to a more robust dirt removal system. They are especially efficient at removing greasy stains. An example of a cationic surfactant used in this category is the mono alkyl quaternary system.

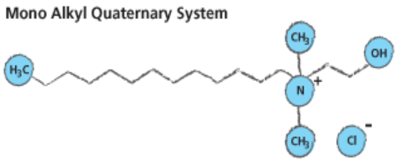


Fig.1.5. Mono alkyl quaternary system

In household and bathroom cleaners, cationic surfactants contribute to the disinfecting/sanitizing properties.

- ***Non-ionic surfactants***

These come as a close second with about 45% of the overall industrial production. They do not ionize in aqueous solution, because their hydrophilic group is of a non dissociable type, such as alcohol, phenol, ether, ester, or amide. A large proportion of these nonionic surfactants are made hydrophilic by the presence of a polyethylene glycol chain, obtained by the poly condensation of ethylene oxide. These surfactants do not have an electrical charge, which makes them resistant to water hardness deactivation. They are excellent grease removers that are used in laundry products, household cleaners and hand dish washing liquids. Most laundry detergents contain both non-ionic and anionic surfactants as they complement each other's cleaning action. Non-ionic surfactants contribute to making the surfactant system less hardness sensitive. The most commonly used non-ionic surfactants are ethers of fatty alcohols.

- ***Amphoteric/zwitterionic surfactants***

When a single surfactant molecule exhibit both anionic and cationic dissociations it is called amphoteric or zwitterionic. These surfactants are very mild, making them particularly suited for use in personal care and household cleaning products. They can be anionic (negatively charged), cationic (positively charged) or non-ionic (no charge) in solution, depending on the acidity or pH of the water. They are compatible with all other classes of surfactants and are soluble and effective in the presence of high concentrations of electrolytes, acids and alkalis. These surfactants may contain two charged groups of different sign. Whereas the positive charge is almost always ammonium, the source of the negative charge may vary (carboxylate, sulphate, sulphonate). These surfactants have excellent dermatological properties. They are frequently used in shampoos and other cosmetic products, and also in hand dishwashing liquids because of their high foaming properties. An example of an amphoteric/zwitterionic surfactant is alkyl betaine.

1.2 What is Surfactant Adsorption?

One of the characteristic features of the surfactant is their tendency to adsorb at the surface/interfaces mostly in an oriented fashion. The phenomenon of surfactant adsorption has been studied to determine:

(1) A measure of coverage of surface/interface by the surfactant, which in turn determines the performance of surfactant in many industrial processes such as foaming/defoaming detergency and emulsification.

(2) The orientation of the surfactant molecules at the surface/interfaces, which in turn determines how the surface/interface will be affected by the adsorption, i.e. whether it will become more hydrophilic or hydrophobic. These properties provide information on the type and the mechanism of any interactions involving the surfactant molecules at the surface/interface and its efficiency as a surface-active agent.

1.2.1 General behaviour of surfactant and its effect on various physical properties

Aqueous dilute solution of an ionic surfactant acts as a normal electrolyte at low concentration, but beyond a specific concentration it forms organized aggregates of a large number of molecules called ‘micelles,’ and this specific concentration is called critical micelle concentration (CMC). Above the CMC, sudden changes in many physicochemical properties have been observed in aqueous solution of surfactants. These changes are illustrated schematically in Fig 1.6.

Adsorption of more than one surfactant significantly enhances the efficiency of many interfacial properties compared to the adsorption of a single surfactant. Although the adsorption of single surfactants at solid- liquid interface has been investigated intensively, there have been only a few studies of mixed systems, in spite of their great importance. Adsorption of surfactants from the mixed systems mainly depends on the solution properties of mixed surfactant system. Many researchers have studied the solution properties of mixed surfactant systems and the resulting adsorption. The physical properties like surface tension, interfacial tension and detergency changes below the CMC with concentration but there is no change in these properties above CMC. Some other physical properties like density, equivalent conductivity show a change in slope below and above the CMC.

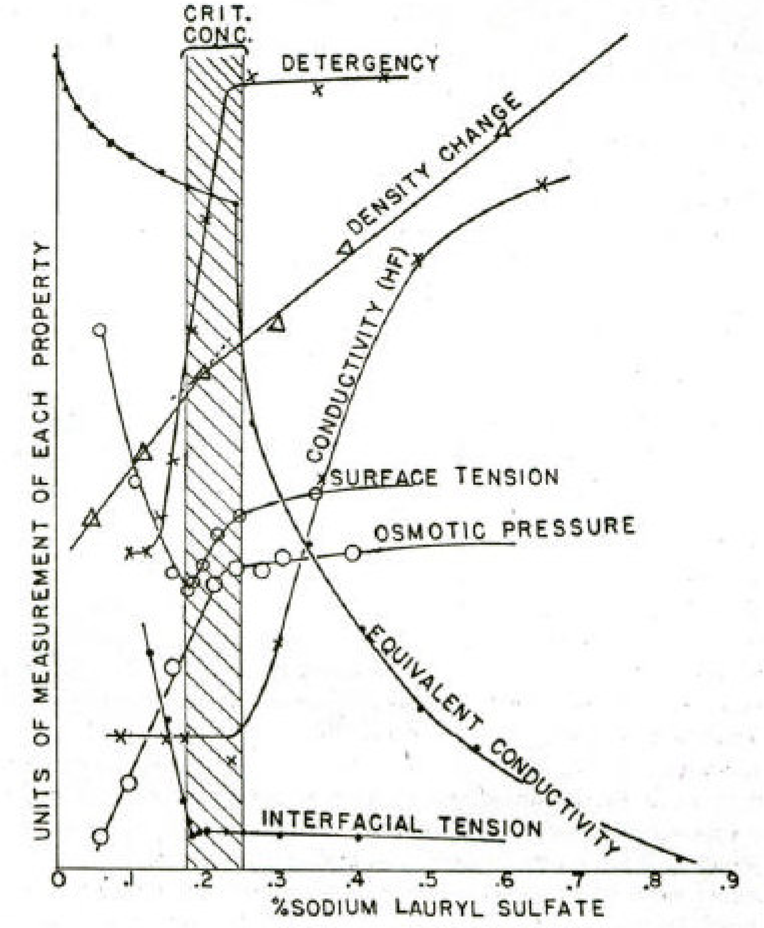


Fig 1.6 Physical properties changes for Sodium dodecyl sulfate at 25-28^{0}C[3]

1.2.2 Adsorption of Surfactant at the Solid/Liquid Interface

The adsorption of surfactants at the solid/liquid interface is strongly influenced by the number of factors:

(1) The nature of structural groups on the solid surface, i.e. highly charged sites or non-polar sites.

(2) The nature of surfactant molecule i.e. the nature of hydrophilic (ionic or nonionic) or hydrophobic groups.

(3) The environment of the aqueous phase i.e. presence of electrolyte, pH, and presence of other additives.

- **Mechanisms of adsorption**

There are several mechanisms by which surface-active molecules may adsorb onto the solid substrates from aqueous solution (Rosen, 1978)[1]. In general, adsorption of surfactants involves single ions rather than micelles (Griffith and Alexander, 1967)[2].

(i) Ion exchange: Replacement of counter ions adsorbed onto the substrate from the solution by similarly charged surfactant ions.

(ii) Ion pairing: Adsorption of surfactant ions from solution onto oppositely charged sites unoccupied by counter ions.

(iii) Hydrophobic bonding: Adsorption occurs by this mechanism when there is an attraction between the hydrophobic group of an adsorbed molecule and a molecule present in the solution.

(iv) Adsorption by polarization of electrons: When the surfactant contains electron rich aromatic nuclei and the solid adsorbent has strongly positive sites, attraction between electron rich aromatic nuclei of the adsorbate and positive sites on the adsorbent results adsorption.

(v) Adsorption by dispersion forces: Adsorption by London-van der waals force between adsorbate and adsorbent increases with increasing the molecular weight of the adsorbate.

- **Hydrophilic solid surface chemistry**

The hydrophilic solid is a characteristic of materials exhibiting an affinity to water. The surface chemistry allows these materials to be wetted forming a water film or coating on their surface. The surface functional groups have the ability to form the hydrogen bond with water. In general, mineral oxides and silica surfaces are used for studying surfactant adsorption at the hydrophilic surfaces. The solid–liquid interface is considered to develop a surface charge as a result of surface equilibrium involving potential determining ions which give rise to positive, negative and for some systems, neutral surface sites. The charge on the mineral colloids depends on the nature of the colloid, pH, ionic strength, and other solution conditions[3]. For oxides in simple electrolyte solution the charge is typically positive at low pH, the charge decreases and eventually becomes negative as pH increases. This charge variability is caused by the release and uptake of protons or hydroxyls. Generally, the H^+ and OH^- are the potential determining ions. Like other mineral oxide surfaces, the principal mechanism by which silica surfaces acquire a charge in contact with water and potential determining ions (H^+ and OH^-) is shown by the following equations[2]:

$SiOH + H^+ \rightarrow SiOH_2^+$ (i)

$SiOH + OH^- \rightarrow SiO$ (ii)

The isoelectric point of silica occurs at approximately pH 2 and the charge becomes negative between pH 6 and 11.

- **Adsorption isotherm:**

At the solid-liquid interface, the plot of amount of surfactant adsorbed per unit mass or unit area of the solid vs. equilibrium concentration is called adsorption isotherm. A number of studies have been conducted on solid liquid interface. The study of equilibrium of surfactant adsorption is important to determine the maximum amount adsorbed per unit area or mass of the adsorbent and to determine the adsorption isotherm. This is a measure of extent of surface of the adsorbent that is covered by the adsorbent molecules at a given condition, and hence determines the interfacial properties in many applications. Most of the interfacial processes are related to the equilibrium adsorption of the surfactant.

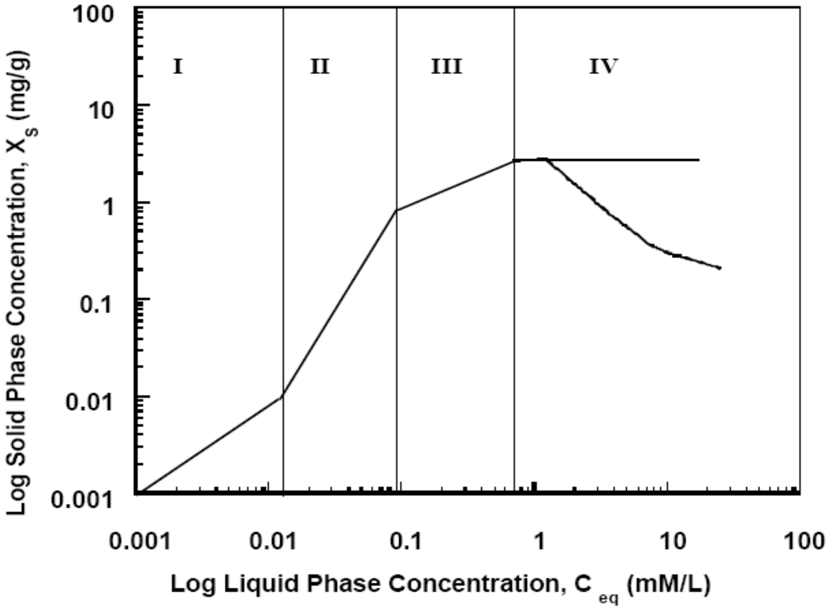


Fig 1.7 Schematic presentation of typical four-regime adsorption isotherm depicts the typical isotherm of adsorption of surfactants on the solid-liquid interface in a rather wide range of concentration of surfactants going beyond the CMC.

The solid surfaces are either positively or negatively charged in the aqueous medium by ionization/dissociation of surface groups or by the adsorption of ions from solution onto a previously uncharged surface. So, electrical double layer at the solid- liquid interface is usually an important phenomenon for the adsorption of ionic surfactants.

In general, a typical isotherm can be subdivided into four regions when plotted on a log-log scale .In region I, the adsorption obeys Henry's law, adsorption increases linearly with concentration. Region II shows a sudden increase in adsorption due to surface aggregation of the surfactants, while region III shows a slower rate of adsorption than region II. Region IV is the plateau region above the CMC.

- **Application of surfactant adsorption**
  - ✓ **Soil and ground water remediation**

The improper disposal, accidental spills, and leaks of petroleum hydrocarbons and organic solvents have resulted in long-term persistent sources of contamination of soil and groundwater, which has become a serious environmental concern because of their impact on health. Surfactants have recently been studied by several investigators for their ability to act as soil-washing agents and as facilitators of subsurface remediation of hydrocarbon spills. When surfactant is added at concentrations more than the cmc, the number of micelles increases, thereby enhances the contaminant solubility. This process solubilization will be equally appropriate for enhancing the desorption of highly hydrophobic contaminants and for dissolution of residual saturation.

✓ **Mineral / particulate floatation**

Ore or mineral floatation is currently the most industrially important example of a particulate flotation process and may be considered as a model for the other particulate process. Particulates, which have been successfully removed from suspension by floatation, include bacterial spores, algae, clays and colloidal precipitates. Like ore flotation, each of these processes requires the addition of a suitably charged surfactant and either adjustment of pH or addition of an ion that promotes the adsorption of surfactant on the surface of the particulate. 1.3.2. Surfactant-enhanced carbon regeneration Adsorption beds containing activated carbon are widely used to remove organic pollutants from wastewater streams. The adsorber will not be effective when breakthrough occurs and the carbon must be regenerated, this involves the removal of adsorbed organics from the carbon surface. In this method, a concentrated surfactant solution is passed through the adsorber containing the spent carbon, and the adsorbate desorbs and gets solubilized in the micelles

✓ **Herbicide dispersions**

In the present-day, the success of weed control technology in agriculture is attributable to the development and effective use of organic herbicides, followed by the use of herbicide adjuvants, particularly, the surfactants. Surfactants perform a number of different functions in herbicide dispersions. Surfactants are primarily used in aqueous dispersions, where they reduce the surface tension and consequently increase the spreading and wetting of the weed surface. This results in a uniform coverage of weed surface, greater absorption, reduced rate of evaporation, and other desirable effects. Surfactants help herbicide molecules to penetrate through the waxy surface of leaf. In nitrogen containing fertilizer (ammonium sulfate)-surfactant blends help the nitrogen compound to penetrate through the leaf surface. Generally, mixture of non-ionic surfactants is used in these applications.

✓ **Deinking from paper and plastic film**

Floatation deinking is the most important method for recycling of the paper. In this process, the surfactants are necessary for the removal of ink from the fibre during pulping step and to cause the pigment particles to be separated from the paper fibres by flotation. It is also important for the plastic recycling. The cationic surfactants are the most effective while the anionic surfactants are the least effective in removing the printing ink from plastic film, probably because the binder is an acidic acrylate with a negative charge.

✓ **Filtration of ultra fine particles**

The removal of particulate contaminants is very important in many industries, such as water reclamation facilities, water treatment, microelectronics and pharmaceutical industries. As the size of the particles decreases particle removal becomes very difficult. Adsorption of proper surfactant on the filter surface can lower the energy barrier between the particles and the filter surface; and thus increase the deposition of small particles on the surface of the filter. One example of such phenomenon is micro porous polypropylene membrane filters which are modified with a cationic surfactant, dimethyl dioctadecyl ammonium bromide (DDAB), to create a charged surface. Negatively charged nanoparticles can then be filtered by utilizing the electrostatic interaction between the charged particles and the polar head of the surfactants adsorbed on the filters

✓ **Stability of particulate suspension**

The stability of particle and colloidal slurries is an important phenomenon in many industries such as paint, printing ink, pharmaceutical, etc. Particle settling, which destabilizes the suspension, is often caused by the shielding of surface charges on the particles which would result in coagulation and subsequent settling. It has been found that the effects of addition of conventional stabilizing agents (e.g. ionic surfactants, polymers) increase the stability of the particle. However, sometimes the synergistic effects of mixed ionic–non-ionic surfactant systems are used to improve the stability of particle suspension especially when the system has high ionic strength.

✓ **Detergency**

Surfactants molecules are adsorbed on both soil and fabric surface in the process of detergency. The adsorption of surfactants plays a dual role in the removal of soil. They reduce the attraction between soil and fabric by attaching themselves to both. This way they not only loosen the soil from the fabric but also deflocculate the particles at the same time, i.e. they break up into colloidal particles and stabilize their aqueous dispersion. The soil, which forms a fine and stable dispersion in the wash liquor, is much less prone to attach itself to the fabric during remaining wash cycle than the soil present as a coarse and unstable dispersion. The detergency of a surfactant in the absence of electrolyte can be enhanced if the surfactant adsorption is enhanced.

CHAPTER 2

LITERATURE SURVEY

2.1 Surfactant adsorption kinetics

Reported studies on the surfactant adsorption kinetics on the solid–liquid interface are limited when compared to that on the fluid–fluid interface. Studies of surfactant adsorption or desorption kinetics from water at the hydrophilic solid surface, have been conducted mostly by using silicon oxide (silica), as this model hydrophilic surface has been well characterized. Adsorption kinetics on cotton, on filter paper and on active carbon have also been studied.

There seems to be consequences in the literature to the time variations on extent of adsorption can be divided into three different regimes, they are:

(1) linear increase in adsorption with time,

(2) transition regime where the rate of adsorption levels off and

(3) a plateau regime.

The range over which the regions extend varies with the bulk concentration, nature of surfactant, presence of salt and so on. The nature of solid surface, that is the hydrophobic or hydrophilic, and the electrical interactions play an important role in the kinetics of adsorption of surfactant at the solid–liquid interface.

2.1.1 Adsorption kinetics of ionic surfactant

Biswas and Chattoraj [4] have studied the adsorption of cationic surfactants (C_{16}TAB, C_{14}TAB, C_{12}TAB) on silica– water interface at different bulk concentration, pH, ionic strength, temperature and electrolyte. It is shown that the adsorption follows a two-step first order rate process with two different process rate constants. We have studied the adsorption kinetics of anionic, cationic and non-ionic surfactant at the cellulose–water interface is shown in Fig. 2.1. It is shown that the rate of adsorption kinetics of cationic surfactant is very fast and the final amount adsorbed is higher than the anionic and non-ionic surfactant at the cellulose–water interface. The order of rate of adsorption is cationic >anionic >non-ionic. As the cellulose surface is negatively charged in the aqueous medium, so the cationic surfactant can preferably be adsorbed on the cellulose surface. Adsorption kinetics of anionic surfactant on cotton shows that the total equilibrium time is approximately 2–3 hr. and at least 50% adsorption was complete within 10 min and the rate of adsorption of anionic surfactant on cotton increases with the increasing temperature . Biawas and Chattoraj [4] have also observed the rate constant of adsorption of CTAB, MTAB and DTAB on silica increases with increasing temperature.

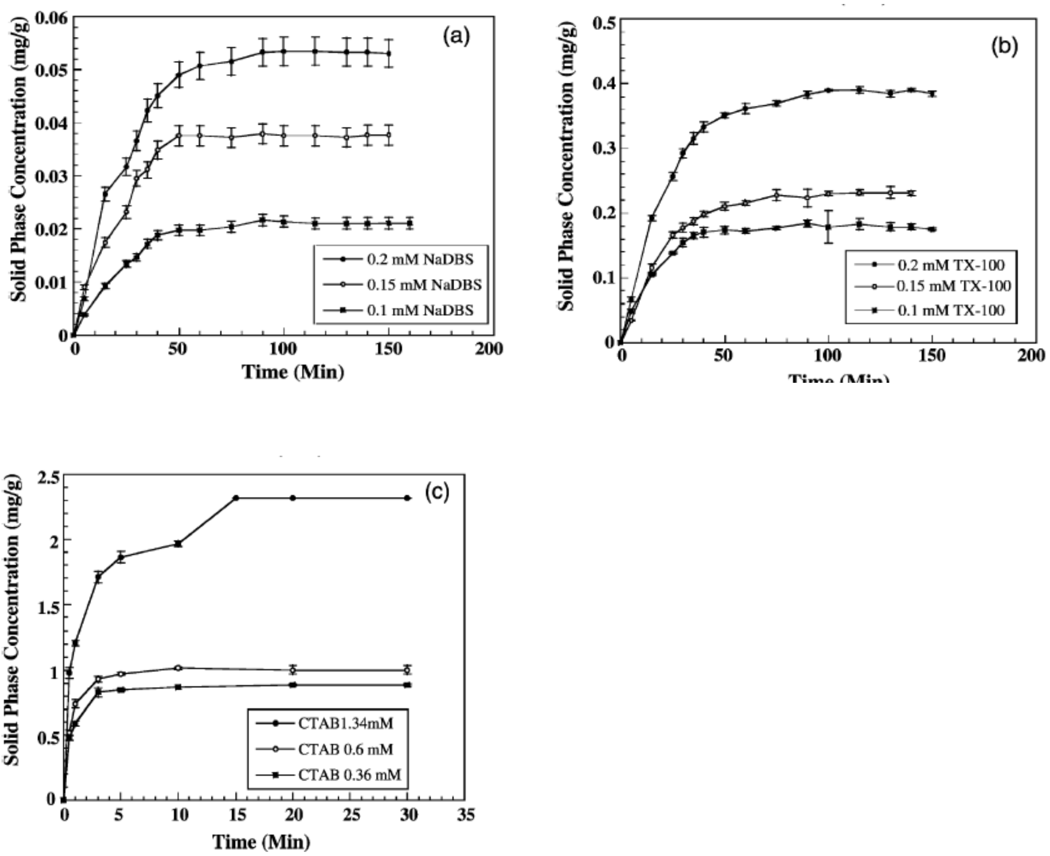


Fig 2.1. (a)Adsorption kinetics of NaDBS (b) Adsorption kinetics of TX-100 (c) Adsorption kinetics of CTAB on filter paper[5]

Adsorption kinetics of non-ionic surfactant on silica has been studied by ellipsometry technique and by UV absorption. Fig. 2.2 shows the adsorption kinetics of $C_{14}E_6$ on silica–water interface.

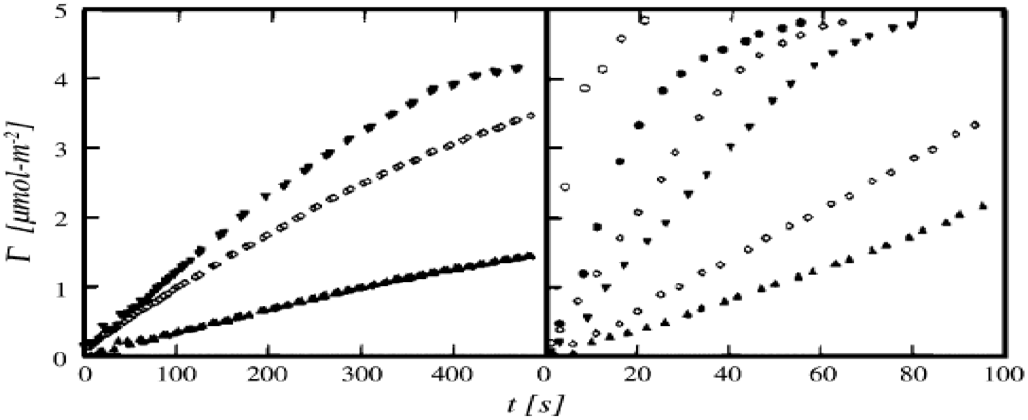


Fig. 2.2. Evolution of the adsorbed amount, G, of $C_{14}E6$ with time at different surfactant concentrations V cmc, left side, and concentrations >cmc, right side.

The initial adsorption rate increases with the increasing surfactant concentration. The initial adsorption rate increases steadily with the surfactant concentration, which is 0.007, 0.009, and 0.01 mmol l^{-1}, respectively, in the graph on the left side. The corresponding values in the plot on the right side are 0.02, 0.025, 0.05, 0.1, 0.25, and 1 mmol l^{-1}, respectively[10]

2.2 Groundwater Remediation

The improper disposal, accidental spills, and leaks of petroleum hydrocarbons and organic solvents have resulted in long term persistent sources of contamination of soil and groundwater, which has become a serious environmental concern because of their impact on health.

The pump-and-treat process was initially used for cleanup soils that were contaminated by both organic and inorganic contaminants. However, some limitations of this approach have been recognized recently due to the presence of strongly sorbed hydrophobic organic compounds HOCs, residual saturation RS, or non-aqueous phase liquids NAPLs. To overcome these mass transfer limitations, the surfactant aided soil washing process has been proposed to improve the performance of subsurface remediation.

Various techniques, including soil vapor extraction, bioremediation solidification/stabilization, and soil washing, have been used to remediate contaminated sites.

Surfactants have recently been studied by several investigators for their ability to act as soil washing agents and as facilitators of subsurface remediation of hydrocarbon spills. A general goal of subsurface remediation by pump and treat is extraction of subsurface contaminants with above-ground treatment for waste processing and management. The hydrophobic sink provided by the cores of surfactant micelles can significantly increase the mass of contaminant extracted per volume of water pumped, thereby overcoming the mass transfer limitations historically experienced in conventional pump-and-treat efforts. As surfactant is added at concentrations exceeding cmc, the number of micelles increases, thus enhances the contaminant solubility. This process solubilization will be equally appropriate for enhancing desorption of highly hydrophobic contaminants and for dissolution of residual saturation. Mobilization micro emulsification will have an even more dramatic effect in enhancing the extraction of residual saturation as the interfacial tension becomes negligible and the solubility enhancement escalates the phases become virtually miscible. Thus, both these mechanisms can significantly enhance the efficiency of contaminant extraction over water alone. For *in situ* soil flushing, reported that the concentration of the hydrophobic contaminants naphthalene, a biphenyl solubilized in surfactant solutions is a linear function of the total surfactant concentration, providing the cmc is reached. Vigon and Rubin evaluated surfactant selection and dose optimization through evaluation of parameters such as surface tension, cmc, extent of hydrophilic-hydrophobic balance, solubilization efficiency and partition coefficient.

Much attention has been paid to the performances of surfactant-aided soil washing of HOCs contaminated soil or sediment and to the investigation of chemical remediation of surfactant/HOCs mixtures extracted from soils and sediments The extent to which surfactants influence HOC distribution in environmental systems depends on HOC sorption to solid phases HOC solubilization by micellar or monomeric surfactant , and surfactant interactions with sediment or soil components.

2.2.1 Soil washing

When surfactant is added to a contaminated soil system, the partitioning of an HOC between different phases becomes complicated. Theoretically, the distribution of an HOC between the solid phase (soil or sediment) and the liquid phase ($[P]_w + [P]_{surf}$) may be described by an overall distribution coefficient, K_d :

$$K_d = \frac{[P]_s}{[P]_w + [P]_{surf}} \tag{1}$$

Where $[P]_s$, $[P]_{surf}$ and $[P]_w$ stand for concentration of HOCs in the soil (mol/kg) solubilized by both monomeric and micellarphases mol/L!, and in the water (mol/L). A K_d value can be easily measured in a laboratory, and the reciprocal of K_d can be used as an index to quantify the efficiency of a surfactant-aided soil-washing system.The surfactant-aided soil remediation has been investigated for some typical HOCs. The resulted soil-washing performances are shown in Fig. 2.3. It is interesting to note that the performance

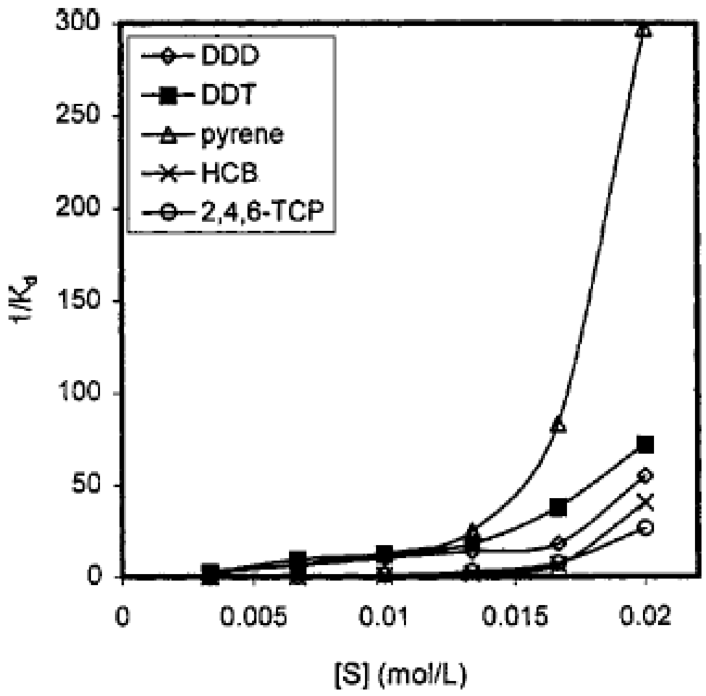


Fig. 2.3 Soil-washing performance curve ($1/K_d$) for HOCs at variousBrij35 concentrations, where 3.75 g of Tai Mo Shan soil at various concentrations of Brij 35 surfactant solutions (higher than CMC soil21.0031023 mol/L) were used in test.[7]

It is assumed that there are two main sources of HOC in the soil system before the washing is initiated. One is the fixed HOC that is physically or chemically adsorbed or bonded in the soil media, and another is the RS that resides in the liquid phase due to partitioning.

- **Solubilization of HOC using surfactant**

Apparently, the remediation of contaminated soils by surfactant aided soil washing for HOCs does not have a linear correlation with the surfactant dose, which makes the prediction work difficult. A practical model, therefore, is proposed for such predicting purpose. Solubilization of HOC by surfactant may be analogous to similar reactions of HOC with aqueous organic matter. Almgren et al[8] have shown that, for HOC solubilized within micelles, solubilization of one molecule does not affect the solubilization of another. Solubilization of HOCs is generally initiated at the cmc and is proportional to the surfactant concentration in bulk solution beyond this point, which can be described by a micelle-water partition coefficient, *Km* (L/mol)

$$K_m = \frac{[P]_{\text{mic}}}{[P]_w[S]_{\text{mic}}} \text{ or } K_m = \frac{[P]_{\text{surf}}}{[P]_w[S]} \tag{2}$$

where $[P]_{\text{mic}}$= concentration of solubilized pollutant in micelles(mol/L); $[S]_{\text{mic}}$= concentration of micellar surfactant (mol/L); and$[S]$=concentration of surfactant in both monomeric and micellar form (mol/L). The partitioning of HOC into a surfactant solution involves both the micellar phase and the monomeric phase .

Another important study was conducted by Lizhong Zhu[6] etal about the solubilization of nonionic organic compounds (NOCs) like phenol,p-nitrophenol and naphthalene o Betonite and soil using Myristylpyridium bromide (MPB) surfactant.The results obtained are shown in Fig 2.4.

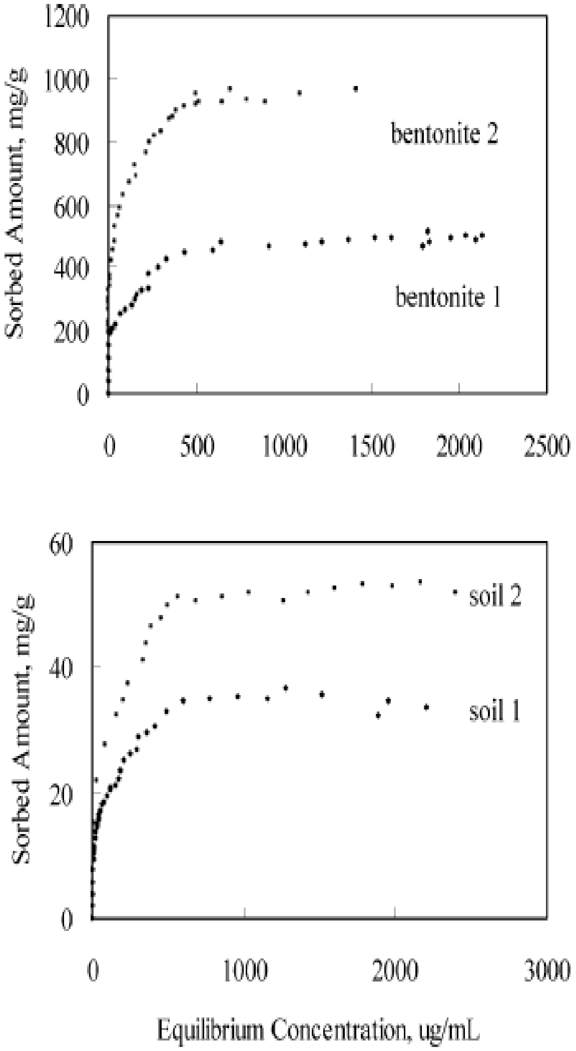


Fig 2.4 Sorption of MPB onto two betonites and two soils[6]

2.3 SEAR (Surface Enhanced Acquifer Remediation) Model

Pumping groundwater for above ground treatment is a standard remedy for groundwater contamination. However, remediation with pump-and-treat methods can require periods of years to decades to reach treatment goals due to persisting sources of contamination. These persistent sources were determined to be NAPLs, which are undissolved organic contaminants that become trapped in the subsurface due to capillary forces. Many NAPLs have low aqueous solubility and are biologically recalcitrant; therefore mass removal from the dissolved phase is slow. SEAR was developed as a method to increase the solubility and mobility of NAPL and enhance the removal rate achievable with pumped groundwater. Surfactants are surface active agents that have two different active sites, a water-liking (e.g., hydrophilic) head and a water-disliking (e.g., hydrophobic) tail. Thus, they exhibit solubility in both water and oil and help to improve NAPL recovery. SEAR technology can be used to clean up a wide variety of NAPL contamination. Over the past few years, the greatest demand for the SEAR technology has been for remediating chlorinated hydrocarbon DNAPLs such as trichloroethylene (TCE) and tetrachloroethylene (PCE). This is due to their prevalence as groundwater contaminants, the risk associated with their presence in the subsurface, and the lack of other established remedial alternatives. Industrial solvents were often released to the environment as spent solvents laden with oily contaminants. SEAR has been used to remove these variable density contaminant mixtures and contaminants such as creosote, gasoline, jet fuels, and polychlorinated biphenyls (PCBs)

SEAR can be considered a chemical enhancement to pump and treat in which a surfactant solution is pumped through a contaminated zone by introduction at an injection point and removal from an extraction point. To cover the entire contaminated zone, a number of injection and extraction wells are used; the well configuration is determined by the subsurface distribution of DNAPL and the hydrogeologic properties of the aquifer. A conceptual picture of SEAR application is shown in Figure 2.5. Application of SEAR technology removes the contaminant source by removing the residual DNAPL contamination that dissolves to form the groundwater plume. Once the DNAPL sources impacting a particular groundwater plume are entirely removed, an intermediate and long-term reduction in dissolved phase contaminant concentrations will occur through natural attenuation. Thus complete delineation of the existing DNAPL sources is requisite to effective management of source control removal measures such as SEAR.

At suitable sites, a water flood is applied first to remove any easily recoverable mobile DNAPL. The more tightly held, residual DNAPL is then removed through injection of the surfactant solution into the DNAPL source zone. A post surfactant-injection water flood is conducted to recover injected chemicals and solubilized or mobilized DNAPL remaining in the aquifer. The extracted fluids are then treated above ground to remove free-phase (i.e., separately mobile phase) and dissolved phase contaminants and any other constituents necessary to meet disposal requirements. The surfactant can be recovered for re-injection, if desired. The primary difference between a SEAR system and a pump and treat system is the importance placed on maintaining hydraulic control over the injected fluids and contaminants. To this end, a SEAR well field consists of closely spaced injection and extraction wells and often includes hydraulic control or tap water injection wells to prevent the escape of injected chemicals and solubilized/mobilized contaminant. As shown in Figure 2.5 below, injected fluids and contaminants are captured at extraction wells screened within the DNAPL-contaminated zone.

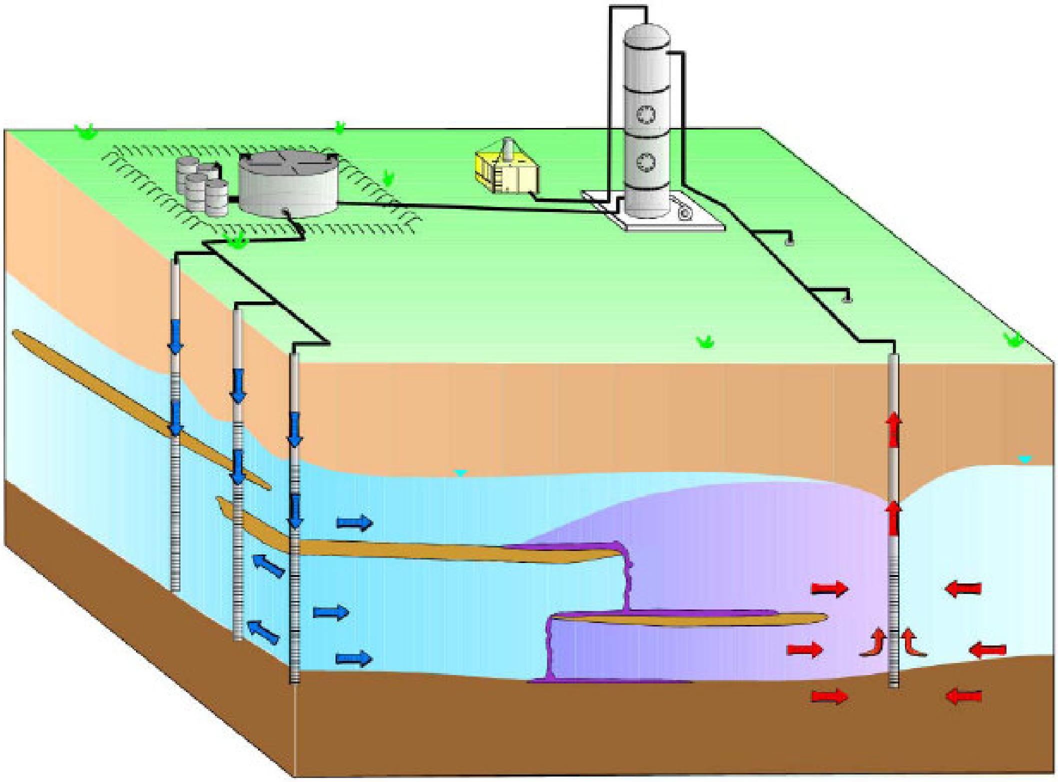


Fig 2.5. Conceptual Design for a SEAR Application[9]

CHAPTER 3

EXPERIMENTS

3.1 Materials

Non-ionic surfactant-Triton X-100 [$C_{14}H_{22}O$ (C_2H_4O) $_{10}$] (chemical name-Glycol Tertoctylphenyl ether) of scintillation grade ,Anionic surfactant- Sodium Lauryl Sulphate ($C_{12}H_{25}$ NaO_4S) were obtained from Ranbaxy Chemicals and were used as received. Naphthalene was used as an organic poly aromatic hydrocarbon. In all the experiments performed ultra pure water (pH=7) was used.

3.2 Sand sieving and cleaning

The sand was sieved in the sieve shaker and the 212-500 μm sized sand as taken for the experiments. The sand was cleaned firstly by thorough water washing and then followed by immersion in sodium dithionite solution (0.1M $Na_2S_2O_4$) for 2 hrs to remove metallic compounds such as iron oxide and manganese oxide. Organic impurities were removed by soaking sand in hydrogen peroxide (5%) for 3 hrs followed by washing with water and subsequent overnight soaking in HCl (12N). The sand is then rinsed thoroughly with pure water until the pH of the wash water shows the value of pure water (6.8-7). The cleaned sand was then dried in an oven at 100^0C for 24 hrs

3.3 Surfactant Analysis

The stock solution of 10mM and 50mM of Triton X-100 and Sodium Lauryl sulfate were prepared respectively. Care should be taken while preparing such solutions so that the solution is of desired concentration. Formation of foam wile preparation should be avoided. The calibration plot (Absorbance vs Concentration) was obtained by measuring UV absorbance of surfactant at 223 nm wavelength (for Triton X-100) against different surfactant concentrations in UV Spectrophotometer. Thus the relation between absorbance of surfactant and concentration of surfactant is obtained from the plot. Here water was taken as a reference for UV spectral analysis.

Since anionic surfactant being UV spectra insensitive, they cannot be quantified and thus their adsorption studies on sand–water interface cannot be studied by this method.

Similar procedure was used for calibration of naphthalene solution prepared in methanol (below 1% by volume) and the required relationship between absorbance and concentration of naphthalene was obtained. Here a sufficiently high concentrated solution of (400mM) naphthalene solution was prepared in methanol which would be sufficient to saturate the surfactant solution under test.

Precautions to be taken before conducting spectral analysis:

- The cubets should be cleaned properly before using.
- Separate microtips should be used for different solution while using micro pipette.
- Baseline correction should be done taking ultra fine water as a reference before starting the spectral analysis
- Auto zero should be executed before starting with the spectral analysis.
- Cubets should be cleaned with ultra fine water between two successive concentrations solution.

3.4 Surfactant solubilization of PAH's

Batch experiments were conducted in duplicate to determine the solubility enhancement of PAHs by surfactants. A volume of 10ml surfactant solutions with a series of concentration were placed in 15ml Tarson centrifuge tube and 0.1ml of naphthalene solution (400mM) was subsequently added to each tube to saturate the solutions. These samples were then equilibrated on a reciprocating shaker for 24hrs at around 25^0C. and were subsequently centrifuges at 4000 rpm for 30 mins to completely saturate the undissolved solute. An appropriate aliquot of the supernatant was then carefully withdrawn with a volumetric pipette and the concentration of PAHs in the solution was analyzed using UV spectrophotometer using water as a reference in the cubet**.**

3.5 Sorption of surfactant onto sand

Batch experiments were conducted to determine surfactant equilibrium sorption isotherms using plastic bottles of 100ml volume. 20ml of different concentration surfactants are taken in the bottles and then 10 g of cleaned sand is poured into each such bottle containing surfactants of different concentrations. Then they are left to attain equilibrium state for around 12hrs. Once the equilibrium state is reached then the aliquot of the supernatant is decanted into a centrifuge tube and centrifuged at 4000rpm for 30mins to completely separate the small sand particle from the surfactant solution. Then the aliquot is analyzed for the concentration of surfactant using neat surfactant solution as a reference for UV analysis. The amount adsorbed on sand is given by

$$\text{Amount adsorbed(mmol/g)} = (C_0 - C_{eq})v/m$$

where,

v- volume of solution used

C_0&C_{eq}-Initial and equilibrium surfactant concentration (mM/L) respectively

m-mass of sand in grams

Thus, the sorption amount of surfactant onto soil was computed simply from the difference of the initial and final surfactants concentration in solution.

3.6 Distribution of PAH in sand-water-surfactant system

Equilibrium sorption experiments for naphthalene onto sand in the presence of surfactant were conducted in duplicate using 50ml plastic bottles. Different concentration of surfactant (20 ml) & 10 gm of sand were taken to which 0.2 ml of naphthalene solution (400mM) was added to make it saturated. These bottles were kept for 12-14 hrs to reach the equilibrium stage. The solution and the solid phase was separated by centrifugation at 4000 rpm for 30mins.An appropriate amount of aliquot of the supernatant was removed and analyzed for naphthalene. The sorbed amounts of naphthalene were computed simply from the difference of initial and final naphthalene concentrations.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1Quantization of surfactant

Different concentrations of surfactant solution some below the CMC value and some above it were taken. (for e.g. 0.1, 0.15, 0.5, 0.2 (mM)) for Triton X-100. The peak adsorption was found to be at wavelength of 223 nm. Thus obtained values of absorbance at different wavelength corresponding to different concentration of surfactants are plotted as shown in Fig 4.1

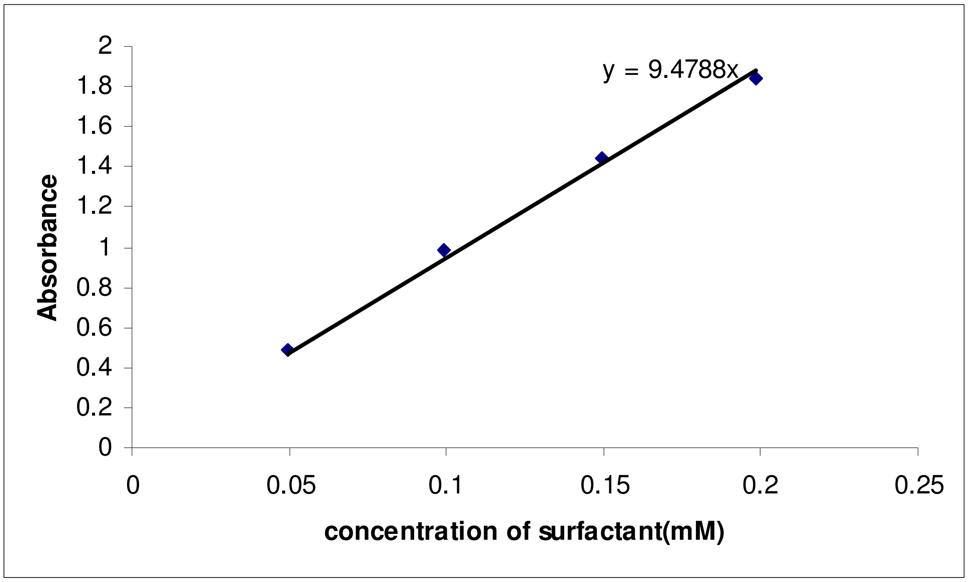


Fig 4.1 Calibration curve of Triton X-100

Similar approach was followed for quantifying Naphthalene and the relation between concentration of naphthalene and concentration of surfactant was found to be

$$y=5.2275x$$

where,

y- Concentration of naphthalene

x- absorbance

4.2 Surfactant solubilization of Naphthalene

Different concentrations of surfactants were taken keeping into consideration the limitations of UV spectrophotometer and sufficient amount of Naphthalene solution was added to saturate the solution (0.2ml of 400mM naphthalene solution).

The CMC value for Triton X-100 is 0.2 mM. So concentrations like 0.05, 0.1, 0.2, 0.5, 1.0, 1.5, 2.0 (mM) were taken.

Thus obtained solubilization curve is shown in Fig 4.2.Similarly the solubilization curve for anionic surfactant (Sodium Lauryl Sulfate) was obtained as shown in Fig 4.3.It can be inferred from both the plots that solubilizing ability of non ionic surfactant is more than anionic surfactant. Thus it can be said that anionic surfactant are more efficient in PAHs removal from sand by solubilization mechanism Below the CMC, surfactant exists as a monomer and have minimal effects on the aqueous solubility of organics . Micellar solubilization occurs when the surfactant concentration exceeds the CMC, where the aqueous solubility of organics are enhanced by the incorporation of hydrophobic molecules into the micelle. The extent of micellar solubilization depends on various factors including surfactant structure, micelle geometry, ionic strength, temperature and the size and chemistry of the solubilizate.

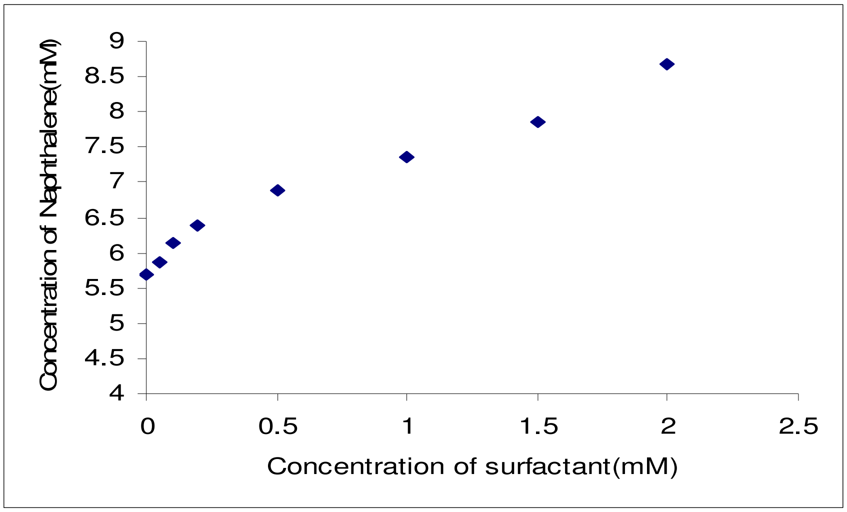


Fig. 4.2 Solubilization curve of Naphthalene in Triton X-100

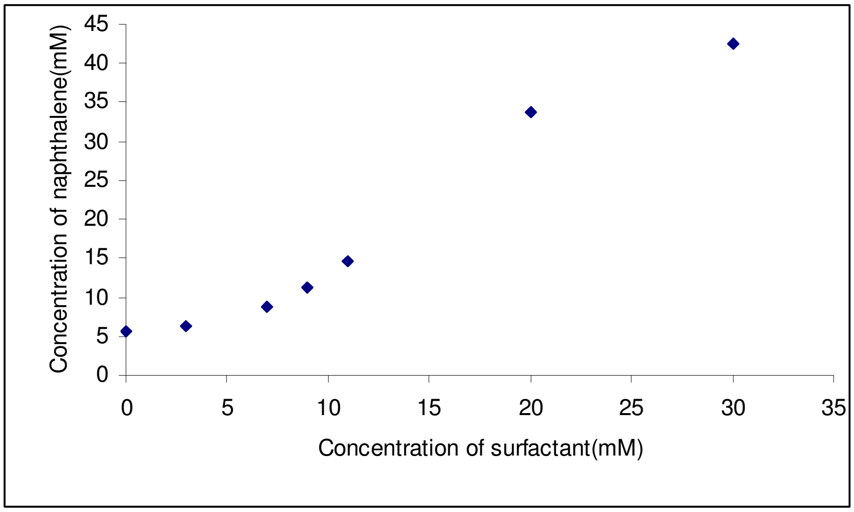


Fig 4.3. Solubilization curve of Naphthalene in Sodium Lauryl Sulfate

The critical micellar concentration is nearly 0.18 which is comparable to the value of 0.2mM [10] for Triton X-100.and CMC value for Sodium lauryl sulfate is nearly 8mM which is comparable to 10mM obtained from literature. Since the CMC value of Non ionic surfactant is lower than anionic surfactant so former has a better solubilization tendency than the latter.

4.3 Sorption of surfactant on sand

Adsorption of surfactant is studied to measure the coverage of surface/interface by the surfactant. Surfactants are adsorbed onto the sand surface to increase the organic content of the sand. The surfactant sorption isotherm is shown in Fig 4.4 below.

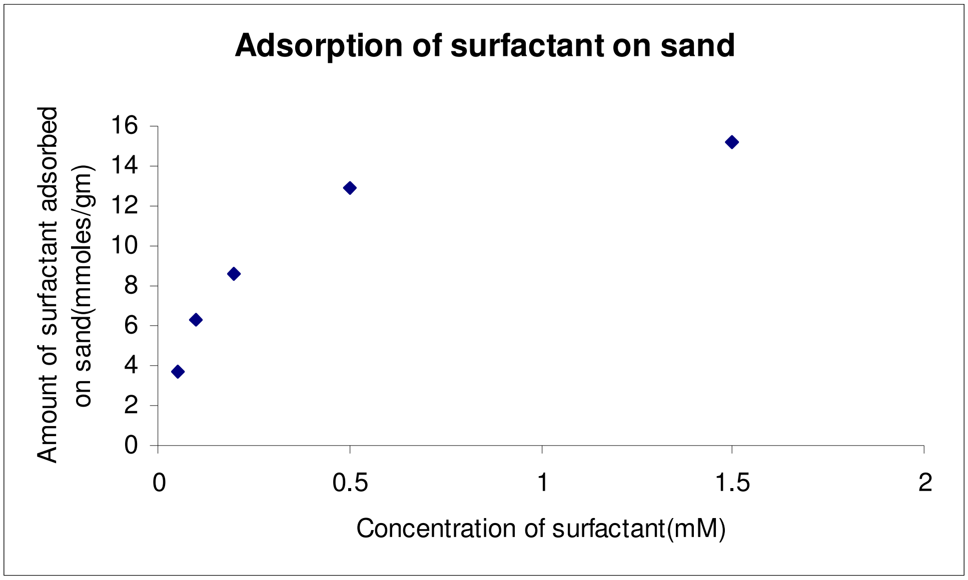


Fig 4.4 Adsorption isotherm of surfactant (Triton X-100)

The adsorption isotherm of Sodium Lauryl Sulfate could not be investigated using UV spectrophotometer as it UV insensitive.

4.4 Sorption of Naphthalene on sand

Adsorption of Naphthalene onto sand surface with and without surfactant was studied and adsorption isotherms thus obtained are shown in Fig 4.5, Fig 4.6

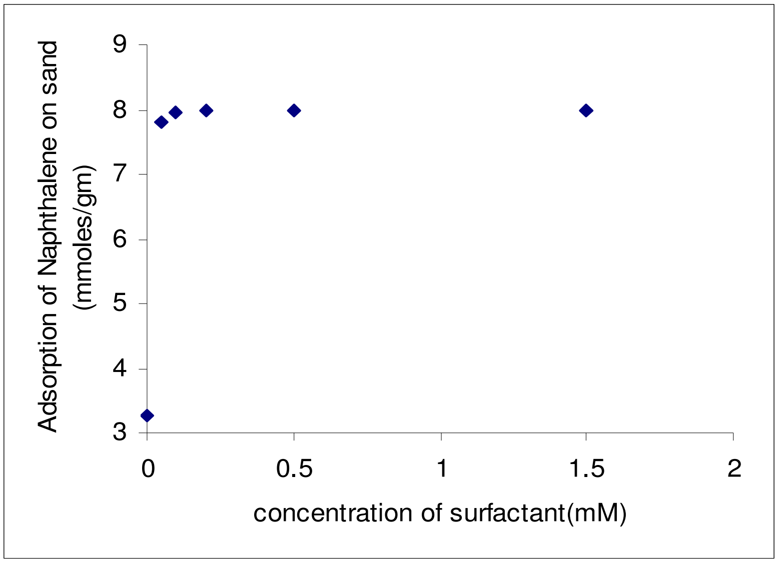


Fig 4.5 Adsorption isotherm of Naphthalene in presence of Triton X-100

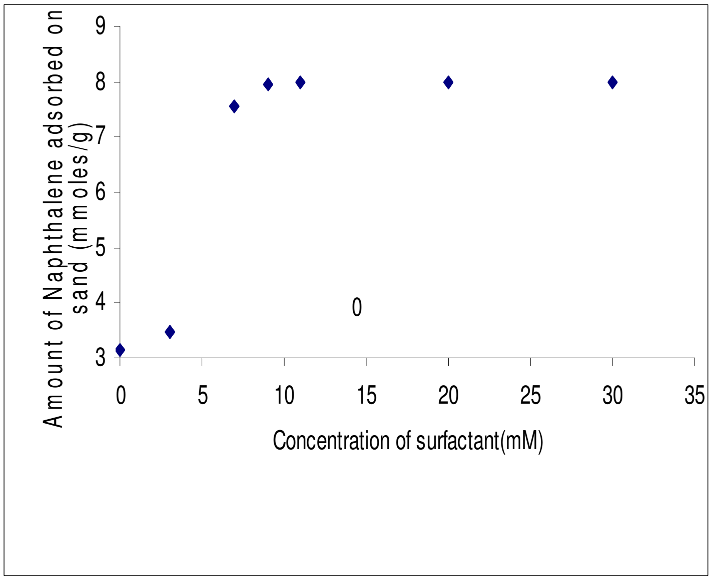


Fig4.6 Adsorption isotherm of Naphthalene in presence of Sodium Lauryl Sulfate

From both the isotherms it can be inferred that anionic as well as non ionic surfactant are equally capable of removal of PAHs.But from literature it is believed that anionic surfactant are better than non ionic surfactants. Thus sand surface should be covered with anionic surfactant which increases the hydrophobicity of the sand and helps in extracting PAHs.

As the surfactant concentration is relatively low for extracting PAHs, the low performance of sand washing likely resulted from the loss of surfactant to the sand due to adsorption. In addition, due to the hydrophobic properties of the HOC, the fixed HOCs that originally sorbed in the sand have a higher affinity to be retained in sand particles, whereas the RS if any, in the liquid phase is more easily trapped in the hydrophobic cores of the surfactant micelles. Under this circumstance, only internal relocation of HOCs from RS to surfactant micelle occurs. Because such transfer only takes place within the aqueous phase, no effective washing really occurs.

As the micellar concentration in the system progressively increases, the remaining RS in the liquid phase is reduced, which allows a better chance for the fixed HOC to make contact with the unoccupied micelles. This will move the performance curves upward. As the surfactant concentration is at a relative high level, RS has been completely dissolved in the micellar phase, and the fixed HOC in the sand turns out to be the only source being extracted by surfactant micelles, which results in a rapid reduction of HOC in the sand media. A sudden rise of the performance, therefore, is observed.

CHAPTER 5

CONCLUSIONS

Conclusions

- The solid-sorbed surfactant was not used to simply increase the functional organic carbon content of solid for PAHs sorption. When the sorption of surfactants onto the sand reached saturation the solid surface was completely covered with the surface micelle or bilayer. Similar to the partition of PAHs to surfactant micelle in solution, the sorption of the sorbed surfactant is attributed to PAHs partitioning to the surface micelle.
- Solubilization capacity of Naphthalene in aqueous phase can be enhanced using surfactants.
- Comparison between anionic and non ionic surfactant shows that non ionic have higher solubilization capacity
- A key aspect in using surfactants for in situ soil remediation is the effect of soil matrix on the behaviour of the surfactant solution. The interaction between surface and the surfactants plays a major role in determining the solubilization capacity, and therefore the removal efficiency of organics in sand matrix.
- Surfactant enhanced remediation is a promising technology for removing organic contaminants from aquifers.

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