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Dear Dr. Santanu Paria,

I am pleased to confirm that the revided version of your paper "Surfactant-Enhanced Remediation of Organic Contaminated Soil and Water" has been accepted for publication in Advances in Colloid and Interface Science.

Thank you for submitting your work to this journal.

With kind regards,

John Berg
Editor
Advances in Colloid and Interface Science

Comments from the Editors and Reviewers:

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Surfactant-Enhanced Remediation of Organic Contaminated Soil and Water

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Abstract

Surfactant based remediation technologies for organic contaminated soil and water (groundwater or surface water) is of increasing importance recently. Surfactants are used to dramatically expedite the process, which in turn, may reduce the treatment time of a site compared to use of water alone. In fact, among the various available remediation technologies for organic contaminated sites, surfactant based process is one of the most innovative technologies. To enhance the application of surfactant based technologies for remediation of organic contaminated sites, it is very important to have a better understanding of the mechanisms involved in this process. This paper will provide an overview of the recent developments in the area of surfactant enhanced soil and groundwater remediation processes, focusing on (*i*) surfactant adsorption on soil, (*ii*) micellar solubilization of organic hydrocarbons, (*iii*) supersolubilization, (*iv*) density modified displacement, (*v*) degradation of organic hydrocarbon in presence surfactants, (*vi*) partitioning of surfactants into soil and liquid organic phase, (*vii*) partitioning of contaminants into soil, and (*viii*) removal of organics from soil in presence of surfactants.

Surfactant adsorption on soil and/or sediment is an important step in this process as it results in surfactant loss reduced the availability of the surfactants for solubilization. At the same time, adsorbed surfactants will retained in the soil matrix, and may create other environmental problem. The biosurfactants are become promising in this application due to their environmentally friendly nature, nontoxic, low adsorption on to soil, and good solubilization efficiency. Effects of different parameters like the effect of electrolyte, pH, soil mineral and organic content, soil composition etc. on surfactant adsorption are discussed here.

Micellar solubilization is also an important step for removal of organic contaminants from the soil matrix, especially for low aqueous solubility organic contaminants. Influences of different parameters such as single and mixed surfactant system, hydrophilic and hydrophobic chain length, HLB value, temperature, electrolyte, surfactant type that are very important in micellar solubilization are reviewed here. Microemulsion systems show higher capacity of organic hydrocarbons solubilization than the normal micellar system. In the case of biodegradation of organic hydrocarbons, the rate is very slow due to low water solubility and dissolution rate but the presence of surfactants may increase the bioavailability of hydrophobic compounds by solubilization and hence increases the degradation rate. In some cases the presence of it also reduces the rate. In addition to fundamental studies, some laboratory and field studies on removal of organics from contaminated soil are also reviewed to show the applicability of this technology.

Keywords: Surfactant adsorption, solubilization, surfactant-enhanced remediation, biodegradation, density modified displacement.

Contents

1. Introduction

Widespread use, improper disposal, accidental spills and leaks of organic hydrocarbons like petroleum hydrocarbons, organic solvents, and polyaromatic hydrocarbons (PAHs) have resulted in long-term persistent sources of contamination of soil and groundwater, which becomes a major environmental issue because of their adverse effect on human health. Subsurface contamination by the organic compounds is a complex process and difficult to treat due to many reasons like the tendency of adsorption of contaminants onto the soil matrix, low water solubility, limited rate of mass transfer for biodegradation and so on. As many organic compounds have low solubility in water, so they may leach from the soil for a longer period of time and thus ultimately becomes a continuous source of the soil and groundwater contamination. Since the identification of the pollutants based on toxicity is most important, U.S Environmental Protection Agency (EPA) has listed some toxic organic compounds as "priority pollutants" [1]. The organic contaminants according to physical state can be classified as two types: (i) solid and (ii) liquid. The liquid organic contaminants are remain as a separate phase in aqueous medium are called nonaqueous phase liquids (NAPLs). NAPLs those are denser than water are called DNAPLs, and those that are lighter are called LNAPLs. LNAPLs include hydrocarbon fuels such as gasoline, heating oil, kerosene, jet fuel, and aviation gas. DNAPLs include chlorinated hydrocarbons such as carbon tetrachloride, 1,1,1-trichloroethane, chlorophenols, chlorobenzenes, tetrachloroethylene, and PCBs. NAPLs are frequently enter into the unsaturated zone as a discrete liquid phase and transported downward because of gravitational and capillary forces [2]. DNAPLs will tend to migrate vertically through the saturated zone and will rest on the bottom of the water table. In contrast, LNAPLs will tend to spread laterally along the water table. During the transportation of NAPLs through the subsurface, a portion of the organic phase also retained with in the pores of the soil matrix as an immobile ganglia or globules due to interfacial forces.

There are different technologies available for remediation of the sites contaminated with both organic and inorganic contaminants. U.S. EPA has listed different suitable technologies for remediation of RCRA-listed (Resource Conservation and Recovery Act) organic and inorganic hazardous wastes contaminated sites. The technologies used for remediation of those sites are solidification/stabilization, incineration, soil vapor extraction, bioremediation, chemical treatment, solvent extraction etc. Among those technologies, Cement-based solidification /stabilization (S/S) technology has been identified by U.S. EPA as the best demonstrated available technology for RCRA-listed hazardous wastes. S/S was reported as an established technology, and about 24% of the superfund sites are used S/S technology in the United States. The surfactant-based technologies are under innovative technology, and about 2-3% of the superfund sites are used this technology (see Fig. 1) [3]. A recent review on this topic shows that S/S is mainly useful for the inorganic contaminates but not very effective for the organic contaminates, unless the soil is treated with surfactants [4]. Surfactant based technologies may be useful for the organic contaminants.

1.1 Hazardous waste

A hazardous waste can be defined as a waste with a chemical composition or other properties that make it capable of causing illness, death, or some other harm to humans and other life forms when mismanaged or released into the environment [5]. The common sources of hazardous wastes are: (a) industrial wastes, (b) agricultural wastes, (c) household or municipal waste, and (d) medical wastes. Hazardous wastes may pollute the soil, air, surface water, or ground water. Underground pollutants can be carried by underground water flow and can mix with underground water table. Municipal Solid Waste (MSW) can be as hazardous as industrial-generated wastes, and pose serious health problem in storage, handling, and disposal. Waste control, disposal standards, and requirements are not well established in many countries. As a result, absence of clear and comprehensive regulations makes it difficult to exercise proper control. Presently, initiatives have been taken by many countries via legislation or recommended guidelines and/or standards for neutralization and detoxification of the waste streams to be implemented before discharge. Table 1 shows typical hazardous components in industrial waste streams.

1.1.1 Sources of organic contaminants

Potential sources of organic contaminants include: (i) industrial leaks and spills, (ii) leaks from oil and chemical storage tanks, (iii) improper application of pesticides, (iv) careless disposal of cleaners, oil and antifreeze, (v) improper disposal of household wastes, (vi) landfills and garbage dumps. Petroleum hydrocarbons are common groundwater pollutants as a result of leaking underground storage, spillage from the storage tanks and during transportation. The organics like pentachloro phenol (PCP) is a toxic material used as wood preservative. There are many wood preservative sites are contaminated with PCP in Canada [6]. The major sources of other organic contaminants like PAHs are in coal storage sites, coking sites and tar ponds. In addition, organic contaminants are also generated from the industrial wastes like in the manufacturing process of halogenated phenols and other halogenated compounds, pesticides or pesticide derivatives, halogenated benzene under alkaline conditions. The maximum contaminants limits (MCL) of organic contaminants in drinking water and their health effects are given in Table 2 suggested by U.S. EPA [7].

1.2. Soil

Knowledge of physical and chemical properties of soil is most important for designing the parameters of remediation process. The mechanisms of interaction between the soil and contaminants are also important to know. Soil can be defined as loose material composed of weathered rock, other minerals, and also partly decayed organic matter, that covers large parts of the land surface [8].

1.2.1 Chemical and physical properties of soil

The soil is composed of three phases: a solid, liquid, and gas phase. The soil components include about 50% by volume mineral particles, 25% water, 20% air and 5% organic matter. With the exception of a few organic soils, the bulk of soil material is mineral in character, and has been derived from solid geological deposits. Table 3 gives the general chemical formula of the minerals present in the soil. As a result of weathering and the addition of organic debris, soils contain minerals and organic matter. The clay minerals and humus is usually bear a negative charge because of their structure and chemical composition. The occurrence of negative charge is due to the dissociation of protons from the surfaces and edges of the clay minerals (aluminosilicates and hydrous (hydrated) oxides of iron and aluminium) and from acidic groups in humus, which increases as pH is raised. In presence of water orthoclase and albite hydrolyzed and clay or kaolinite is formed. The weathering process can be represented by the following reactions [9]:

$$KAlSi_3O_8 + H^+ \rightarrow HAlSi_3O_8 + K^+ \qquad (1)$$

Orthoclase clay

$$2KAlSi_3O_8 + 3H_2O \rightarrow H_4Al_2Si_2O_9 + KOH + 4SiO_2 \qquad (2)$$

Orthoclase kaolinite

$$2KAlSi_3O_8 + 3H_2O \rightarrow HAlSi_3O_8 + Na^+ \qquad (3)$$

Albite Clay

The mineral constituents of the soil are represented by the particles of widely varying size, shape and chemical composition. Three groupings of soil particles are in common use, namely sand, sit, and clay. The groups are subdivided according to requirements. The different size limits of the particles are given below in Table 4.

1.2.2 Contaminant-soil interactions

The contaminant-soil interaction is mainly occurred by (i) sorption, (ii) complexation, and (iii) precipitation [10]. The general term sorption is used to indicate the process in which the solutes (ions, molecules, and compounds) are partitioned between the liquid phase and the soil particle interface. Physical adsorption occurs when the contaminants are attracted to the soil constituent's surfaces (from the aqueous solution present inside the pore) because of the unsatisfied charges (attractive forces) of the soil particles. Chemical adsorption occur by chemical bonding. In specific adsorption, the ions penetrate the coordination shell of the structural atom and are bonded by covalent bonds via O and OH groups to the structural cations. The interaction by complexation and precipitation is occurred by the inorganic contaminants. Organic contaminants like petroleum hydrocarbons are adsorbed physically due to hydrophobic forces on the soil surface. The different physical forms possible for organic contaminants in soil are illustrated in Fig. 2.

1.3 Site Characterization

Site characterization is the first and most important step in determining the effectiveness of soil washing. In addition, proper site characterization is most essential for taking decisions about the design and execution of bench-and pilot scale tests that yield the best possible data at the least cost. The following soil information is necessary to characterize a site [13]:

- Site geology and hydrogeology
- Hydraulic conductivity of soil
- Soil type, composition vs. depth, and characterization of the aquifer material (grain size distribution and organic carbon content),
- Soil chemistry
- Aerial extent of soil contamination (vertical and horizontal profiles)
- Total amount of contaminated soil to be treated
- Range, concentration, and variability of contaminants in the soil
- History, process, and time frame of the conditions leading to the contamination.

In addition, it is also important to know how soil type and contaminant concentrations change with latitude and depth so that an accurate profile of the feedstock soil can be developed. Detailed knowledge of site hydrogeology is also crucial to understanding of ground water flow and contaminants transport in the subsurface [3].

1.4 Surfactants

The term surface-active agent or "surfactant" represents a heterogeneous and long-chain molecule containing both hydrophilic (head) and hydrophobic (tail) moieties. The hydrophilic group of surfactant is an ionic or highly polar group. Depending on the nature of the hydrophilic group, surfactants can be classified as anionic, cationic, zwitterionic, and non-ionic [14]. In an aqueous medium, when the concentration of surfactants exceeds a certain critical value, the monomer molecules form organized aggregates of a large number of molecules called 'micelles', and this specific concentration is called critical micelle concentration (CMC). The physical properties like surface tension, interfacial tension, adsorption, and detergency change below the CMC with the concentration but there is no change in these properties above the CMC. Surfactant solutions exhibit a striking change in some other physical properties like density, equivalent conductivity, and solubilization of organics in below and above CMC when polled against the concentration. Based on the origin of the surfactants they can be classified as synthetic or biosurfactants.

1.4.1 Synthetic surfactants

It has been mentioned earlier that depending on the nature of the hydrophilic group, synthetic surfactants are classified in four types. The hydrophilic group is usually a sulphate group, a sulfonate group, or a carboxilate group (for anionic surfactants), a quaternary ammonium group (for cationic surfactants), polyoxyethylene, sucrose, or polypeptide (for nonionic surfactants. The most common hydrophobic parts of the synthetic surfactants are paraffins, olefins, alkylbenzenes, alkylphenols, and alcohols.

A group of synthetic surfactants have recently received considerable attention are the molecules those contain more than one hydrophobic tails and hydrophilic heads. These surfactants are called gemini surfactants or twin surfactants or dimeric surfactants. In gemini surfactants two surfactants are linked by a spacer unit at or in close proximity to the head groups. The spacer may be rigid or flexible, hydrophilic or hydrophobic, typically 2 - 8 bridging atoms [15, 16]. The schematic presentation of gemini surfactants are shown in Fig. 3. Mostly the gemini surfactants are symmetrical in nature with two identical surfactants connected by a spacer group, but some unsymmetrical gemini surfactants with three or more polar groups or tails have recently been reported [17, 18]. The zwitterionic surfactants are special type of gemini surfactants, containing both anionic and cationic surfactants. The zwitterionic gemini surfactants contain no counterions. The gemini surfactants are drawing attention due their superior performances in some respect than those of the corresponding monomeric surfactants. Generally, the gemini surfactants have remarkably low CMC values, more surface active, high solubilization capacity, better mono- or di-valent ions tolerance, etc.

1.4.2 Biosurfactants

Biosurfactants are biologically available compounds those exhibit surface-active properties [19]. Biosurfactants are mainly produced by bacteria or yeast, and also available from plants, animals, including human. Recently biosurfactants have gained more attention over synthetic surfactants due to environmental compatibility nature of those compounds. Those can be classified according to different molecular structures. The hydrophobic part of the molecule is based on long-chain fatty acids, hydroxy fatty acids or ∝-alkyl-β-hydroxy fatty acids. The hydrophilic portion can be a carbohydrate, amino acid, cyclic peptide, phosphate, carboxylic acid or alcohol [20]. These compounds can be produced by a wide variety of microorganisms. Some major types of biosurfactants and their origin are listed in Table 5. Most of the biosurfactants are anionic or nonionic. Only a few are cationic such as those containing amine groups. The potential environmental applications biosurfactants have been reviewed by some researchers [12, 20, 23, 24]. The structure of biosurfactant is a characteristic of the producing species and the availability of carbon source during the growth of the microorganisms [25].

2. Mechanism of groundwater pollution by organics

Groundwater is used in many countries of the world as a cheap source of drinking water. Even, over 50% of the drinking water in United States comes from groundwater [26]. Groundwater is very susceptible to contamination, unless protected by a low permeability layer such as clay. The organic contaminants like petroleum hydrocarbons, halogenated organic compounds, PAHs or other organic compounds are bind strongly inside the soil matrix and present for long time at the contaminated sites. Many of those organic hydrocarbons are sparingly soluble in water, so they can mix with water during the flow of water through the soil matrix. Ultimately when the contaminated water reached to the groundwater table that contaminate groundwater. Moreover, when the spillage of liquid organic hydrocarbon is sufficient, the spill liquid can reach the ground or surface water table. If the liquid is LNAPL that will float on the water surface and slowly solubilize in water. Even, when the surface water is contaminated and that may pass through the soil matrix with low organic content (less sorptive capacity of the organics), the contaminated water reached to the ground water table with out purification and contaminate that. Since there is also a flow in groundwater in the subsurface, the contaminate water moves away from the contaminated site of the spill [26]. Fig. 4 shows schematic presentation of ground water contamination by LNAPL.

Similar to LNAPL, if the DNAPL spill is sufficiently large, it continues to move downward and finally deposit at the bottom of the water table. Many sites are contaminated with other types of DNAPLs including coal tar and creosotes (complex hydrocarbon mixtures consisting of polycyclic aromatic hydrocarbons and other aromatic hydrocarbons), polychlorinated biphenyl (PCBs), and certain pesticides. These DNAPLs are not only toxic and lead to a risk of drinking water resources, but they are also very difficult to remediate with classical remediation techniques [27].

2.1 Role of surfactants

The physical characteristics of organic contaminants commonly found in soil important for the remediation technologies are (i) solubility in water and (ii) interfacial tension with water (iii) biodegradability, and (iv) vapor pressure. The first two factors (i) low solubility in water and (ii) high interfacial tension with water decrease the efficiency of in situ soil remediation during water flushing and bioremediation process [28]. Surfactants are used to enhance the rate of remediation. Surfactant systems often exhibits complex behavior in removing organic contaminants whereas, mobilization by lowering interfacial tension and micellar solubilization by surfactants are accepted as main mechanisms of NAPLs removal [29-31]. The organic hydrocarbons and poly aromatic hydrocarbons (PAHs) are bind strongly to the soil, and also sparingly soluble in water, as a result their removal by various subsurface treatments is difficult. The use of surfactants have shown to increase the desorption rates of sorbed contaminants from soil, hence also making them available for remediation [29, 32]. Soil washing using surfactants was originally developed in petroleum recovery operations. Afterwards the surfactants are used for remediation of organic contaminated sites. The schematic presentation of the SER process is shown in Fig. 5. For this remediation scheme, the surfactant solution is injected below the ground to enhance the extraction of the contaminant. Once the surfactant-contaminant stream comes above ground, separation processes are necessary for either re-injection of the surfactant solution or disposal of the waste stream. The main factors should be consider for the surfactant selection in this process are cost, biodegradability, low toxicity, low adsorption to soil, effective at concentrations lower than 3%, low soil dispersion, and low surface tension [22]. The used surfactants must be recovered and reused for the process to be economic.

Cationic surfactants have also been suggested for potential use in the remediation of aquifers contaminated with organics. Surface water contaminated with organics can also be purified by sorption of the organics onto soil from water, when the contaminated water will passes through underground soil matrix. The sorption of organic contaminants from water by soil is controlled by the soil organic matter content [34]. Low organic matter soils have very little sorptive capability for common groundwater contaminants. Cationic surfactants can be readily adsorbed onto negatively charged soil grains, resulting in more hydrophobic surfaces, which can, in turn, enhance the removal of organic contaminants from water [35].

3. Importance of surfactant adsorption in remediation

Surfactants are used as potential agents for enhanced solubilization and removal of contaminants from soil and sediments [36-40]. In a surfactant-enhanced remediation process surfactant adsorption on soil and/or sediment is an important parameter. The effectiveness of surfactant is decreased when a significant amount is adsorbed by the soil, since amount of surfactant available for solubilizing the contaminants decreases, and its mobility through the medium to which it is applied is reduced [41, 42]. In addition to that, adsorption of surfactant increase the hydrophobicity of the soil, as a result, removed solubilized organic will be re-adsorbed on soil surface. To facilitate the application of surfactant-based technologies in soil and groundwater remediation as well as water purification, it is important to develop a better understanding of surfactant adsorption and desorption on soil [43]. Another reason for investigating surfactant adsorption onto soil and its component is to understand the transport of surfactants and organic compounds in side soil matrix. Most of the mineral surfaces are negatively charged in neutral aqueous medium, as a result, anionic surfactants and nonionic surfactants are expected to be sorbed less than cationic surfactants, and have usually been chosen in SER technologies [44, 45].

3.1 Anionic surfactant adsorption

There are several studies on the adsorption of anionic surfactants on soil [45-50] or soil constituents like alumina [52-55], clay [56-58], sediment [59-61]. Among the anionic surfactants, LAS is the surfactant used extensively in detergents in throughout the world because of its effectiveness, versatility, cost/performance ratio and environmental safety. In general, LAS are not strongly adsorbed on soil surfaces [60]. There are different interactions mechanisms proposed for the adsorption of LAS by different researchers such as hydrophobic [48, 60, 62], specific [46, 60], hydrogen bonding [46], precipitation [37, 58, 63], and electrostatic [60] depending on the soil-specific properties such as, pH, organic matter content, clay content, cation exchange capacity (CEC) and amorphous iron content [64]. Wolf and Feijtel [61] have reviewed the fate of linear alkylbenzenesulfonate (LABS) to terrestrial organisms.

Adsorption isotherms are commonly used to describe adsorption processes and these represent a functional relationship between the amount adsorbed and the activity of the adsorbate at a constant temperature [52].

3.1.1 Adsorption isotherm of anionic surfactants: The nature of adsorption isotherm of anionic surfactants on soil or soil constituents is depending on the soil nature or the experimental conditions like pH, presence of electrolyte, organic content of the soil etc. Adsorption of anionic surfactants onto positively charged site of alumina [52, 53, 65] and soil [50] shows typical four-regime isotherm, similar to general adsorption isotherm of ionic surfactants onto oppositely charged solid surfaces. The mechanism of occurrences of typical three or four-regime isotherms have been discussed by many researchers [52, 53, 65, 66].

Adsorption of sodium dodecylbenzene sulfonate (SDBS) on sodium saturated montmorillonite shows no significant amount of SDBS adsorbed (< 0.2 mg/g) but the amount adsorbed is significant when Ca^{2+} – montmorillonite is used [58]. Adsorption isotherm of SDBS on Ca^{2+} – montmorillonite shows (Fig. 6) SDBS sorbed sharply to a maximum at its equilibrium concentration about 1.5 CMC (~1400 mg/L) and then decreased rapidly to zero when equilibrium concentration is about to that of maximum. The shape of the isotherm is similar to that of precipitation curve between SDBS and Ca^{2+} in $CaCl_2$ solution as the precipitation of $Ca(DBS)_2$ appears to be the primary mechanism for the sorption of SDBS [57, 58]. In further, X-ray diffraction (XRD) study shows SDBS could not enter into the interlayer of the montmorillonite.

An organic matter (OM) content of the soil has a significant effect on the adsorption of anionic surfactant on soil. The adsorption of anionic and nonionic surfactants by soil shows a positive relationship between adsorption and the OM contents of soil [47, 49, 67, 68], and also there is a relationship between the adsorption and the clay content [46, 69-71]. A recent study shows the adsorption coefficient of SDS increased with increasing the OM content of the soil [49].

The adsorption isotherms of SDS on different soils can be fitted well with the Freundlich isotherm equation [46, 49].

$$q_m = K_f C_e^{n_f} \tag{4}$$

where q_m is the adsorption capacity, C_e is the equilibrium surfactant concentration, K_f is the adsorption coefficient (measure of adsorption capacity), n_f is a constant (an indicator of the curvature of isotherm). The adsorption coefficient (K_f) values of different OM soils (OM ranges between 0.052-10.3%) ranged between 1.77 and 82.1. In general, the higher K_f values corresponding to the soils with elevated OM content. It is proposed, SDS and LABS are adsorbed through hydrophobic interaction with the OM of the soil and by ligand exchange and/or electrostatic attraction with kaolinite [45, 49]. Ligand exchange occur according to following mechanism [46]:

(5)

(6)

Adsorption of LABS with different alkyl chain length on sludge shows a linear relationship between the $\log K_i$ [55]. K_i is the partition coefficient, defined as the ratio of the amount of SDS in the soil and in the equilibrium solution for a given equilibrium concentration. The increase in K_i with increasing alkyl chain length is indicative of hydrophobic interaction controlling the adsorption of LABS on sludge.

3.2 Cationic surfactant adsorption

Adsorption of cationic surfactants at solid/liquid interfaces has a wide range of applications, such as detergency, fabric softeners, wetting, ore flotation, and corrosion inhibition etc. Moreover, cationic surfactants have also been suggested for potential use in the remediation of contaminated soils and aquifers [35, 72]. Cationic surfactants are adsorbing strongly onto soil and sediments because of favorable electrostatic interactions with the predominately negatively charged soil mineral surfaces [73]. Thus, the surface of the clay may be greatly modified to become strongly hydrophobic after adsorption of cationic surfactants. Several researchers have studied the adsorption of a variety of cationic surfactants on silica [43, 74-78], soil, clay, and mineral surfaces [35, 48, 72, 79-87].

3.2.1 Adsorption isotherm of cationic surfactants: The general shape of the cationic surfactant adsorption on soil using a specific example of HDTMA is discussed here. The HDTMA adsorption on soil can be divided into four distinct regions, shown in Fig. 7. In region-I (equilibrium concentration, $C_{eq} < C_1$), shape of the isotherms varied, depending on the type of cations initially saturating soil clays. The calcium saturated soil shows a linear isotherm in region I, where as non-monotonic isotherm for Na-saturated soil. The shape of the adsorption isotherm on cation type is depending on the degree of clay dispersion. Na-clays are well dispersed in water, and HDTMA can access all exchange sites. As a result, HDTMA cations are more randomly distributed on the surfaces. Adsorption in this region is strictly by cation exchange as the adsorption resulted in equivalent cation release. In the Ca-soil suspensions, clay particles are associated through face-to-face aggregation prior to HDTMA addition. This restricts the initial replacement of HDTMA to the outer surface and the interlayer regions. In region III, the adsorption isotherm is linear for both Na- and Ca-saturated soil. In this region, the amounts of HDTMA adsorbed exceed the cation release, indicating that hydrophobic bonding is the sole mechanism responsible for the increase in HDTMA adsorption. Region II is the transition between regions I and III, having both the adsorption mechanisms. When C_{eq} is grater than C_3 the plateau region (region IV) is reached.

Some parameters like the effect of exchangeable cation type in soil, type of electrolyte and concentration on adsorption of cationic surfactants (HDTMA) onto soil have been studied extensively by Xu and Boyd [81]. In the case of adsorption of cationic surfactants on silica, it has been reported that, increasing the hydrocarbon chain length by four methylene units, from C_{12} to C_{16}, lowers the concentration at which characteristic features of the adsorption isotherm occur by approximately an order of magnitude [88]. In case of adsorption of alkylammonium cations on montmorillonite, the Gibbs free energy change for the exchange of inorganic cations increases linearly with the molecular weight of the organic cations [89]. The cation exchange mechanism also occurs for adsorption of small alkylammonium compounds such as *n*-butylammonium on clay minerals [90].

3.2.2 Nature of clay and d-spacing: Effect of clay type is an important parameter on the adsorption of cationic surfactants [82]. Adsorption of quaternary ammonium compound (QAC) surfactants on clays depend on the clay type, the nature of exchangeable cations initially saturating the clay, and the ionic strength of the aqueous solution. The stability of QAC-clay complexes depends on the nature of both QAC and clay, and composition of aqueous solution [82]. Adsorption of cationic surfactants on swelling clays (e.g. montmorillonite) is a more complex process than the nonswelling clays (e.g. kaolinite). The adsorption of surfactants changes the spacing of clay layers. The basal spacing of the clays due to adsorption of surfactant can be determined by X-ray diffraction. Fig. 8 shows the change in basal spacing (*d*-spacing) of Na-montmorillonite (Na-SWy-1) as a function of HDTMA adsorbed is a three-step curve. The *d*-spacing of wet (100% relative humidity), partially air dried (95% relative humidity) and dry (≤ 1% relative humidity) clays were nearly identical at high HDTMA loadings, but different at low HDTMA loadings (≤ 1 CEC). The *d*-spacing for wet clay samples was increased 17.6 to 22.1 Å by changing HDTMA loading from 0.1 CEC to 0.75 CEC. Partially air-drying clays show the *d*-spacing ~14.1 to 15 Å at ≤ 0.3 CEC loading levels and resulting stepwise *d*-spacing vs. HDTMA loading curve. The thickness of the montmorillonite platelet is 9.6 Å and the gallery height of a flat lying alkyl chain in the clay interlayer can be 4 or 4.5 depending on the orientation of the molecule. In the three step *d*-spacing curve a monolayer arrangement is formed (13.6 or 14.1 Å) at HDTMA loading ≤ 0.54 CEC, when the loading is beyond 0.55 CEC a bilayer arrangement (17.6 and 18.1 Å) is formed. A pseudotrimolecular layer is (21.6 and 22.1 Å) resulted from further increase in HDTMA loading beyond 1.05 CEC.

The *d*-spacings of Ca-SWy-1 are different than Na-SWy-1, for wet sample. For example, at 0.2 – 0.95 CEC *d*-spacing (17.6 to 18.1 Å) were several angstroms less than that for Na-SWy-1 at similar HDTMA loading. In addition, *d*-spacings are more gradual in case of Ca-SWy-1. So, it is concluded that the characteristic of the structure of adsorption layer of cationic surfactants in the interlayer of clay is very complex, mainly depends on nature of the clay (swelling or nonswelling), initial electrolytes condition (Na-saturated clay or Ca-saturated clay), types of anion present (Cl^-, Br^- or SO_4^{2-}) in the solution.

3.2.3 Effect of electrolytes in batch study: The studies of effect of electrolytes show adsorption of cationic surfactants on soil or sand increased with the ionic strength of the solution [43, 80], and a change of companion anion from Cl^-, Br^-, or SO_4^{2-} also increased the adsorption of cationic surfactant via hydrophobic bonding [80]. The presence of electrolyte can change the critical concentration for different regions (C_1, C_2, and C_3) of HDTMA isotherm on soil mentioned in the previous section. The anion type lowered C_2 and C_3 in the order: $SO_4^{2-} < Br^- < Cl^-$ [80]. The slope of the linear portion of the isotherm in region III and the HDTMA adsorption plateau in region IV is also depended on anion type, the order of increasing slope and maximum HDTMA adsorption is reverse to that of previous: $SO_4^{2-} > Br^- > Cl^-$. The change in adsorption behavior in presence of different anions can be attributed to the variation of screening ability to screen the positively charged head groups. The divalent counterions are more effective in charge screening than monovalent ions, so HDTMA adsorption via hydrophobic bonding presence of SO_4^{2-} was higher than with monovalent ions. Similarly, amount of adsorption was more in presence of Br^-, since it has more charge screening efficiency than Cl^-.

In case of adsorption of cationic surfactants on negatively charged surfaces, two types of electrostatic interactions play a critical role: (i) that between the surfactant and the solid surface (attraction) and (ii) that among the surfactant heads (repulsion). To find the dominating force for cationic surfactant adsorption, the effect of electrolytes (in presence of NaCl, Na_2SO_4, and $CaCl_2$) on the adsorption of C_{14}PB (tetradecyl pyridiniumbromide) on sand have been studied [43]. Fig. 9 shows the variation of specific adsorption as a function of Debye-Hückel parameter (κ). The increasing ionic strength weakens the electrostatic interaction, but it is observed that specific adsorption increases with κ; attributes that electrostatic repulsion among surfactant heads is the dominant interaction in determining the adsorption of alkyl-PB on sand surfaces. Since the sand is hydrophilic, adsorption of cationic surfactant initially occurs mainly by cation exchange [80, 81] and a few with the hydrophobic bonding with the surface. In the presence of electrolyte, adsorbed surfactant molecules are placed densely due to increased lateral interactions between the tails (hydrophobic bonding), as electrical repulsion between the headgroups is weakened.

In the study of Paria and Yuet [43] the electrostatic repulsion, Φ_r, among surfactant heads was estimated using the expression given by Verwey and Overbeek [91] for the electrostatic interaction between two charged spheres of radius a separated by a center-to-center distance r, namely,

$$\frac{\Phi_R}{a\varepsilon\psi_0^2} = \frac{e^{-\kappa a(s-2)}}{s} \tag{7}$$

where, ψ_0 is the surface potential and $s = r/a$. Using the area per molecule, A_m, calculated above, the equilibrium value of s can be estimated as $s_{eq} = r_{eq}/a$, where $r_{eq} = (4A_m/\pi)^{1/2}$ is the distance between two adsorbed surfactant molecules in a saturated monolayer. Thus, the reduced potential energy, $\Phi_r^{'}$, *at* $r = r_{eq}$ can be expressed as

$$\Phi_r^{'} = \frac{e^{-\kappa a(s_{eq}-2)}}{s_{eq}} \tag{8}$$

Thus the role of head-group repulsion is assessed, by considering the variation of $\Phi_r^{'}$ as a function of κ as shown in Fig. 10. The strong linear correlation between $\Phi_r^{'}$ and κ clearly indicates that head-group repulsion decreases with increasing ionic strength, which is consistent with the observed adsorption behavior.

3.2.4 Effect of electrolytes in column study: With the continuation of the previous study [43] in column show the starting of the breakthrough time was delayed in presence of electrolyte compared to the case without electrolyte. The behavior is consistent with the batch experiments, which indicate that the amount adsorbed increases in the presence of electrolyte. Since the starting of breakthrough is delayed with increasing amount adsorbed when the concentration and flow conditions are remain unchanged.

The study of desorption of surfactants from the column when eluted with the pure water after adsorption in presence of different electrolytes are shown in Fig. 11. Fig. 11 shows that, after approximately one pore volume (7 min), there is a sudden increase in outlet surfactant concentration, showing in the form of a peak for all three electrolytes studied. The maximum peak height for NaCl–water (adsorption-desorption sequence, e.g. adsorption was performed in presence of NaCl, and followed by desorption with pure water) and $CaCl_2$–water are very similar ($C_t/C_0 \approx$ 6-6.8), but that for Na_2SO_4–water is significantly lower ($C_t/C_0 \approx 3$). The times required for maximum amount released are almost the same for all three electrolytes (9 – 10 min.), but after the maximum desorption the rate of desorption is lower for Na_2SO_4–water. The appearance of a peak in the desorption curve is consistent with the notion that adsorption in the presence of electrolytes is enhanced due to reduced repulsion between the adsorbed head groups. When pure water was then injected into the column, the adsorbed surfactant molecules began to experience stronger repulsive force similar to that without electrolyte. Consequently, the excess molecules adsorbed on the surface desorbed immediately, resulting in the observed increase in outlet surfactant concentration after one pore volume. The lower peak height of the Na_2SO_4–water desorption curve is probably caused by the higher valence of the anion.

It was also shown that no elution peak was found when desorption occur in presence of similar electrolyte condition to that of adsorption (NaCl–NaCl and Na_2SO_4–Na_2SO_4) systems, and the rates of desorption in both cases were lower than that for the NaCl–water and Na_2SO_4–water systems. The figure 11 also shows the difference between the NaCl–NaCl and Na_2SO_4–Na_2SO_4 systems at smaller time scale between 10 and 25 minutes, where the rate is lower for

Na_2SO_4–Na_2SO_4, probably because of the difference in the valence of the counter-ions as noted above.

3.2.5 Retention of surfactant in column study: Surfactant retention is an important factor in various applications. In soil remediation, for example, surfactant retention is not desirable due to environmental concerns, whereas retention is a key parameter in other applications such as soil modification for groundwater purification [35]. Fig. 12 shows the amount of surfactant retained in the column after desorption under different conditions. Comparing the cases of water–water and water–NaCl, the water–NaCl system shows a very small amount of surfactant retained in the column. The amount of surfactant retained after desorption is mainly determined by the electrostatic attraction between the negatively charged surfaces and the cationic surfactants. When desorption was performed in the presence of NaCl, the thickness of the electrical double layer on the sand surface was significantly reduced, resulting in a weaker electrostatic attractive force between the surface and the surfactant molecules, and therefore a lower retention. The amounts retained for NaCl–NaCl and Na_2SO_4–Na_2SO_4 are similar and lower than those of NaCl–water and Na_2SO_4–water, due to the same reason as mentioned in the water–NaCl system. Xu and Boyd [83] have also studied the desorption of HDTMA from soil and found the rate of desorption depends on the loading level of HDTMA and the conditions under which HDTMA was adsorbed. At high HDTMA loading levels (> 0.8 CEC) or high ionic strength solutions, rate of desorption is low.

3.3 Nonionic surfactant adsorption

Nonionic surfactants are often used in SER process because of their lower CMC compared to ionic surfactants, higher degree of surface-tension reduction, and relatively constant properties in the presence of salt, which result in better performance and lower concentration requirement. In particular, the nonionic ethoxylate surfactants have been suggested for the removal of organic contaminants from soil because of their high solubilization capacity and biodegradability. In addition to these factors, in selecting surfactants for use in SER processes, considerations must also be given to the environmental impact and retention of surfactants [37]. Surfactants retained in the soil matrix after the SER processes are themselves acted as environmental contaminants. Since surfactant retention is closely related to adsorption on soil particles, insight into the adsorption behavior of nonionic surfactants is therefore critical in facilitating the application of SER technologies. Due to the importance of this surfactant class, many researchers have been investigated the sorption of nonionic surfactants onto soil [41, 49, 50, 57, 67, 71, 92-97], sand [98-105] subsurface media [106] using batch and/or column experiments.

3.3.1 Importance of mineral and organic content: Some researchers have reported the adsorption of nonionic surfactants on soil is increased with increasing organic matter of the soils [49, 67, 2] and some others have found a relation ship between adsorption amount and the clay content but not directly to fraction of organic carbon [49, 70, 71, 96, 107]. The adsorption of nonionic surfactants (TX-100) on 18 different soils of a wide ranges of organic and clay content have been studied by Rodríguez-Cruz et al. [49]. They have found different shape isotherms depending on the composition of the soils. The soils with very high OM content (> 5%) are of S type indicating an increase in adsorption with increasing concentration of surfactant. The isotherms corresponding to the soils with a medium and low OM content and very low clay content are in general of L type. When the soils contain very low OM and high clay content H type isotherms are formed due to high affinity between adsorbate and adsorbent, such that all surfactant molecules adsorbed from the solution. They have also found most of the cases the isotherms can be fitted with the Freundlich equation. Fitting of Freundlich equation on 15 different soils show the values of n_f are lower than unity, with the exception of one soil sample ($n_f = 2.86$) with highest OM content (10.3%). The K_f values also changer in a wide range (0.01 to 913), in general, the highest values corresponded to the soils with high clay contents. Liu et al. [92] also showed Freundlich type isotherm for adsorption of different nonionic surfactants on natural soil. Similar to the study of Rodríguez-Cruz et al. [49], Liu et al. [92] have found the values of n_f are less than unity for three micelle forming surfactants and grater than unity for one lamellae forming surfactant (shown in Table 6). It was not clear to the authors whether any other factors were determining the values of n_f. The researchers have found different types of adsorption isotherms of nonionic surfactants on soils like Langmuirian type [41, 71, 96, 97], and four-region type [50].

3.3.2. Importance of soil composition: Hydrogen bonding may be considered the major driving force for nonionic surfactant adsorption on soil or mineral surfaces, as ionic and chemisorbing groups are absent in the nonionic surfactants [71, 108]. Mathur and Moudgil [109] have reported that polyethylene oxide shows strong adsorption on SiO_2 via hydrogen bonding but not on some oxides such as Al_2O_3 and Fe_2O_3. The study of the dependence of nonionic surfactant (Polyethylene glycol mono-*p*-nonylphenyl ether, A_9PE_{10}) adsorption on soil mineral composition indicates that there is a correlation exists between the atomic ratio of Si:(Al + Fe) on soil mineral surface and A_9PE_{10} sorption [71]. The sorption of A_9PE_{10} on three soils shows the increasing sequence of red soil (q_m = 0.13 mg m^{-2}) < kaolinite (q_m = 1.18 mg m^{-2}) < bentonite (q_m = 2.60 mg m^{-2}). The bentonite is a clay with 2:1 structure, containing an octahedral aluminum layer, sandwiched between tetrahedral silicon sheets. This 2:1 structure implies the dominance of Si sites and consequently high Si:Al ratio. Red soils are iron-rich (laterite) and aluminous (bauxite) deposit usually develops in heavily leached area with intensive rainfall and high temperature. Intensive leaching removes soluble H_4SiO_4 from soils and leaves aluminum and iron rich residue in soils showing low Si:(Al + Fe) ratio. The relation between Si:(Al + Fe) and A_9PE_{10} sorption capacity are shown in Fig. 13.

3.4 Gemini surfactant adsorption

Gemini surfactants are a relatively new class of surfactant molecules, because of that there are relatively less literature available on adsorption of gemini surfactants. At the same time they are also drawing more scientific interest due to their effectiveness in the modification of interfacial properties, interesting aggregate structures both in solution and at the solid-aqueous interface, excellent solubility and stability in concentrated electrolytes, and remarkably resistant to oxidative and thermal degradation. Different types of gemini surfactants and their properties have been discussed recently in a review article [110]. A gemini surfactant consists of two surfactant molecules (anionic, cationic, or nonionic) joined by an alkyl spacer group (s). The surfactant molecules are in general identical in gemini surfactant. The spacer group can be hydrophilic or hydrophobic, flexible or rigid, and it generally connects two surfactant moieties at, or near the head group. The properties of the Gemini surfactants are greatly influenced by the length of the spacer group [111]. The dimeric surfactants have CMC values 10 to 100 times less than those of monomeric surfactants [112]. Most of the adsorption studies are of cationic gemini surfactants on silica [63, 111-117] and few studies on clay and lime stone [118, 119]. Studies on anionic gemini surfactants are also very few [54, 119, 120].

3.4.1 Effect of spacer length of cationic gemini surfactant: S. Partyka and his group [112-115] have reported adsorption of dimeric cationic gemini surfactants (12-*s*-12) onto silica surfaces. They have investigated with particular emphasis on the effect of state of the silica surface, raw and HCl-treated silica (SiNa and SiH, respectively), and the effect of length of spacer group. Adsorption of alkanediyl-α,ω-bis (dodecyldimethylammonium bromide) dimeric cationic surfactants or 12-*s*-12 with alkanediyl groups C_2H_4, C_4H_8, C_6H_{12}, and $C_{10}H_{20}$ (corresponding structures are referred as, 12-2-12, 12-4-12, 12-6-12, 12-10-12) on silica are shown in Fig. 14a. The isotherms are typical "S" shaped and amount of maximum surfactant adsorbed at saturation is nonlinear in nature with the change of the length of the spacer group. Figure 14b clearly indicates the decrease in amount of surfactant adsorbed at saturation as the length of spacer group increases [111, 112]. The rearrangement of data indicates the variation of maximum amount adsorbed with 1/s is nearly linear. The behavior indicates the surface area occupied by one surfactant molecule rapidly increase at silica surface. In the first step of the "S" shaped adsorption isotherm exchange of the residual sodium ions bound to the silica surface occur by the surfactant cations. The end of this step corresponds to the point of zero charge of the particle reached for an amount of surfactant, which is independent of the length of the alkanediyl spacer groups (C_2H_4 to $C_{10}H_{20}$). In the second adsorption step, there is a sharp drop of pH of the supernatant phase from 6.5 to about 4.0, and by an increase of the concentration ratio [free bromide ion]/[free surfactant ion]. The decrease in pH of the supernatant is due to the decrease in pK_a of the silanol groups because of the induction of the positive charge of the adsorbed aggregates resulted in an increase of their ionization. The ionization occurs according to $SiOH \longrightarrow SiO^- + H^+$.

The comparison of monomeric (DTAB) and gemini surfactant (12-2-12) surfactants on different silica surface (SiNa and SiH) show the shape of the isotherms are same but the maximum amount adsorbed is about 20 and 10% less respectively for DTAB [111]. It has been shown during the ion exchange step of the adsorption, the short spacer dimeric surfactants 12-2-12 adsorbs by only one charged head group onto one charged site of the surface and that shows release of one sodium ion from the surface [113, 114, 118]. The analysis of equilibrated supernatant after adsorption shows one bromide and one sodium released from the surface are present. This indicates only one hydrophilic group in the gemini molecule is adsorbed onto the surface and the second hydrophilic group is oriented towards the aqueous medium accompanying the bromide ion. In contrast, when the spacer group is long and flexible ($s \geq 10$), two head group is attached to the surface. The analysis of supernatant was found to contain two bromide and two sodium ions for each adsorbed surfactant ions. The mechanism is shown schematically in Fig. 15. After saturating the adsorption sites present on the surface a second adsorption step occurs due to hydrophobic interaction between the alkyl chains of the adsorbed surfactants. Atkin et al. [111] showed the adsorbed aggregates of 12-*s*-12 are flattened ellipsoidal for $s = 2$ and 3, and the aggregates are become more flattened as the spacer length is increased (Fig. 15c). Rosen and Li [119] have found the maximum amount of cationic gemini surfactants adsorbed on clay increases in presence of electrolyte.

3.4.2 Effect of structure of anionic gemini surfactant: Adsorption of C_{12}MADS, C_{16}MADS (MADS = monoalkyl disulfonate), C_{10} DADS (DADS = dialkyl disulfonate), C_{10}MAMS (MAMS = monoalkyl monosulfonate) on soil show Langmuirian isotherm [120]. The comparison of maximum amount of surfactants adsorbed between mono and disulfonated, and that between different chain lengths surfactants are shown in Table 7. Comparison of C_{10}MAMS and C_{10}MADS shows DS (disulfonated) surfactants adsorbed less due to increased in electrostatic and steric hindrances to sorption. Comparisons between different chain lengths show higher adsorption for longer chain length due to increased hydrophobicity of the surfactant.

3.4.3 Zwitterionic surfactant: The zwitterionic geminis contain no counterions, similar to amino acids they are in the form of 'inner salts' [121]. The zwitterionic surfactants are also called as heterogemini surfactants [122]. The zwitterionic geminis can be seen as a combination of an anionic surfactant and a cationic surfactant. There are only limited experimental studies on adsorption zwitterionic surfactants on solid-liquid interface [121-124] also a few theoretical studies [125, 126]. The adsorption of zwitterionic surfactant N-dodecyl betaine or NDB ($C_{12}H_{25}N^+(CH_3)_2$-CH_2-CO_2^-) on silica show the formation of bilayer like adsorption aggregate structure. They proposed, the first step is the direct interaction of the individual monomers with the surface sites and second step is the interfacial aggregate formation. Similar observation was also found by other researchers [121]. It was found by Seredyuk et al. [122] the amount of surfactant adsorbed at the hydrophilic surface (silica) is much higher than the hydrophobic surface (silica treated with dichlorodimethylsilane) and suggested the formation of aggregates in the form of either continuous bilayer structure or micelle like structure at the hydrophilic surface.

3.4.3.1 Effect of pH on zwitterionic surfactant adsorption: The effect of pH on the adsorption of zwitterionic surfactant on hydrophilic surface is interesting. It has been found that the effect of pH on adsorption zwitterionic surfactant on sand is negligible as long as the surfactants carry no negative charge [123]. However, interestingly, as the surfactants with a net positive charge start to increase at low pH values (≈ pK_a) the surface excess is observed to decrease rapidly. The study shows there is a correlation between the pH value at which the surface excess is drastically altered and the pK_a value of the surfactant carboxyl group. The effect of pH on adsorption of zwitterionic surfactants, $C_{12}H_{25}$-$N^+(CH_3)_2$-$(CH_2)_nCO_2^-$ ($n = 1$ and 5, are referred as $C_{12}N_1CO_2$ and $C_{12}N_5CO_2$ respectively), on sand is shown in Fig. 16. The adsorption amount is unaffected between pH 7 to 4 for both the surfactants but start decrease rapidly further lowering of pH and $C_{12}N_5CO_2$ shows almost zero at pH 2. The adsorption of $C_{12}N_1CO_2$, on the other hand, is much less sensitive to pH. For $C_{12}N_5CO_2$ surfactant, pK_a value is 4.37 while for $C_{12}N_1CO_2$ is ~ 2. The properties of adsorbed layer of surfactants are usually unaffected by pH if the surfactants are in the zwitterionic form in that pH range. However, as the lowering of pH of the solution below pK_a results in rapid desorption due to transformation of surfactant zwitterionic to cationic or anionic form. This resulted in increase in electrostatic repulsion between the adsorbed aggregates and/ or a decrease in attractive interaction between adsorbed aggregate and the silica surface (as zero surface charge is around pH 2).

3.5 Biosurfactant

3.5.1 Structure of biosurfactant: Generally the structure of biosurfactants includes a hydrophilic moiety composed of amino acids or peptides, anions or cations, or mono-, di-, or polysaccharides [127]. The hydrophilic portion is generally consists of either a carbohydrate, a hydrophilic amino acid such as such as glutamate, aspartate, lysine, or arginine, or a hydrophilic peptide. The hydrophobic portion is generally made of saturated, unsaturated, or hydroxylated fatty acids, an isoprenoid structure such as cholesterol, or a hydrophobic amino acid or peptides including amino acids such as phenylalanine, leucine, isoleucine, valine, or alanine [128]. The structure of different rhamnolipids, the most widely studied biosurfactants are shown in Fig. 17. Two types of rhamnolipids contain either two rhamnoses attached to β-hydroxydecanoic acid or one rhamnose connected to the identical fatty acid [20].

3.5.2 Biosurfactant adsorption: Types of biosurfactants, their microbial origin, and their application in different area including environmental pollution have been reviewed by some researchers [20, 22, 127]. Although there are many biosurfactants, most of the adsorption studies are concentrated on rhamnolipid surfactant [129, 130, 131, 132]. Adsorption of rhamnolipid biosurfactant on soil depends on different soil parameters like clay, metal oxides, and organic mater of soil [131, 132]. The observed isotherm of rhamnolipid adsorption onto soil are composed of three regions [130], similar to that of synthetic surfactants [52]. Adsorption isotherm of R_1 on different clay, like illite and Ca-montmorillonite are typical two-step adsorption showing the formation of hemimicelle like anionic surfactants. The fitting of Freundlich equation of the isotherm of R_1 on different clay shows kaolinite is concave (n_f = 0.33) but those for illite and Ca-montmorillonite are convex (n_f = 1.67 and n_f = 1.22 respectively) [132]. The adsorption isotherms of R_1 on four different metal oxide, hematite (Fe_2O_3), MnO_2, gibbsite ($Al(OH)_3$), and iron-oxide coated silica (FeO_x-Si) were nonlinear (Freundlich isotherm) and followed the order of nonlinearity (n_f): $Fe_2O_3 > MnO_2 > Al(OH)_3 > FeO_x$-Si. A comparison of the rhamnolipid adsorption isotherms for different soil parameters indicate both aluminosilicates, iron oxide, and clay content are critical for to the adsorption of a anionic biosurfactant [132]. Moreover, since the adsorption is non-linear in nature, there are large differences in adsorption at low and high concentrations of rhamnolipid. The studies on effect of electrolyte show the amount of rhamnolipids adsorbed strongly depend on the ionic strength and adsorption increases with increasing ionic strength [129].

3.5.3 Adsorption from mixture of biosurfactants: The results on adsorption of R_1 and R_2 mixture on soil are more interesting [129, 131, 132]. The mixture of R_1 and R_2 shows less sorption of R_1 than R_1 alone due to the presence of more hydrophilic nature of R_2 (see Fig. 18). Specifically, for kaolinite, FeOx-Si (iron oxide coated silica), and HA-Si (humic acid coated silica) show that R_1 form adsorbed 3-fold, 10-fold, and 30-fold more respectively alone than when in presence of R_2. So, the use of R_1/R_2 mixture should decrease the sorption of the R_1 form by several orders of magnitude depending on the predominant soil constituent present. Noordman et al. [130] have studied the adsorption isotherms of a mixture of different rhamnolipid surfactants for the total and individual components on soil. They have found due to the preferential adsorption of the hydrophobic components, the composition of the multicomponent rhamnolopid surfactant mixture remaining in the solution phase in both batch and column studies have been changed. The adsorbed amounts of the components at higher surfactant concentration in the column studies at full breakthrough were lower by certain factor under continuous flow conditions than the batch studies. The lower degree of surfactant adsorption in column experiments may be attributed to the presence of shear stress during continuous flow conditions, which might counteract formation of surface aggregates and thereby reduce adsorption.

4. Importance of solubilization

Solubilization in micellar solution is a promising method for significantly increasing the efficiency of remediation of aquifers contaminated with NAPLs or solids like PAHs [133]. PAHs are hydrophobic pollutants often introduced into subsurface from the sites of creosote wood treatment, coal storage, coke oven plants, and coal tar spillage. Because of the low solubility of these organic contaminants in water, they present in the soil matrix as a long-term source of contaminants, and also pump-and-treat remediation of soils polluted with such contaminants are become difficult. In that case, SER have been proposed as a promising technology for removing low soluble residual organics from contaminated aquifers [2, 37]. This technology is based primarily on two processes: (i) micellar solubilization and (ii) mobilization of entrapped NAPLs due to reduction in interfacial tension. The aspects of solubilization in micellar solution will be discussed in this section and mobilization in the next section.

The surfactants exist as monomers below the surfactant's CMC and have only minimal effects in the aqueous solubility of organics [134, 135]. Micellar solubilization occurs when the surfactant concentration exceeds the CMC, where the aqueous solubility of organics is enhanced by the incorporation of hydrophobic molecules into surfactant micelles [134-136]. The extent of micellar solubilization depends on many factors, including surfactant structure, aggregation number, micelle geometry, hydrophile/liophile balance (HLB) value, ionic strength, temperature, and the size and chemistry of the solubilizate [14, 137].

4.1 Micellar solubilization: To quantify the effectiveness of a surfactant in solubilizing a given solubilizate, the molar solubilization ratio (MSR) is used. MSR is defined as the number of moles of organic compound solubilized per mole of surfactant added to the solution. When both the concentrations (surfactant and solubilizate) are expressed in same unit, the MSR is dimensionless. The MSR can be calculated as [135]

$$\mathrm{MSR} = (S - S_{\mathrm{CMC}})/(C_{\mathrm{S}} - \mathrm{CMC}) \quad (9)$$

where S is the apparent solubility of organic compounds at surfactant concentration C_{S} ($C_{\mathrm{S}} >$ CMC) and S_{CMC} is the apparent solubility of the organic compounds at the CMC. MSR can be determined from the slope of the linearly fitted line of solute concentration vs. surfactant concentration curve above the CMC. Partitioning of the organic compounds between micelles and monomeric solution is an alternative approach in quantifying the surfactant solubilization. The micelle phase/aqueous-phase partition coefficient (K_{mw}) is based on the mole fraction ratios, the ratio of mole fraction of the compound in the micellar pseudophase (X_{m}) to the mole fraction of the compound in the aqueous pseudophase (X_{a}). K_{mw} also can be defined as [133, 138]

$$K_{\mathbf{mw}} = \frac{X_m}{X_a} = \frac{C_{\mathbf{m}}}{C_{\mathbf{a}}} = \frac{n_{\mathbf{m}} / V_{\mathbf{m}}}{n_{\mathbf{a}} / V_{\mathbf{a}}} \quad (10)$$

where C_{m} is the concentration of the hydrophobic solute in the micelle, C_{a} is the concentration of that in the aqueous phase, n_{m} is the number of moles of solute present in the micellar phase, n_{a} is the number of moles of solute in the aqueous phase, V_{m} is the micellar volume, and V_{a} is the aqueous volume. Edwards et al. [135] have defined the mole fraction of organic compound in the micellar pseudophase can be calculated as

$$X_{\mathrm{m}} = (S - S_{\mathrm{CMC}})/(C_{\mathrm{S}} - \mathrm{CMC} + S - S_{\mathrm{CMC}}) \quad (11)$$

or, in terms of MSR,

$$X_{\mathrm{m}} = \mathrm{MSR}/(1+\mathrm{MSR}) \quad (12)$$

The mole fraction of organic in aqueous pseudophase can be approximated for dilute solution,

$$X_{\mathrm{a}} = S_{\mathrm{CMC}}\, V_{\mathrm{w}} \quad (13)$$

where V_{w} is the molar volume of water, e.g., 0.001805 L/mol at 25 °C, S_{CMC} is the apparent solubility of organic compound at the CMC. K_{mw} can be represented as

$$K_{\mathrm{mw}} = X_{\mathrm{m}}/\, X_{\mathrm{a}} = (S - S_{\mathrm{CMC}})/[(C_{\mathrm{S}} - \mathrm{CMC} + S - S_{\mathrm{CMC}})(S_{\mathrm{CMC}}\, V_{\mathrm{w}})] \quad (14)$$

The solubilization of organic contaminants by single surfactants has been studied extensively [2, 68, 103, 120, 135, 136, 139-158], in compare to that, there are less study on mixed surfactant system [105, 159-166]. The MSR and K_{mw} values of different organic contaminants in different surfactant solutions are shown in Table 8.

4.1.1 Solubilization in single surfactant system: During micellar solubilization, polar solutes can accumulate close to the micelle surface, amphiphiles in the palisade layer, and nonpolar oils in the hydrophobic core of the micelle. The apparent or pseudophase solubility of the compounds have been referred as the total solute present in the aqueous and micellar phase increases linearly with increase in concentration above the CMC [120, 133, 135, 160]. The increase in solubility of organic compounds in presence of micelles is almost entirely due to hydrocarbon partitioning into the micellar core. As a result, the amount of hydrocarbon dissolved in the aqueous phase is essentially unaffected by the presence of surfactants as long as excess hydrocarbon will present [147]. Morri et al. [170] found the increase in association constant between solubilizate monomer and vacant micelle with increase in hydrophobicity of the solubilizate molecules, indicate the solubilization is mainly controlled by hydrophobic interaction between the solubilizate and micelle. The rate of exchange of hydrophobic compounds between the micellar phase and aqueous phases generally is considered to be fast. The solubilization of hydrocarbons in micellar solutions of ethoxylated nonionic surfactants has been the subject of several experimental and theoretical investigations [135, 143, 145, 158, 171-173]. The researchers are given efforts on the effects of hydrocarbon, surfactant molecular structure, solution composition, and temperature on solubilization capacity.

4.1.1.1 Effect of hydrophilic chain length: There is a contradiction on effect of hydrophilic chain length of the nonionic surfactants on the solubility of the organic compounds in aqueous medium. Some researchers have found the effect of hydrophilic chain length of nonionic surfactants is not significant, since the hydrophobic micellar core is the most important part in the solubilization process. Paria and Yuet [105] have studied the effect of EO (ethylene oxide) of a homologues series NP surfactants and found that changing of EO groups in a wide range (9, 12, 15, and 40) there is no significant change in the batch solubilization of naphthalene. Similar results were also found by others [174, 175]. Tokiwa [174] also found the solubilization of Yellow OB was unchanged in dodecyl polyoxyethylene ethers by changing the EO groups 6 to 20. Xiarchos and Doulia [176] found the solubility of alachlor pesticide was increased with increasing the hydrophilic chain length of the nonionic surfactants in a homologue series. They used two homologues series nonionic surfactants octylphenol ethoxylates (Triton X-114 (EO = 8), Triton X-100 (EO = 10), and Triton X-102 (EO = 12)) and ethoxylated decyl alcohols (Neodol 91-5E (EO = 5), Neodol 91-6E (EO = 6), and Neodol 91-8E (EO =8)) in their study. In terms of solubilization capability, the nonionic surfactants of each homologue series were ranked as follows: Neodol 91-8E > Neodol 91-6E > Neodol 91-5E and Triton X-102 > Triton X-100 > Triton X-114.

On the other hand, the anionic surfactant sodium dodecyl polyoxyethylenesulphates ($C_{12}H_{22}(OC_2H_4)_xSO_4Na$, where $x = 1\text{-}10$), shows increased solubilization with increasing the polyoxyethylene chain [174]. The polyoxythylene group in this case acts as similar to that of hydrocarbon part, as CMC values decreases with increasing that group.

4.1.1.2 Effect of hydrophobic chain length: Any factor that causes an increase in the diameter or aggregation number of the micelle can be expected to produce increased solubilization. The solubilization of hydrocarbons in aqueous medium is strongly depending on the hydrophobic tail length of the surfactants since the micellar aggregation number and micellar size increases with increasing surfactant tail length [105, 135, 175-178]. The study of effect of tail length on solubilization shows in a homologues series of a cationic surfactant (alkylpyridinium bromide) MSR and K_m increases with increasing the tail length. It has been also found that the values of MSR increase linearly with increasing the tail length [105]. Similar observation was also found by Abu-Hamdiyyah and Rahman [177, 178]. Solubilization tendency of benzene, cyclohexane, and *n*-hexane increases linearly as a function surfactant chain length of an anionic surfactant ($C_nH_{2n+1}SO_4Na$). The standard free energy of solubilization of benzene, cyclohexane, and *n*-hexane decreases (more negative) with increasing surfactant chain length. The amphiphilic additives tend to solubilize in the outer region of the micelle and the nonpolar additives present in the interior of the micellar core, which is composed of the portions of the hydrocarbon chains. They have concluded from their study that per CH_2 of surfactant chain (a) the sum of the change in the standard free energy component resulting from strengthening of the hydrophobic effect by amphiphilic additives and the corresponding change in the electrostatic free energy as a result of the positioning of the additive between the ionic heads is more negative than the change in the standard free energy of micellization; (b) the change in the standard free energy of micellization is more negative than the change in the standard free energy component resulting from strengthening of the hydrophobic effect by nonpolar additives; and (c) the change in the standard free energy component resulting from strengthening of the hydrophobic effect by amphiphilic additives is more negative than the change in the corresponding component resulting from nonpolar additives.

The branched hydrophobic chain surfactants have less solubilization power of hydrocarbons than the isomeric straight chain surfactants, because of their shorter effective chain length. This may also account for the observation that unsaturated soaps have less solubilizing power for hydrocarbons than the corresponding saturated ones [14].

In the study of Edwards et al. [135] it has been found that for nonionic surfactants also there is an increase in solubility with increasing hydrophobic chain length. Saito and Shinoda [179] also report similar results, but they have mentioned that the hydrocarbon chain length of nonionic surfactants is less important than that for ionic surfactants.

4.1.1.3 Effect of HLB value: The HLB number of a surfactant is one of the most widely used indicators for a given application [14]. The tendency of surfactant partitioning between oil and aqueous phase is also depends on the HLB value, the higher the HLB value, more tendency of partitioning into water. For an ethoxylated nonionic surfactant, the HLB value may be expressed as [14]

$$\text{HLB} = \frac{E}{5} \tag{15}$$

where, E is the percentage of EO in the surfactant on a mass basis. The HLB scale ranges from 0 to 20. A hydrophobic group has an HLB of 0, where as EO head group has an HLB of 20. For the industrial applications HLB values used from 10 to 20 [145, 180]. There are some studies related to solubilization of organic compounds in surfactant solution depending on their HLB values [143, 145, 179, 181, 182]. There is a maximum in solubilization against HLB number of surfactants observed by many researchers for different surfactants and hydrocarbons [143, 145, 179, 181, 182]. Zhou and Rhue [182] have studied the PCE (perchloroethylene) solubility in presence of 42 different surfactants based on their HLB values and found 12 surfactants have higher solubility. These 12 surfactants were HLB values in the range of 10.8 – 13.2. It has been also found that PCE solubilization is decreased when the surfactant HLB values exceeded about 13.2 or below 10.8. The decrease is faster in the lower end than in the higher end. Diallo et al. [145] found a similar trend for solubilization of dodecane, decane, hexane, and cyclohexane in presence of dodecyl alcoholethoxylate surfactants. The core volume of the micelle decreases with increasing the HLB value. The core volume of a micelle, V_c (Å^3) can be calculated as [183]

$$V_c = N_a(27.4 + 26.9(N_c - 1)) \tag{16}$$

where N_a is the aggregation number and N_c is the total number of carbon atoms of the surfactant lipophile. Fig. 19 shows the effect of HLB on the core volume of dodecyl alcohol ethoxylate micelle in dilute solution at 25 ºC. The trend of variation of HLB with MSR (for solubilization of dodecane, decane, hexane, and cyclohexane) is also similar to that of micellar core volume shown in Fig. 19. It has been found that the higher the molar volume (V_m) of a hydrocarbon the lower it's MSR [144]. Diallo et al. [145] have pointed out that for solubilization of alkane and aromatic hydrocarbon maxima in MSRs with HLB shows only for aromatic hydrocarbon sine they can be solubilized in both hydrophobic micellar core and hydrophilic shell. For any particular oil, the maximum MSR is found when the HLB of the surfactant fits that of the oil [146, 184].

The effects of HLB on micelle-water partition coefficient depend on the surfactant type and hydrocarbon type. The effect of HLB on micelle-water partition coefficients of the alkanes show the value of log K_{mw} for alkanes decreases with increasing HLB. The more hydrophobic alkanes (i.e. higher octanol-water partition coefficient, log K_{ow}) have higher micelle-water partition coefficient. When the HLB values of surfactants increase, log K_{mw} for chlorinated alkanes (trichloroethylene and tetrachloroethylene) also go through a maximum [146]. More hydrophobic compound has again the largest micelle-water partition coefficient.

4.1.1.4 Effect of temperature: Temperature also has a significant effect on solubilization of organic compounds in presence of surfactant. For both ionic and nonionic surfactants an increase in temperature generally results in an increase in the extent of solubilization for both polar and nonpolar solubilizates. As an example, an increase in temperature from 10 to 25 ° C resulted in about 30% increase in weight solubilization ratios (WSR) of DCB, PCE, and dodecane in presence of witconol 2722 surfactant. The effect was attributed to (a) the changes in the aqueous phase solubility of the organic compound (b) changes in the surfactant micelles with temperature [144]. The later mechanism is predominant due to the tendency of increase in micellar aggregation number with increase in temperature [185]. As the temperature increases, the micelles of nonionic surfactants become larger and larger until they are so large that the solution becomes visibly cloudiness and followed by separation of the surfactant-rich phase. This point is called cloud point of nonionic surfactants. For a particular hydrophobic group, larger the percentage of oxythylene in the surfactant molecule, higher the cloud point. There is an optimum temperature, at which the nonionic surfactants show maximum solubilization, the optimum temperature is also dependent on the hydrophilic chain length [180].

4.1.1.5 Effect of electrolyte: The addition of electrolyte at low level does not change the solubility of organic compounds in presence of nonionic surfactants but the small changes occur at high electrolyte concentration [144]. At high electrolyte concentration there is a decrease in cloud point and increase in aggregation number due to the "salting out" of the nonionic surfactant [185]. It is well known that increasing the ionic strength increases the micelle aggregation number and decreases the CMC for ionic surfactants, as a result solubilization power also increases. It has been found that the solubilization power of pyrene in SDS increases by approximately 16% as the NaCl concentration is increased from 0 to 100 mM.

4.1.1.6 Effect of surfactant type: The nonionic surfactants are better solubilizing agents than ionics in very dilute solution, because of lower CMC. In general, the order of solubilizing power of hydrocarbons and polar compounds that are solubilized in the inner core are: nonionics > cationics > anionics, with same hydrophobic chain length [180, 175, 186]. In the study of Paria and Yuet [105] solubilization capacity of naphthalene in presence of cationic surfactants with different head group have been studied. Comparison of solubilization capacity of naphthalene in cationic surfactants, $C_{14}PB$ and $C_{14}TAB$ show there is no difference in solubility as the tail length is similar and the head group area and charge are almost similar. Comparison of solubilization of naphthalene between cationic ($C_{12}PB$) and anionic (SDS) surfactants with identical hydrocarbon chains (C_{12}) show that the MSR for SDS is lower, about half of that for $C_{12}PB$. The difference in solubilization is probably due to the adsorption of naphthalene at the micellar surface by electrostatic interactions between the π-electrons of naphthalene and cationic micelle.

4.1.2 Solubilization in mixed surfactant system: It has been mentioned earlier that there are few literature available on mixed surfactant systems, most of these studies are concentrated on poly aromatic hydrocarbons [105, 161, 162-164, 166] and a few on chlorinated hydrocarbons [165, 167, 187].

4.1.2.1 Anionic-nonionic mixed surfactant system: In general, ionic-nonionic mixed surfactants show better solubilization efficiency, exhibiting higher cloud points than those of the single nonionic surfactant, as well as lower Kraft points than those of the single ionic surfactant. As a result, mixed surfactants could be useful for the application of SER over a wide range of temperature, salinity, and hardness conditions than the individual surfactants [162]. The studies on solubilization of PAHs in anionic-nonionic surfactant mixture show the higher solubility of PAHs in mixed surfactant systems than those in single surfactant solutions at comparable surfactant concentrations [161, 162].

Zhou and Zhu [162] have reported the pyrene solubilization efficiency in mixed surfactant systems in terms of deviation ratio (R) between the $\mathrm{MSR}_{\mathrm{exp}}$ and the $\mathrm{MSR}_{\mathrm{ideal}}$ ($R = \mathrm{MSR}_{\mathrm{exp}}/\mathrm{MSR}_{\mathrm{ideal}}$). When the value of R is greater than 1, there will be a positive mixing effect of mixed surfactants on the solubilization and positive deviation of MSRs from the ideal mixture. In their study, the values of R for pyrene are larger than 1 at any solution composition studied, which indicates that the four anionic-nonionic mixed surfactants studied by them have the positive deviation from ideal mixture (see Fig. 20a). The positive deviation of MSRs from ideal mixture follows the order of SDS-TX-405 > SDS-Brij-35 > SDS-Brij-58 > SDS-TX-100. This mixing effect was found to increase with an increase in the HLB value of nonionic surfactants, also there was a strong negative deviation of the CMC values from the ideal mixture. The larger the HLB of nonionic surfactants in the mixed system, the grater the attractive interaction between the components of mixed surfactants, which result in the greater negative deviation of the CMC from ideal mixture, and then the mixing effect of anionic and nonionic surfactants on solubilization of pyrene becomes grater. In addition, the positive deviation of MSRs from ideal mixture has a maximum for all four mixed systems at the mole fraction of nonionic surfactant between 0.1 and 0.3. Similar results in positive deviation and maximum in R was also found by others [105, 164, 188]. The mole fraction of nonionic surfactants at which maximum in R occurs depending on the surfactant molecular structure.

The addition of inorganic ions in ionic-nonionic mixed surfactant systems increases the solubility of organic hydrocarbons [161]. Higher the valence of the inorganic ions higher the efficiency of the solubilization enhancement.

4.1.2.2 Cationic-nonionic mixed surfactant system: Paria and Yuet [105] have studied the solubilization of naphthalene in presence of cationic-nonionic and anionic-nonionic surfactant mixtures. In the mixed systems nonionic surfactant (NP-9) was same, and different chain length cationic surfactants (C_{10}PB, C_{12}PB, and C_{14}PB) were used. The negative deviation in R

(R < 1) was found in this study (see Fig. 20b). The deviations are more pronounced at low mole fractions of NP-9, with the extent of deviation in the cationic surfactant series increasing as C_{14}PB < C_{12}PB < C_{10}PB. In addition, a comparison between similar hydrocarbon chain length cationic and anionic surfactants, C_{12}PB and SDS, show the deviation is more pronounced with cationic surfactant. The negative deviation of R in the cationic-nonionic surfactant mixtures can be attributed as (i) a reduction in surface adsorption of the naphthalene molecules and (ii) the close packing of molecules in the mixed micelle due to a reduction in electrostatic repulsion among surfactant heads. The close packing of surfactant molecules also occurs when the hydrophobic chain lengths are very similar, which may contribute to the increase in deviation from C_{10}PB to C_{14}PB. The difference in deviation between SDS and C_{12}PB may also be explained in terms of adsorption of naphthalene molecules at the micellar surface.

4.1.3 Solubilization in biosurfactant: Biological surfactants have advantages relative to synthetic surfactants for specific applications due their structural diversity, biodegradability, and effectiveness at extreme temperature, pH, and salinity [128]. Due to the environmental friendly nature of the biosurfactants, many researchers have studied solubilization of organic hydrocarbons in presence of biosurfactants for the application in remediation process [22, 128, 189-193]. Most of the researchers have used rhamnolipid biosurfactant for their studies. In the comparison of the effectiveness of anionic rhamnolipid biosurfactant (CMC = 0.0342 mM) and a synthetic anionic surfactant (CMC = 0.424 mM) in solubilizing hexadecane, Thangamani and Shreve [128] found the MSRs for solubilization of hexadecane in rhamnolipid biosurfactant was approximately 20 times more effective that the alkylbenzene sulfonate (ABS) synthetic surfactant. Kanga et al. [193] have compared the effect of biosurfactants and synthetic surfactants on solubilization of naphthalene and methyl substituted naphthalenes (see Fig. 21). The synthetic surfactants have a lower solubilization potential than the biosurfactant, as shown lower enhancement factor E. Although biosurfactants have a higher solubilization potential, the rate coefficients are lower than the synthetic surfactant. They have found that kinetics of solubilization of naphthalene and methyl-substituted naphthalenes in bio (Glycolipids from *Rhodococcus* strain H13-A) and synthetic (Tween-80) surfactants follow first order rate law

$$\frac{dC}{dt} = k(EC^* - C) \tag{17}$$

where C^* and C are the saturation concentration, and time-variable concentration of the hydrocarbon respectively, k is the first-order rate constant, E is the aqueous phase solubility enhancement factor due to presence of surfactants. As a result, the potential for solubilizing power is much greater for biosurfactants as compared to synthetic, and these effects are more pronounced with increases in methyl substitution. The reason for greater solubilization was attributed to the larger micellar volume of the biosurfactants.

The effect of structure of rhamnolipid biosurfactants show monorhamnolipid has more solubilization capacity of phenanthrene than dirhamnolipid [189]. The solution pH is also an important parameter for solubilization of hydrocarbons in biosurfactants. Solubilization of phenanthrene in presence of rhamnolipid biosurfactants show solubilization is maximum in the pH range 4.5-5.5. Specifically, the apparent solubility at pH 5.5 was 3.8 times greater than at pH 7 in the presence 240 ppm rhamnolipid, due to formation of different pH-dependent structures of anionic biosurfactant [190].

McCray et al. [192] have studied the solubilization behavior of two- and three-component NAPL mixtures in biosurfactant solutions. They found the relatively hydrophobic compounds in the mixture experienced solubility enhancements with respect to pure water that were greater than those predicted by ideal enhanced solubilization theory, while the solubility enhancements for the relatively hydrophilic compounds were less than predicted. The degree of nonideality is shown to be a nonlinear function of the NAPL-phase mole fraction. They have developed an empirical equation to predict the multicomponent partition coefficients.

Kommalapati et al. [194] have studied suitability of a plant based natural surfactants derived from *Sapindus mukorossi*, commonly known as “soapnut” or “Ritha” to solubilize hexachlorobenzene (HCB). The mass of dry ritha powder required to solubilized 1 mg/L of HCB in water was comparable to SDS and other commercial surfactants.

4.2 Relationship between octanol- and micelle-water partition coefficients: The octanol-water partition coefficient (K_{ow}) is the ratio of the concentration of a compound in octanol and in water at equilibrium and at a specified temperature. The octanol-water partition coefficient has been correlated to water solubility; therefore, the water solubility of a substance can be used to estimate its octanol-water partition coefficient. It has been shown by different researchers [135, 136, 144, 195] that there is a linear relationship between log K_{mw} and log K_{ow} for various organic compounds in a micellar surfactant solution. The slope of the linear relationship depends on the type of surfactant. Edwards et al. [135] found the mole fraction of the organic compound in the micellar pseudo phase in different surfactant solutions is negatively correlated with log K_{ow}. To investigate the role of surfactant and organic properties in the solubilization of hydrophobic organic compounds, an empirical correlation was made to relate the micelle-water partition coefficient and surfactant molecular structure to the octanol-water partition coefficient of the organic compound by Jafvert et al. [173]:

$$K_{\mathrm{mw}} = K_{\mathrm{ow}}\,(bN_{\mathrm{c}} - cN_{\mathrm{h}}) \qquad (18)$$

where b and c are fitted coefficients, N_{c} is the total number carbons in the hydrophobic group, and N_{h} is the number of hydrophilic groups (Sorbitan carbons and ethoxy groups).

4.3 Microemulsion and supersolubilization: Microemulsion is defined as a thermodynamically stable phase consists of ternary mixtures of oil-surfactant-water or quaternary mixtures of oil-surfactant-cosurfactant-water. Microemulsion can be of three basic types: (i) microemulsion corresponds to oil solubilized in aqueous micelle (Winsor-I), (ii) microemulsion corresponds to water solubilized in reverse micelle present in the oil phase (Winsor-II), and (iii) microemulsion corresponds to oil and water bicontinuous phase that is stabilized by a surfactant membrane (Winsor-III) [196]. The typical transition is possible from Winsor type I to type III and to Type II microemulsions shown in Fig. 22 [197, 198]. The tracsitions are well correlated with the interfacial tension (IFT) of the system. The Winsor type I microemulsion can be transform to a Winsor type III microemulsion by decreasing the system HLB (e.g., increasing salinity for ionic surfactants systems). When the HLB values decreases further, the system transforms Winsor type III to Winsor type II microemulsion. Microemulsions have higher solubilization ability of hydrophobic organic compounds (HOCs) than the normal micellar system with the similar micellar solubilization concept called super solubilization. In microemulsion, reduction in the micelle curvature allow increased oil solubilization in the core of these “swollen” micelles [199]. Solubilization capacity of these swollen micelles can be higher up to 1 or 2 orders magnitude than the regular micelle solubilization [200-202]. Supersolubilization is becoming more attractive in many applications like hard surface cleaners, detergency, surfactant enhanced remediation of oil contaminated sites etc. due to its increased solubilization capacity.

D.A. Sabatini, J.H. Harwell and their coworkers [196, 199, 203, 204, 205, 206] have done significant work on supersolubilization. Using this technique, the aqueous contaminants solubility in water is increased by the presence of surfactant micelles, as a result the removal of more contaminant is possible with less water flushing through the contaminated area. Graciaa et al. [207, 208] have showed a very lipophilic amphiphile additive (the long chain alcohol) may substantially improve the solubilization of microemulsion. Improvement in the solubility is due to the presence of the additive, is called a lipophilic linker. The role of the linker is to extend the reach of the surfactant tail deeper into the oil phase, thus providing additional interaction. Uchiyama et al. [204] have reported the effect of linker molecules on solubilization capacity of hydrocarbon and chlorinated hydrocarbon microemulsions using an anionic surfactant (sodium dihexylsulfosuccinate or Arerosol-MA or AMA). They found as the chain length of lipophilic linker (alcohol molecule) increases the solubilization capacity of the anionic surfactant system increases. More specifically, the longer chain alcohol is more effective at linking oil molecules for hexane than for chlorinated hydrocarbon oils, as the linker effect is more effective for higher equivalent alkane carbon number (EACN) oils. The hydrophilic linkers are more effective to enhance the solubilization of lower EACN oils and the combination of lipophilic and hydrophilic linkers synergistically enhances the solubiliozation capacity of chlorinated hydrocarbon microemulsions. Acosta et al. [196] showed the optimum mixed linker performance is reached at equimolar ratio of lipophilic and hydrophilic linker.

5. Mobilization of NAPLs: It has been mentioned earlier that surfactant enhanced remediation technology is based primarily on two recovery mechanisms (a) increased aqueous solubility of the organic compound due to micellar solubilization and (b) mobilization or displacement of NAPLs due to interfacial tension (IFT) reduction. Mobilization has been shown to be an extremely efficient means for recovering NAPLs from sand and aquifer materials than solubilization [209]. Utilization of this approach in the field is difficult due to uncontrolled migration of mobilized NAPL phase. Particularly, the displacement of DNAPLs is problematic due to the tendency of downward migration and redistribution of the mobilized DNAPLs. In order to overcome the risk of downward migration of DNAPLs while still achieving efficient recovery, the density modified displacement (DMD) method is developed [209 - 213]. The concept of displacing entrapped NAPL through low IFT surfactant flooding was originated in the field of enhanced oil recovery. Immiscible displacement is referred as mobilization, offer the advantage of reduced flushing volumes which may dramatically reduced the remediation time and cost. Partitioning alcohols can reduce, or reverse the density difference between the organic and aqueous phase, therefore minimizing or eliminating the risk of downward DNAPLs migration. In the DMD process partitioning of sufficient quantity of alcohols into a DNAPL to lower the density and efficiently convert the DNAPL to LNAPL. In addition to density conversion, NAPL displacement and recovery is achieved by flushing with a low interfacial tension surfactant solution. The alcohol utilized for partitioning in most applications was n-butanol, which is relatively soluble in water.

Kostarelos et al. [214] introduces the concept of *natural buoyancy* using low microemulsion density to control vertical migration of DNAPL. They used isopropanol to reduce the microemulsion density. Kibbey et al. [211] have studied the partitioning alcohol (*n*-buranol) into DNAPLs (TCE and PCE) in presence and absence of surfactants and found alcohol concentrations near saturation are necessary for inversion of DNAPLs to LNAPLs. The use of surfactants also increases the solubility of alcohol in water. They have suggested in their study, there is no apparent benefit to the using surfactants for density modification. Although surfactants increase the partitioning of alcohol to DNAPL contaminate zones, they also change the equilibrium to required more alcohol for density conversion. Moreover, the combination of surfactants with alcohols may also lead to unwanted interfacial tension reduction and downward mobilization. They have suggested the use of an alcohol macroemulsion for DMD is an effective method [211 - 213]. Ramsburg et al. [212] also showed the use of 1-butanol macroemulsion reduced the volume of preflood (predisplacement flood) solution required for in situ TCE-NAPL density modification in aquifer cell experiments from ~ 5 pore volume with 6% (wt) 1-butanol aqueous solution to ~ 1.2 pore volumes.

6. Biodegradation of organic hydrocarbons: HOCs generally have low aqueous solubilities, and because of less availability of those compounds biodegradation is very difficult. In presence of surfactants the solubilities of HOCs increased and micellized HOCs have increased bioavailability to microorganisms, as a result, improved the biodegradation rate. The surfactants affect the rate of hydrocarbon biodegradation in two ways: (i) by increasing dissolution of the molecules in aqueous phase and (ii) changing the affinity between the microbial cells and hydrocarbons by increasing cell surface hydrophobicity [12, 25, 215-217]. For very low-solubility hydrocarbons microbial cells may attach to the surface and secrete surface-active agents to increase the mass transfer and result in increasing degradation. The microorganisms may or may not have ability to secrete surfactants but adhesion of cell to the surface is one of the major mechanisms [218]. However, it has been shown that increased dispersion does not always lead to increased biodegradation. Which indicate three-way interaction among the biosurfactant, substrate, and cell that is crucial to achieving enhanced biodegradation rates [25].

In some cases, surfactants show inhibitory effects on biodegradation [189, 193, 218-224]. It has been shown that surfactants inhibit the biodegradation of hydrocarbons by detaching the cells from the liquid/solids-water interface [12, 218]. In some cases surfactants used as a preferential growth substrate by degrading microorganisms [221, 225, 226] and toxicity of the surfactants [227, 228] cause the inhibitory effects on biodegradation. Even, the toxicity of the surfactants to the pollutant degrading bacteria also depends on the surfactants binding to the soil constituents. As an example, the HDTMA adsorbrd to the clay is essentially nontoxic to the pollutant-degrading bacteria in soils whereas aqueous-phase HDTMA shows considerable toxicity [229]. There are many studies on biodegradation of organic hydrocarbons in presence of synthetic [162, 218, 221, 225, 230-237] and biosurfactants [25, 189, 218, 237-239]. It has been found that surfactants have facilitate, retard, or no effect on biodegradation of organic hydrocarbons. The summary of some research work on effect of surfactants on biodegradation of organic hydrocarbons are presented in Table 9, mostly taken from the paper of Liu et al. [232], indicates the effects of surfactants on microbial degradation of HOCs are neither consistent nor have a general trends. Different bacteria used for degradation of organic hydrocarbons are listed in Table 10.

6.1 Effect of surfactant structure and type on biodegradation: In the surfactant enhanced biodegradation process surfactant should not be biodegradable and should be nontoxic to the biodegradable bacteria. Biodegradation of nonionic surfactants is difficult when the hydrophobic part of the molecule is branched, an aromatic group is present within the hydrophobic part, or ethoxylate chain length of hydrophilic portion is more [249, 221]. Toxicity of surfactants to several soil bacteria related to the HLB values, for a similar chain length higher the HLB values lower the toxicity. Toxicity of nonionic surfactants with ethylene oxide chains lower than six monomers were related to buried in the lipid layer of liposome and caused damage the membrane, long ethylene oxide chains (e.g. 30 monomers) had no effect on membrane permeability [221, 250]. Liu et al. [232] have studied the availability of naphthalene to PAH degrading microorganism when solubilized inside the surfactant micelle. They observed the presence of Brij-30 and TX-100 surfactants above the CMC were not toxic to the PAH-degrading bacteria and the presence of surfactant micelles did not inhibit mineralization of naphthalene. The presence of micelles do not inhibit the degradation rate as the residence time of naphthalene inside the micelle is very short compare to high exit rate of the molecule from the micelle, which makes the molecule available to the microorganisms. In this process, Brij-30 was degraded as the naphthalene degradation process proceeded but TX-100 was unaffected.

In general, it has been found that presence of biosurfactants enhanced the biodegradation of different organic hydrocarbons [25, 189, 239]. However, pH near 7 is not always optimal for solubilization or bioavailability. As an example, solubilization and biodegradation of phenanthrene in presence of rhamnolipid was found maximum around a pH 4.5-5.5 [239].

7. Surfactant partitioning to NAPL: In SER processes, solubilization and mobilization have been studied extensively, but limited information is available on partitioning of single [128, 132, 154, 251] and mixed [153, 164, 166, 187] surfactants between aqueous and organic phase. Most of these studies related to partitioning of surfactants are focused on the nonionic surfactants since they have relative high solubilization capacity and have potential use in the surfactant enhanced remediation process. The partition coefficient of surfactants (K_{ps}) can be represented as the ratio of the equilibrium organic-phase surfactant monomer concentration (C_m^o) to the equilibrium aqueous-phase surfactant monomer concentration (C_m^w). Significant partitioning of surfactants to NAPL phase leading to a substantial loss of surfactant and less available for solubilization.

7.1 Single surfactant system: Partitioning isotherm (the plot of concentration of surfactants in NAPL phase vs. that in aqueous phase) shows there is a gradual increase in concentration of surfactants in NAPL phase with increasing the concentration of surfactants in aqueous phase and after a limit there is a plateau region [133, 251, 153]. Generally, plateau region occurs near CMC region of the surfactants. In general, surfactant partitioning is found to be strongly correlated with surfactant hydrophobicity, mixture polydispersity, and NAPL/water interfacial tension [153]. The extent of surfactant partitioning is increased with decreasing NAPL/water interfacial tension [251]. The nonionic surfactants with less number of EO groups or longer hydrophobic chain length are more hydrophobic in nature and have higher tendency to partition into NAPL phase. In a mixed surfactant system, more hydrophobic compounds selectively partitioning into the NAPL, leaving a significantly more hydrophilic surfactants in aqueous phase [133]. The partitioning also increases with increasing NAPL polarity [153, 251]. Effect of surfactant mixture polydispersity on partitioning shows polydisperse surfactant mixture continues to partition above the CMC to a greater extent than does the single pure surfactant [153]. They have also developed an empirical relation for calculating partitioning plateau concentration (C_p) in terms of CMC and IFT:

$$C_p = \frac{\varphi}{\mathrm{CMC}^{\alpha}\mathrm{IFT}^{\beta}} \tag{19}$$

where C_p is the partitioning plateau concentration of surfactant (mg/L of NAPL); CMC is the aqueous critical micellar concentration (mg/L); IFT is the NAPL/water interfacial tension (dyn/cm); φ, α, and β are empirical constants. The empirical constants can be determined by performing a least square nonlinear regration on the experimental data. Predicted values are reasonably fit well with the experimental values.

7.2. Mixed surfactant system: Some recent studies show reduction in partitioning loss of nonionic surfactants in presence of anionic surfactant [164, 166, 187]. In general, anionic surfactants does not partition into the organic phase [14, 164]. In addition, the solubilization capacity of anionic surfactants is significantly less for NAPL or organic hydrocarbons than nonionic surfactants [136, 174, 179, 182], but anionic-nonionic mixed surfactant systems show higher solubilization efficiency than the individuals [153, 164, 166, 187]. Since the mixed anionic-nonionic surfactants could reduce partitioning loss of nonionic surfactants and increase in solubilization efficiency, mixture may be the potentially better system for SER application. In the study of Zhao and Zhu [164], they found TX-100 losses into TCE (trichloroethelene), CB (chlorobenzene), and 1,2-DCB (1,2-dichlorobenzene) phases were more than 99, 97 and 97%, respectively, when single TX-100 was used. In a single or mixed system it was observed that no anionic surfactant (SDBS) was partitioned into DNAPLs. In addition, SDBS decreased greatly the partition loss of TX-100 into DNAPLs. As an example, the extent of TX-100 partition into 1,2-DCB was decreased with increasing the amount of SDBS addition (shown in Fig. 23). Similar observation was also found in other studies [166, 187]. The reduction in partition loss for TX-100 was attributed to poor SDBS partition into DNAPL and to the formation of TX-100-SDBS mixed micelles.

8. Partitioning of contaminants to soil: Although it has been well known that the surfactant enhance the desorption of HOCs and facilitated transport of HOCs by solubilizing inside mobile micellar pseudophase, the surfactant also adsorbed on the soil matrix and thereby lead to HOCs partitioning into immobile adsorbed surfactants [105, 106, 252-254]. The later would help to enhance the sorption of HOCs onto soils. For soils and sediments the most common measure of HOC sorption capacity is the HOC solid-water distribution coefficient, K_d [252]. In presence of a surfactant, the distribution coefficient of contaminant in solid-water (K_d^*) may be expressed as [106, 252, 255]

$$K_d^* = \frac{K_{oc} f_{oc} + f_{soc} K_{ss}}{1 + K_{mn} C_{mn} + K_{mc} C_{mc}} = \frac{K_d + f_{soc} K_{ss}}{1 + K_{mn} C_{mn} + K_{mc} C_{mc}} \qquad (20)$$

where K_d^* is the ratio of bound organic to mobile organic compound, f_{oc} and f_{soc} are the mass fraction of natural organic carbon and the surfactant in a solid respectively, K_{oc} and K_{ss} are the organic distribution coefficient with the natural organic matter and the sorbed surfactant in solid respectively, K_{mn} and K_{mw} are the partition coefficient of the solute between surfactant monomer and water, micellar phase and water respectively. C_{mn} is the concentration of the surfactant as monomer in water (mass/mass, dimensionless) ($C_{mn} = C$, if $C \leq$ CMC; C_{mn} = CMC, if $C >$ CMC); C_{mc} is the concentration (dimensionless) of the surfactant as micelle in water ($C_{mc} = C$ - CMC).

9. Surfactant enhanced HOCs removal: Surfactant enhanced desorption of HOCs from soil in an important step for determining the performance of SER technology for organic contaminated soil and groundwater. The removal of HOCs from soil matrix in presence of surfactants is a complex process, since the surfactants first remove the HOCs from the soil and at the same time surfactants are also adsorbed on the soil surfaces and change the surface characteristic, as a result, some times HOCs are readsorbed on the soil surface. Due to the complex nature of the process many researchers have studied on removal efficiency of the organic compounds from the soil matrix using different surfactants like single synthetic [28, 95, 105, 256-263], mixture of synthetic [105, 260, 264, 265], and biosurfactants [28, 193, 266-268] to improve the basic understanding.

9.1 Laboratory studies: Mostly the contaminant removal efficiency studies are conducted in the laboratory scale. The removal studies were mainly conducted by using single synthetic surfactants, mixed surfactants, and biosurfactants.

9.1.1 Single surfactants: Many researchers have studied single surfactant facilitated removal of HOCs from a soil column in laboratory scale. Yeom et al. [144] have mentioned that there is a strong effect of aging of contaminants on removal efficiency. They report desorption of HOCs from artificially contaminated soil is usually very high in compared to desorption from weathered and aged coal tar-contaminated soil. Paterson et al. [95] have developed a model for calculating the removal efficiency of organic hydrocarbon in presence of surfactant:

$$\text{Efficiency} = 1 - \frac{\left(S_w + K_{\text{unimer}}\text{CMC} + K_{\text{mic}}\left(C_{\text{Surf}} - \text{CMC} - Q_{\max}\dfrac{M_{\text{Soil}}}{V_{\text{a}}}\right)\right)\dfrac{V_{\text{a}}}{M_{\text{Sol}}}}{C_{\text{Soil,Initial}}} \qquad (21)$$

where S_w, K_{unimer}, K_{mic}, C_{Surf} , V_{a}, M_{Soil}, Q_{Max}, and $C_{\text{Soil,Initial}}$ are the water solubility of the HOC (mg/L), equilibrium constant for the binding of HOC to surfactant unimer (L/mol), equilibrium constant for the binding of HOC to surfactant micelles (L/mol), total concentration of surfactant (mol/L), volume of water (L), mass of soil (kg), maximum amount of surfactant sorbed to the soil (mol/kg), initial concentration of the HOC in soil (mg/kg) respectively. In their study, they found for nonionic ethylene oxide (EO)/propylene oxide (PO) block copolymer surfactants removal efficiency for PAH is related to the EO/PO ratio, lower the EO/PO ratio higher the removal efficiency.

In the process of surfactant enhanced desorption of HOCs adsorption density of surfactants onto soil have a strong effect on the efficiency of desorption [105, 260, 261]. Zhou and Zhu [261] have found only when concentration surfactants was greater than corresponding critical desorption concentration (CDC) PAH desorption would enhanced. The CDC is define as the corresponding surfactant concentration when desorption percentage of PAH is equal to the initial desorption percentage with water. Surfactants are more effective in enhancing HOC desorption from the contaminated soil with relative lower clay content and higher organic carbon content. To show the importance of adsorption density of surfactants on removal efficiency of HOCs Paria and Yuet [105] show that the removal efficiency of naphthalene from a sand column using NP surfactants of different EO groups depends on the adsorption density of the surfactants on sand surface. Higher the adsorption density leads to more removal efficiency. The order of removal efficiency was: NP-9 > NP-15 > NP40.

Rothmel et al. [269] and Mulligan and Eftekhari [28] have proposed a new and interesting idea of remediation with surfactant foam for trichloroethylene (TCE) and PCP (pentachlorophenol)-contaminated soil respectively to reduce the consumption of surfactants. The comparison between TX-100 and rhamnolipid biosurfactant (JBR425) showed better efficiency for TX-100, since it has better ability to solubilization of PCP [28]. Specifically, TX-100 (1%) removed 85% and 84% of PCP from two different soil, fine sandy soil and sandy-sit, respectively, contaminated with 1000 mg/kg PCP. These values were 60% and 61% respectively for JBR425 (1%). Urum et al. [270] have studied the removal of crude oil from soil using air sparging assisted stirred tank reactor using rhamnolipid and SDS surfactants. Saichek and Reddy [258] have studied the surfactant enhanced electro kinetic remediation of PAHs under heterogeneous soil conditions.

9.1.2 Mixed surfactants: There are limited studies of HOC removal efficiency of mixed system. SDS-TX-100 mixed system was showed greater phenanthrene desorption efficiency than that by single TX-100 and the presence of SDS also reduce the adsorption of TX-100 on soil [264, 265]. Specifically, using same TX-100 concentration in 3.5 mmol/L, the desorption percentage of phenanthrene were 49.5% with single TX-100 solution and 62.5, 72.5, 78.5, and 87.5% with mixed surfactants, in which mol ratio of SDS to TX-100 were 1:4, 1:2, 1:1, and 2:1 respectively [264]. The CDC values decreases with decreasing SDS to TX-100 mole ratios, the CDC values of corresponding single and mixed surfactant systems mentioned were 1.6, 1.2, 1.0, 0.8, and 0.6 mmol/L. The results are represented in Fig. 24.

The mixture of two similar surfactants also can increase the removal efficiency. It is mentioned before that Paria and Yuet [260] found removal efficiency of naphthalene from a sand column using NP surfactants was greater when the EO chain length was shorter. When two NP surfactants with different EO groups (NP-9 and NP-40) were mixed together (e. g 4:1 to get an average EO of 15) the mixed system showed the adsorption density similar to single NP-15, that was slight higher than single NP-40 but lower than single NP-9 surfactants. In the study of removal efficiency, it was found the mixed system showed removal efficiency very close to that of NP-9 and higher than NP-15 or NP-40. Thus the mixed systems may be useful for the remediation process by minimizing surfactant loss due to adsorption and increasing removal efficiency.

9.1.3 Biosurfactants: The environmental friendly nature of the biosurfactants leads the researchers to study first in the laboratory scale, whether the biosurfactants are comparable with the synthetic surfactants of suitable properties. In the study of Mulligan and Eftekhari [28], removal of PCP using surfactant foam TX-100 showed better results than JBR425 (a rhamnolipid biosurfactant). In another study, comparison between synthetic (Tween 60) and biosurfactants (from *Rhodococcus rubber*) showed biosurfactant was more efficient and also was less adsorbed on the soil [268]. The ability of biosurfactants to remove crude oil entrapped within the soil matrix was 1.9-2.3 times grater than that of a synthetic surfactant. In a general study of removal of pyrene using rhamnolipids (from *P. aeruginosa* 57SJ) showed the removal efficiency of pyrene increases with increasing the concentration of biosurfactants [193]. They found there was a linear increase in the total recovery of pyrene with the concentration of surfactant. Moreover, they have compared the slope of that recovery line with MSR in the batch solubilization experiment and found the dynamic system was 1.3 times grater than the static system, probably due the presence of cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) in the soil.

Kuyukina et al., [268] have reported the removal efficiency of crude oil from soil using biosurfactants depend on the alkane medium where the microorganism (*R. rubber*) was grown, and also on process temperature. The oil removal rate was found maximum (82%) at 28 °C for *Rhodococcus* biosurfactant produced on *n*-hexadecane and decreased by 1.3 times at 22 °C. The comparisons of oil removal efficiency of biosurfactants produced on different alkanes are shown in Fig. 25. Biosurfactant produced by *R. rubber* grown on *n*-dodecane was most effective for oil removal from contaminated soil in colder conditions (at 15 °C), but at higher temperature (22 °C and 28 °C) *R. rubber* grown on *n*-hexadecane was most effective. The inefficiency of *n*-hexadecane-produced biosurfactant was due to freezing of surfactant below 16 °C.

9.1.4 Removal of dissolved HOCs from water: Contaminated surface water containing dissolved nonionic organic compounds (NOCs) is purified when passing through subsoils by adsorption of NOCs onto soil from water. In this natural process, pure groundwater is accumulated from the contaminated water. The sorption of NOCs onto soil from water is mainly controlled by the soil organic matter content [34, 271]. Low organic matter soils, clays, and aquifer materials have very little sorptive capability for sorbing NOCs from water. However, limited sorptive capacity of clay minerals containing low organic matter can be greatly improved by replacing naturally occurring inorganic exchange cations with organic cations [35, 72, 83, 229, 272]. The organic cation like cationic surfactants studied extensively are quaternary ammonium ions of the form $[RN(CH_3)_3]^+$ where R is the alkyl or aromatic hydrocarbon. The HDTMA-modified clays or soils show sorption coefficients of several common organic compounds like benzene, toluene, and xylene increased by more than two orders of magnitude [35, 72], as a result, have also ability to remove organic anions from water. Smith et al. [272] have studied the effect of the molecular structure of quaternary ammonium cations (ten quaternary ammonium cations composed of various alkyl and aromatic groups) associated with a montmorillonitic clay on the sorption of a nonionic organic contaminant, tetrachloromethane. These results suggest that it is feasible to create an in situ sorbent zone within an aquifer using underground injections of QACs [35, 273]. In most situations, the sorbent zone concept needs to be coupled with contaminant degradation processes for sorbent emplacement to be a practical tool in the remediation of groundwater contamination sites. In general, QACs are active biocidal agents used widely as disinfectants [229]. Nye et al. [229] showed that, in the unbound form, HDTMA is toxic and adversely impacts the heterotrophic activities of aerobic soil microorganisms. Once adsorbed to mineral phases, however, toxic effects are largely eliminated.

9.2 Field studies: Although there are many laboratory scale studies are available but there are only a limited field studies are available on SER [45, 104, 274-278]. Mostly the field studies are in-situ [104, 274-278] rather than ex-situ [45]. Lee et al. [278] have reported surfactant enhanced pilot-scale in-situ flushing of nonionic surfactant sorbitan monooleate (POE 20) to remediate the site contaminated with diesel, kerosene, and lubricating oil at Pusan, Korea. The in-situ pilot-scale site (4m × 4m × 4m) surfactant flushing plant is shown in Fig. 26. Surfactant solution was injected trough injection wells continuously at very low flow rate and the effluent solution from the extraction wells was pumped out in certain time intervals. They found total 48 kg of total petroleum hydrocarbon (TPH) (about 88% of the initial TPH) was removed after three pore volume of 2% POE solution flushing and that was more than 75 times the amount removed when flushing with water alone.

Abriola et al. [276] and Ramsburg et al. [277] have studied a pilot-scale surfactant-enhanced aquifer remediation to recover PCE-DNAPL at the Bachman road site located in northeastern Michigan, Oscoda, USA. First they have done the site characterization and the some preliminary laboratory studies to design the pilot-scale process. In site characterization, soil grain size distribution, saturated hydraulic conductivity, and PCE source zone location are the most important parameters. For the field study, aqueous solution of 6% (wt.) Tween-80 surfactant was injected. In their study, it was found after analysis of effluent samples taken from the extraction well that a total of 19 L of PCE and 95% of the injected surfactant were recovered. At the same time, post-treatment monitoring indicated that PCE concentrations at many locations within the treated zone were reduced by as much as 2 orders of magnitude with respect to that of pre-SEAR levels and had not bounce back after 450 days of SEAR operations ceased. They have mentioned that the overall treatment cost per volume of soil in the pilot-scale was higher (~ $\$2100/m^3$) but the cost will reduce for the full-scale operation. In addition, using efficient low-cost surfactant formulations and reusing the surfactants by advanced separation technology may reduce the chemical cost in the process.

Sahoo et al. [275] have reported the field studies of TCE-contaminated (trichloroethene) sites at Picatinny Arsenal, NJ. They have used TX-100 surfactant solution for flushing. They have used three different model (i) equilibrium transport model, (ii) two-site kinetic transport model, and (iii) multisite kinetic transport model to predict the TCE concentration in presence of surfactant at different wells. They observed the equilibrium transport model could not adequately describe TCE desorption and transport but two-site and multisite models could fit the experimental data well. The concentration data from the two wells and the model analysis suggest that the rate of TCE desorption was increased by ~ 30% in presence of TX-100 than that of pure water.

10. Concluding remarks

This comprehensive review summarizes the findings of numerous literatures aiming for the application of remediation of organic contaminated sites (soil and water) using surfactants as an enhancing agent. To improve the basic understanding of overall surfactant enhanced remediation technologies some aspects like (*i*) surfactant adsorption on soil, (*ii*) micellar solubilization, (*iii*) supersolubilization, (*iv*) biodegradation, (*v*) density modified displacement, (*vi*) partitioning of surfactants and contaminants; and different parameters those affecting these phenomena are discussed. The conclusions of this review can be divided into several points as follows:

1. Adsorption of anionic surfactants on soil shows a positive relationship between OM content of soil. The effect of clay type on adsorption of anionic surfactants show significant adsorption by Ca^{2+}-saturated montmorillonite than Na^{+}-saturated montmorillonite.
2. Adsorption of cationic surfactants on clays also depends on the clay type, the nature of exchangeable cations initially saturating the clay, and the ionic strength of the aqueous solution. Adsorption of cationic surfactants on soil in presence of electrolyte increases with increasing ionic strength due to reduction in repulsive force between the adsorbed surfactant head groups and increase in hydrophobic interactions between the tail groups. The characteristic of the structure of adsorption layer of cationic surfactants in the interlayer of clay is very complex, mainly depends on the nature of the clay (swelling or non-swelling), initial electrolytes condition (Na-saturated clay or Ca-saturated clay), types of anion present (Cl^{-}, Br^{-} or SO_4^{2-}) in the solution.
3. Adsorption of gemini surfactants on silica shows the decrease of amount adsorbed at saturation as the length of the spacer group increases. The comparisons between monomeric and gemini (dimeric) surfactants show shape of the isotherms are similar in nature but maximum amount adsorbed is higher for gemini surfactants. The effect of pH on the adsorption of zwitterionic surfactants on hydrophilic surface is very important, since the net charge of the surfactants depend on pH of the medium.
4. Adsorption of rhamnolipid biosurfactant on soil depends on different soil parameters like clay, metal oxides, and organic mater of soil. Adsorption of mixture of monomeric (R_1) and dimeric (R_2) rhamnolipid on soil shows less adsorption of R_1 than R_1 alone due to presence of more hydrophilic R_2. So, use of mixture of rhamnolipids may reduce the surfactant loss due to adsorption for soil washing application.
5. Solubilization of HOCs in a single surfactant system is mainly depends on hydrophobic chain length and less significant on hydrophilic chain length. The branched hydrophobic chain surfactants have less solubilization power of HOCs than the isomeric straight chain surfactants, because of their shorter effective chain length. There is a maximum in solubilization with increasing the HLB number of surfactants. Addition of electrolytes

increases the solubilization of ionic surfactants and increase in temperature caused to increase the extent of solubilization for both ionic and nonionic surfactants.

In general, the order of solubilizing power of hydrocarbons and polar compounds that are solubilized in the inner core are: nonionics > cationics > anionics, with same hydrophobic chain length. Ionic-nonionic mixed surfactants show better solubilization efficiency, exhibiting higher cloud points than those of the single nonionic surfactants, as well as lower Kraft points than those of the single ionic surfactants. As a result, mixed surfactants could be useful for the application of SER over a wide range of temperature, salinity, and hardness conditions than the individual surfactants. The biosurfactants like rhamnolipids are very much effective in solubilizing HOCs and sometime may be more efficient than the conventional synthetic anionic surfactants. Microemulsions have higher solubilization ability of HOCs than the normal micellar system.

6. The surfactants enhance the rate of hydrocarbon biodegradation either increasing solubilization in the aqueous phase or by changing the cell affinity between the microbial cell and hydrocarbons by increasing cell surface hydrophobicity. There is no general rule for effect of surfactants on hydrocarbon biodegradation, it has been found that surfactants have facilitate, retard, or no effect on biodegradation. The surfactants retard the degradation rate when the surfactants are toxic to the bacteria or preferential utilization of surfactants by hydrocarbon degraders as a nutrient.
7. The extent of surfactant partitioning into NAPL phase is increased with decreasing NAPL/water interfacial tension and for the nonionic surfactants with less number of EO groups or longer hydrophobic chain length. In a mixed surfactant system, more hydrophobic compounds selectively partitioning into the NAPL, leaving a significantly more hydrophilic surfactants in aqueous phase. In anionic-nonionic mixed surfactant system, presence of anionic surfactants decreased greatly the partitioning loss of nonionic surfactants into NAPLs phase.
8. Desorption of HOCs from soil using surfactants is greatly influenced by the adsorption of surfactants on soil. Surfactants are more effective in enhancing HOCs desorption from the contaminated soil with relative lower clay content and higher organic carbon content. Anionic-nonionic mixed surfactant system showed better removal efficiency of HOCs than that of single surfactants.

9. Density modified displacement is important for removal of DNAPLs.
10. Although there are limited field studies are available in compare to many laboratory-based studies, but the pilot scale in situ field studies show surfactant based technology can be used to successfully remediate the organic contaminated sites. The cost of the pilot scale treatment may be higher but the cost may be reduced when the plant will run in full scale and in addition, chemical cost may be reduced using efficient low-cost surfactant formulations and reusing the surfactants by advanced separation technology.

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Notations

a = Radius of a charged spheres

A_m = Area per molecule

b, c = Constants

C^*, C = Saturation concentration, and time-variable concentration of the hydrocarbon

C_a = Concentration in the aqueous phase

C_i = Molar concentration of ionic species

C_m = Concentration of the hydrophobic solute in the micelle respectively

C_m^o = Equilibrium organic-phase surfactant monomer concentration

C_mc = Concentration of the surfactant as micelle in water

C_mn = concentration of the surfactant as monomer in water

C_m^w = Equilibrium aqueous-phase surfactant monomer concentration

C_p = Partitioning plateau concentration of surfactant

C_s = Concentration of surfactant in aqueous phase (> CMC)

$C_\mathrm{Soil,Initial}$ = Initial concentration of the HOC in soil

C_Surf = Total concentration of surfactant

DADS = Dialkyl disulfonate

e = Elementary charge

E = Aqueous phase solubility enhancement factor due to presence of surfactant

f_oc, f_soc = Mass fraction of natural organic carbon and the surfactant in a solid respectively

k = First-order rate constant

K_d = HOC solid-water distribution coefficient

K_d^* = HOC solid-water distribution coefficient in presence of surfactant

K_f = Freundlich adsorption coefficient

K_i = Partition coefficient surfactants between soil and aqueous phase

K_mw = Micelle-aqueous phase partition coefficient of HOC

K_mn = Partition coefficient of the solute between surfactant monomer and water

K_oc, K_ss = Organic distribution coefficient with the natural organic matter and the sorbed surfactant in solid.

K_ow = Octanol-water partition coefficient

K_{ps} = Partition coefficient surfactants between organic and aqueous phase

K_{unimer}, K_{mic}, = Equilibrium constant for the binding of HOC to surfactant unimer, equilibrium constant for the binding of HOC to surfactant micelles respectively

M_{Soil} = Mass of soil

N_{a} = Aggregation number of a micelle

N_{A} = Avogadro's number

n_{a} = Number of moles of solute in the aqueous phase

N_{c} = Number of carbon atoms of the surfactant lipophile

NDB = N-dodecyl betaine

n_{f} = Constant

n_{m} = Number of moles of solute present in the micellar phase

PAH = Poly aromatic hydrocarbon

PCE = Perchloroethylene

PCB = Polychlorinated biphenyl

Q_{Max} = Maximum amount of surfactant sorbed to the soil

q_{m} = Adsorption capacity

r = Center-to-center distance of charged spheres

R = Deviation ratio

S = Apparent solubility of organic compound at surfactant concentration C_{S}

S_{CMC} =Apparent solubility of organic compound at the CMC

S_{w} = Aqueous solubility of organic compound

T = Absolute temperature

V_{a} = Aqueous volume

V_{c} = Core volume of a micelle

V_{m} = Micellar volume

V_{w} = Molar volume of water

X_{a} = Mole fraction of organic in aqueous pseudophase

X_{m} = Mole fraction of organic compound in the micellar pseudophase

Greek letters

α, β, φ= Empirical constants

ε = Permittivity in the medium

Φ_r, $\Phi_r^{'}$ = Electrostatic repulsion among surfactant heads, and the reduced potential energy respectively

ψ_0 = Surface potential

κ = Debye-Hückel parameter

Γ_p = Plateau surface excess

Abbreviations

ABS = Alkylbenzene sulfonate

CB = Chlorobenzene

CDC = Critical desorption concentration

CEC = Cation exchange capacity

CMC = Critical micellar concentration

DNAPL = Dense nonaqueous phase liquid

DNT = Dinitrotoluene

DTAB = Dodecyl trimethylammonium bromide

DMD = Density modified displacement

EO = Ethylene oxide

EPA = Environmental protection agency

HCB = Hexachlorobenzene

HDTMA = Hexadecyltrimethylammonium

HLB = Hydrophile/liophile balance

HOC = Hydrophobic organic compounds

IFT = Interfacial tension

LAS = Linear alkylbenzene sulfonate

LNAPL = Light nonaqueous phase liquid

MCL = Maximum contaminants limits

MADS = Monoalkyl disulfonate

MAMS = Monoalkyl monosulfonate

MSR = Molar solubilization ratio

NAPL = Nonaqueous phase liquid

NP = Nonylphenyl

NT = Nitrotoluene
OM = Organic matter
PB = Pyridinium bromide
PO = Propylene oxide
QAC = Quaternary ammonium compound
RCRA = Resource conservation and recovery act
SDBS = Sodium dodecylbenzenesulfonate
SDS = Sodiumdodecylsulfate
SEAR = Surfactant enhanced aquifer remediation
SER = Surfactant enhanced remediation
S/S = Solidification/ stabilization
TCE = Trichloroethelene
XDR = X-ray diffraction

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Figure Captions:

Fig. 1: Technologies selected for source control at superfund remedial action sites (Fiscal year 1982-2002) [3].

Fig. 2: different physical forms of organic pollutants in soil: (I) solid particles; (II) liquid film; (III) adsorbed onto soil; (IV) adsorbed into soil; (V) in soil macro pores; (VI) in soil micro pores [12].

Fig. 3: (a) Schematic representation of a gemini surfactant [15, 16], (b) Molecular scheme of a gemini surfactant molecule composed of two identical hydrophilic headgroups and two hydrophobic tail groups.

Fig. 4: Ground water contamination by (a) LNAPL (b) DNAPL [26].

Fig. 5: Schematic illustration of surfactant enhanced aquifer remediation [33].

Fig. 6: (a) Sorption isotherm of SDBS by Ca^{2+} – montmorillonite at different concentration of Ca^{2+} – montmorillonite (C_s, g/L). (b) Precipitation between SDBS and $CaCl_2$ at different concentrations of $CaCl_2$ solution (C_{Ca}, mmol/L) [58].

Fig. 7: Adsorption isothermes of HDTMA Cl in Na- and Ca-saturated Osthemo B_t. C_1, C_2, and C_3 are the critical concentrations for the different regions [80].

Fig. 8: *d*-spacings of (a) HDTMA-Na-SWy-1 (b) HDTMA-Ca-SWy-1 at different water contents as HDTMA loadings increased (normalized to CEC) [80].

Fig. 9: Variation of specific adsorption of $C_{14}PB$ as a function of Debye-Hückel parameter (κ). The initial concentrations of $C_{14}PB$ were 0.5 mM, and the equilibrium time was taken for 1 hr. at 25 °C [43].

Fig. 10: Variation of reduced potential energy (Φ'_R) of $C_{14}PB$ as a function of Debye-Hückel parameter (κ). The initial concentrations of $C_{14}PB$ were 0.5 mM, and the equilibrium time was taken for 1 hr. at 25 °C [43].

Fig. 11: (a) Desorption of $C_{14}PB$ when eluted with pure water after adsorption at 0.5 mM inlet concentration of $C_{14}PB$ in the presence of electrolytes (The concentrations of NaCl, $CaCl_2$, and Na_2SO_4 used were 100 mM, 50 mM, and 50 mM, respectively). For simplicity, the data are labeled by the solutions used in the adsorption-desorption sequence. (b) Desorption of $C_{14}PB$

when eluted with pure water and in the presence of electrolytes (excluding the peak). Inset shows the same plot at a smaller time scale. Experiments were carried out at 25 °C [43].

Fig. 12: Amount of $C_{14}PB$ retained in the sand column after desorption under different electrolyte conditions at 25 °C. The adsorption was performed at 0.5 mM inlet concentration of $C_{14}PB$ in the presence and absence of electrolytes [43].

Fig. 13: Correlation between Si:(Al + Fe) ratio and A_9PE_{10} sorption capacity [71].

Fig. 14: (a) Adsorption isotherms of 12–2–12 (●); 12–4–12 (▲); 12–6–12 (■); and 12–10–12 (◆) on silica at 25 C. (b) Variation of the maximum amount of adsorbed surfactant with the spacer carbon number *s* [112].

Fig. 15: Schematic presentation of the adsorption of (a) 12-2-12, (b) 12-10-12 dimeric surfactants onto silica during the ion-exchange adsorption step [115], and (c) variation in the adsorbed surfactant layer as the spacer size is increased [111].

Fig. 16: Plateau surface excess (Γ_p) of $C_{12}N_1CO_2$ and $C_{12}N_5CO_2$ as a function of pH. The measurements were performed at a bulk concentration of 4 CMC (pH ≈ 7) [123].

Fig. 17: Structure of four different rhamnolipids produced by *Pseudomonas aeruginosa* [20].

Fig. 18: A comparison of the sorption of R_1 alone (from ATCC 9027) with R_1 when it is in a R_1/R_2 mixture (from UG2) by kaolinite, and humic acid-coated silica (HA-Si). For ATCC 9027, the C20-R_1 form comprises 80% of the rhamnolipids. For UG2 mixture, the C20-R_1 and C20-R_2 forms comprises 25% and 55% respectively [132].

Fig. 19: Effect of surfactant HLB on total and core volumes of dodecyl alcohol ethoxylate micelles in dilute solutions at 25 ° C [145].

Fig. 20: Deviation ratios (*R*) as a function of the solution composition of nonionic surfactants in different mixed surfactants (a) solubilization of pyrene [161], (b) Solubilization of naphthalene [105].

Fig. 21: Aqueous solubility-enhancement factor (*K*), first-order rate coefficient (*k*), and time to reach 99% of the saturation concentration for the naphthalenes family, as calculated by optimizing the first-order saturation model [193].

Fig. 22: Typical phase behavior of microemulsion showing the transition from oil in water (type I) to bicontinuous structure (type III) and water in oil structure (type II); initial volume ratio of oil to water = 1:1 [197].

Fig. 23: TX100 losses into 1,2-DCB organic phases vs. total surfactant concentration at 1:40 phase ratio of 1,2-DCB: water (v/v) [164].

Fig. 24: The desorption percentage (R_d) of phenanthrene by different surfactant systems with various mole ratios of SDS (S) to TX100 (T) [265].

Fig. 25: Biosurfactant-enhanced oil recovery from the model soil at different temperatures. Surfactants used: (1) water (Control); (2) Tween 60 (synthetic surfactant); (3) Rhodococcus biosurfactant produced on ndodecane; (4) Rhodococcus biosurfactant produced on n-hexadecane [268].

Fig. 26: In situ flushing system at the pilot site [278].

Tables:

Table- 1: Typical hazardous substances in industrial waste streams [8].

Industry	Arsenic	Heavy metal	Chlor. H'carbons	Mercury	Cyanides	Selenium	[*]Misc. Organics
Chemical	-	✓	✓	✓	-	-	✓
Electrical and Electronics	-	✓	✓	✓	✓	✓	-
Electroplating metal Ind.	✓	✓	-	✓	✓	-	✓
Leather	-	✓	-	-	-	-	✓
Mining, Metallurgy	✓	✓	-	✓	✓	✓	-
Paint&Dye	-	✓	-	✓	✓	✓	✓
Pesticide	✓	-	✓	✓	✓	-	✓
Pharmaceutical	✓	-	-	✓	-	-	✓
Pulp & Paper	-	-	-	✓	-	-	✓
MSW	✓	✓	✓	✓	✓	✓	✓

[*] Misc. organics include various phenols, benzenes etc.

Table-2: MCL of organic contaminants in water [7]

Contaminant	MCL (mg/l)	Health effect	Source
Alachor	0.002	Eye, liver, kidney or spleen problems; anemia; increased risk of cancer	Runoff from herbicide used on row crops
Benzene	0.005	Anemia; decrease in blood platelets; increased risk of cancer	Discharge from factories; leaching from gas storage tanks and landfills
PAHs	0.0002	Reproductive difficulties; increased risk of cancer	Leaching from linings of water storage tanks and distribution lines, coal storage.
Carbofuran	0.04	Problems with blood, nervous system, or reproductive system	Leaching of soil fumigant used on rice and alfalfa
Carbontetra chloride	0.005	Liver problems; increased risk of cancer	Discharge from chemical plants and other industrial activities
Chlorobenzene	0.1	Liver or kidney problems	Discharge from chemical and agricultural chemical factories
DBCP[a]	0.0002	Reproductive difficulties; increased risk of cancer	Runoff/leaching from soil fumigant used on soybeans, cotton, pineapples, and orchards
O-dichlorobenzene	0.6	Liver, kidney, or circulatory system problems	Discharge from industrial chemical factories
p-dichlorobenzene	0.075	Anemia; liver, kidney or spleen damage; changes in blood	Discharge from industrial chemical factories
Ethylbenzene	0.7	Liver or kidneys problems	Discharge from petroleum refineries
Toluene	1	Nervous system, kidney, or liver problems	Discharge from petroleum factories
1,2,4 Trichlorobenzene	0.07	Changes in adrenal glands	Discharge from textile finishing factories

[a] 1,2-Dibromo-3-chloropropane

Table 3: Common primary minerals in soils ([9, 10]

Primary mineral	Chemical composition
1. Quartz	SiO_2
2. Feldspar	
Orthoclase, Microcline	$KAlSi_3O_8$
Albite (Plagioclase)	$NaAlSi_3O_8$
3. Mica	
Muscovite	$H_2KAl_3SiO_3O_{12}$
Biotite	$(H,K)_2(Mg,Fe)_2(Al,Fe)_2Si_3O_{12}$
4. Ferromagnesians	
Hornblende	$Ca(Fe,Mg)_2Si_4O_{12}$
Olivine	$(Mg,Fe)_2\ SiO_4$
Amphiboles	$Mg, Fe)_7(Si_4O_{11})_2(OH)_2$
5. Magnesium silicate	
Serpentine	$H_4Mg_3SiO_2O_3$
6. Phosphate	
Apatite	$(Ca_3(PO_4))_3\ Ca(F, Cl)_2$
7. Carbonates	
Calcite	$CaCO_3$
Dalomite	$Ca\ Mg\ (CO)_3$

Table 4: Size limits of different soil constituents [11].

Fraction	Size limits expressed as particle diameters (mm)
Coarse sand	2.0 to 0.2
Fine sand	0.2 to 0.02
Sit	0.02 to 0.002
Clay	< 0.002

Table-5: Classification and microbial origin of biosurfactants [20, 21, 22].

Surfactant class	Microorganism
Rhamnolipids	*Pseudomonas aeruginosa*, *Pseudomonas* sp., *Serratia rubidea*
Lipopeptides	*Arthrobacter* sp., *Bacillus pumilis*, *Bacillus subtilis*, *Bacillus licheniformis*, *Pseudomonas fluorescens*
Lipopolysaccharides	*Acinetobacter calcoaceticus*, *Pseudomonas sp.*, *Candida lipolytica*
Phospholipids and Sulfonylipids	*Thiobacillus thiooxidans*, *Corynebacterium alkanolyticum*
Fatty acids (corynomycolic acids, spiculisporic acids, etc.)	*Penicillium spiculisporum, Corynebacterium lepus, Arthrobacter parafineus, Talaramyces trachyspermus*
Sophorose lipids	*Candida apicola, Candida lipolytica*
Trchalose lipids	*Arthobacter paraffineus, Corynebacterium spp.*
Glycolipids	*Arthrobacter sp., Corynebacterium sp.*
Sophorose lipids	*Candida bombicola, Candida lipolytica*
Polyol lipids	*Rhodotorula glutinus, Rhodotorula graminus*
Arthrofactin	*Arthrobacter sp.*
Surfactin	*Bacillus subtilis, Bacillus pumilus*
Alasan	*Acinetobacter radioresistens*

Table-6: Values of Freundlich isotherm coefficients log K_f and n_f [92].

Surfactant	Chemical formula	Log K_f	n_f
Igepal CA-720	C_8PE_{12}	0.058	0.558
Tergitol NP-10	$C_9PE_{10.5}$	0.41	0.599
Triton X-100	$C_8PE_{9.5}$	0.86	0.746
Brij 30	$C_{12}E_4$	7.79	2.12

Table 7: Comparisons of maximum amount adsorption of different anionic gemini surfactants [120].

Component	CMC (mM)	Langmuirian sorption maximum, $Q_{\max}$ (µmol/g)
C_{10}MAMS	0.35	10 ± 1.4
C_{10}MADS	0.14	1.4 ± 0.21
C_{16}MADS	0.25	3.0 ± 0.49
C_{10}DADS	0.13	3.0 ± 0.61

Table 8: MSR and K_{mw} values of organic contaminants in different surfactant solution.

Contaminants	Surfactant	MSR	Log K_{mw}	Ref.
Naph.	TX-100	2.3×10^{-1}	4.61	[161]
	TX-305	2.7×10^{-1}	4.51	[161]
	Brij-35	2.7×10^{-1}	4.59	[161]
	Brij-30	3.17×10^{-1}	4.59	[135]
	Igepal CA-720	3.23×10^{-1}	4.63	[135]
	Tergitol NP-10	3.68×10^{-1}	4.57	[135]
	SDBS	5.16×10^{-2}	4.04	[63]
	C_{10}DPDS	5.40×10^{-2}	4.06	[63]
	C_{12}DPDS	1.045×10^{-1}	4.32	[63]
	C_{16}DPDS	1.32×10^{-1}	4.41	[63]
	SDS-TX-100	2.5×10^{-1}	4.64	[160]
	SDS-TX-305	4.1×10^{-1}	4.78	[160]
	SDS-Brij-35	3.4×10^{-1}	4.65	[160]
	Igepal CO-630 (NP-9)	1.79×10^{-1}	4.582	[105]
	Igepal CO-720 (NP-12)	1.75×10^{-1}	4.574	[105]
	NP-15	1.64×10^{-1}	4.55	[105]
	Igepal CO-890 (NP-40)	1.73×10^{-1}	4.55	[105]
	C_{14}PB	1.98×10^{-1}	4.614	[105]
	C_{12}PB	1.35×10^{-1}	4.315	[105]
	C_{10}PB	1.00×10^{-1}	4.226	[105]
	C_{14}TAB	2.02×10^{-1}	4.59	[105]
	SDS	7.3×10^{-2}	4.19	[105]
	TX-100	9.2×10^{-2}	4.61	[160]

	TX-100	9.2×10^{-2}	4.61	[160]
Acen.	TX-305 Brij-35	9.8×10^{-2} 2.4×10^{-1}	4.81 5.18	[160]
	SDS-TX-100	1.2×10^{-1}	5.24	[160]
	SDS-TX-305	2.5×10^{-1}	4.65	[160]
	SDS-Brij-35	1.3×10^{-1}	5.36	[160]
	Tergitol 15-S-7	7.2×10^{-2}	5.21	[167]
	Tergitol 15-S-9	4.9×10^{-2}	5.12	[167]
	Neodol 25-7	6.5×10^{-2}	5.23	[167]
An	TX-100	3.1×10^{-3}	5.33	[160]
	TX-305	3.0×10^{-3}	5.09	[160]
	Brij-35	2.8×10^{-3}	5.59	[160]
	SDS-TX-100	3.9×10^{-3}	5.61	[160]
	SDS-TX-305	4.1×10^{-3}	6.01	[160]
	SDS-Brij-35	4.3×10^{-3}	5.9	[160]
Phen	TX-100	4.1×10^{-2}	5.57	[160]
	TX-305	3.7×10^{-2}	5.09	[160]
	Brij-35	8.6×10^{-2}	5.60	[160]
	Brij-30	1.52×10^{-1}	5.57	[135]
	Brij-58	1.8×10^{-1}	6.20	[157]
	Tween-80	1.9×10^{-1}	6.20	[157]
	Tween-20	1.4×10^{-1}	6.10	[157]
	SDS-TX-100	4.7×10^{-2}	5.63	[160]
	SDS-TX-305	1.1×10^{-1}	6.05	[160]
	SDS-Brij-35	1.2×10^{-1}	5.91	[160]
	C_{10}-MAMS	6.7×10^{-2}	5.79	[120]
	C_{10}-MADS	1.6×10^{-2}	5.18	[120]
	C_{12}-MADS	3.5×10^{-2}	5.53	[120]
	C_{10}-DADS	1.70×10^{-2}	6.17	[120]
	Igepal CA-720	1.04×10^{-1}	5.68	[135]
	Tergitol NP-10	1.60×10^{-1}	5.72	[135]
Py.	TX-100	2.9×10^{-2}	5.9	[160]
	TX-305	2.3×10^{-2}	5.65	[160]
	Brij-35	3.8×10^{-2}	5.86	[160]
	Brij-30	7.15×10^{-2}	6.53	[135]
	Brij-58	8.8×10^{-2}	6.70	[157]
	Tween-80	8.6×10^{-2}	6.70	[157]
	Tween-20	6.7×10^{-2}	6.60	[157]
	SDS-TX-100	3.6×10^{-2}	5.99	[160]
	SDS-TX-305	4.1×10^{-2}	6.50	[160]
	SDS-Brij-35	5.2×10^{-2}	6.45	[160]
	Igepal CA-720	4.25×10^{-2}	6.01	[160]
	Tergitol NP-10	5.76×10^{-2}	6.41	[135]
	Rhamnolipid	7.5×10^{-3}	5.7	[169]
	TX-100	9.2×10^{-2}	6.60	[157]
	Brij-35	9.1×10^{-2}	6.60	[157]
	Brij-58	1.3×10^{-1}	6.70	[157]

	Tween-80	1.3×10^{-1}	6.70	[157]
	Tween-20	9.5×10^{-2}	6.60	[157]
	Tergitol 15-S-7	2.9×10^{-2}	6.34	[168]
	Tergitol 15-S-9	3.5×10^{-2}	6.28	[168]
	Neodol 25-7	7.1×10^{-2}	6.49	[168]
4-NT	Tergitol NP-10	3.77×10^{-1}	3.77	[167]
	Tergitol NP-15	3.67×10^{-1}	3.76	[167]
	Tergitol NP-40	2.77×10^{-1}	3.67	[167]
	Brij 35	2.81×10^{-1}	3.67	[167]
	Tween 80	4.08×10^{-1}	3.8	[167]
2,4-DNT	Tergitol NP-10	9.2×10^{-2}	3.75	[167]
	Tergitol NP-15	8.7×10^{-2}	3.73	[167]
	Tergitol NP-40	8.1×10^{-2}	3.7	[167]
	Brij 35	9.7×10^{-2}	3.77	[167]
	Tween 80	1.18×10^{-1}	3.85	[167]

Table 9: Summary of reported effects of surfactants on microbial degradation.

Overall effect[a]	Observation	Explanation	Ref.
+	Enhanced bacterial growth rate and increased rate of n-alkane consumption	Surfactant solubilization increases aqueous solubility of hydrocarbon	[231]
+	Addition of Alfonic 810-60 or Novel 11 1412-56 enhanced biodegradation of phenanthrene and biphenyl in the presence of aquifer material	Enhancement may be due to removal from the solid and subsequent partitioning in the aqueous pseudophase	[240]
+	Extent of biodegradation of phenanthrene in soil increased by low doses of surfactant in absence of surfactant-induced desorption	No explanation	[227]
+	Triton X-100 increased both the rate and extent of mineralization of naphthalene	Although bacterial adherence prevented, there was sufficient aqueous naphthalene concentration	[241]
+	Increased hydrocarbon degradation rate and extent with biosurfactant addition	Reduction in interfacial tension	[242]
+	Microorganisms were able to rapidly incorporate significant quantities of octadecane	Liposomes facilitated substrate transport through the microbial cell wall	[217]

+	Different Tween-type nonionic surfactants enhanced phenanthrene biodegradation	Surfactant solubilization of HOCs increases bioavailability	[243]
+	Nonionic detergents stimulated growth on hexadecane	Emulsifying action permits effective contact between cells and substrate	[244]
+	Enhanced rate of biodegradation of PCBs in ligninsulfonate emulsion	Emulsifying action overcomes interfacial area limitation	[245]
+	Enhancement in biodegradation of chlorinated hydrocarbon in waste water in presence of surfactant	Enhancement in biodegradation due to the amendment of both mineral nutrients and surfactant as a carbon source.	[233]
0	No effect on phenanthrene mineralization in soilwater systems at low surfactant dose	Surfactant sorbed onto soil	[219]
0	Aromatic biodegradation by pure cultures either unaffected or slightly stimulated by emulsification of oil	Microbial uptake only of solubilized substrate, implying prior adherence not required	[230]
-	Mineralization of phenanthrene inhibited at higher surfactant doses	Possible bacterium-surfactant interactions and/or competitive substrate utilization	[219]
-	Reduced effectiveness or inhibition observed at higher surfactant concentration	Toxicity of surfactants to microorganisms	[227]
-	Triton X-100 completely prevents mineralization of hexadecane dissolved in heptamethylnonane	Surfactant prevented bacterial adherence to solvent-water interface and/or affects cell membranes	[241]
-	Decreased biodegradation of HC in emulsantreated oil	Surfactant prevents adherence to hydrophobic surfaces	[230]
-	Degradation of phenanthrene in SDS-TX-100 mixture decreases as the mole fraction of SDS in mixture was greater.	Preferential utilization of SDS by phenanthrene degraders.	[264]
-	Solubilization of phenanthrene was increased in presence of SDS but degradation of phenanthrene decreased in presence of SDS.	SDS was preferred as a growth substrate, primary degradation and subsequent mineralization occurred.	[221]

[a] + beneficial effect, – detrimental effect, 0 = no effect.

Table 10: Different bacteria used for degradation of organic hydrocarbons

Organic hydrocarbon	Microorganism	Ref.
Naphthalene	Gram negative *E. Coli*	[232]
Hexadecane, Octadecane	*P. aeruginosa* ATCC 9027	[25]
Phenanthrene	*Pseudomonas putida* CRE 7	[189, 190]
	Bacillus sp. B-UM	[218]
	Mycobacterium sp.	[221, 228]
	Sphingomonas sp	[228].
	Sphingomonas paucimobilis EPA505	[246]
Fluoranthene	*Pseudomonas alcaligenes* PA-10	[247]
	Mycobacterium sp.	[221]

	Sphingomonas paucimobilis EPA505	[246]
Pyrene	*Pseudomonas putida*	[250]

Figures:

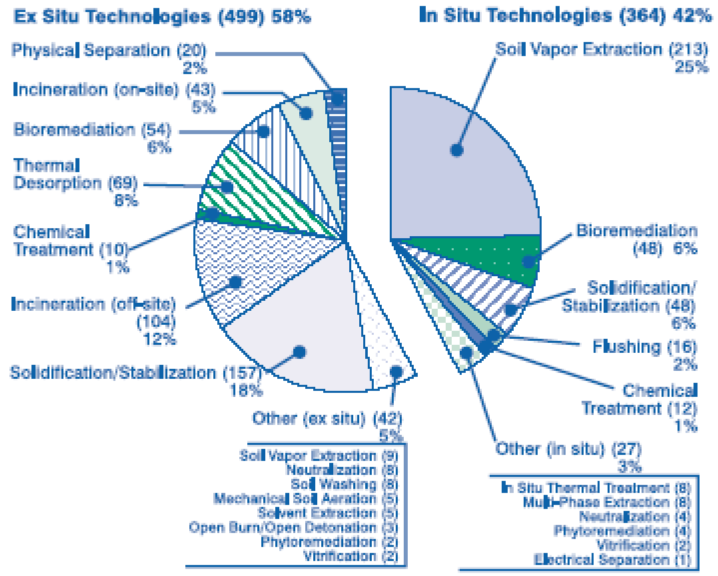


Fig. 1: Technologies selected for source control at superfund remedial action sites (Fiscal year 1982-2002) [3].

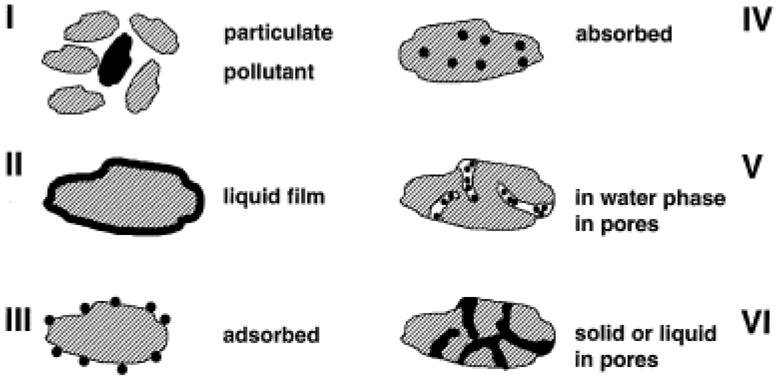
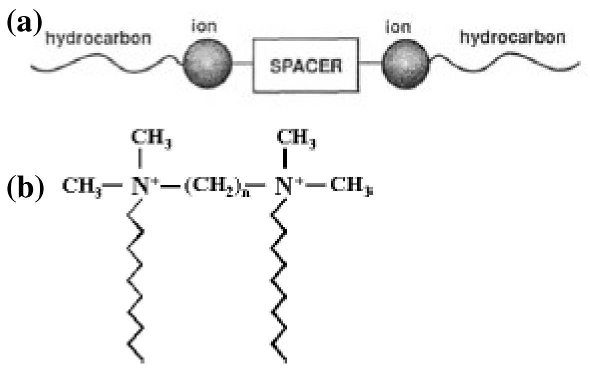


Fig. 2: different physical forms of organic pollutants in soil: (I) solid particles; (II) liquid film; (III) adsorbed onto soil; (IV) adsorbed into soil; (V) in soil macro pores; (VI) in soil micro pores [12].



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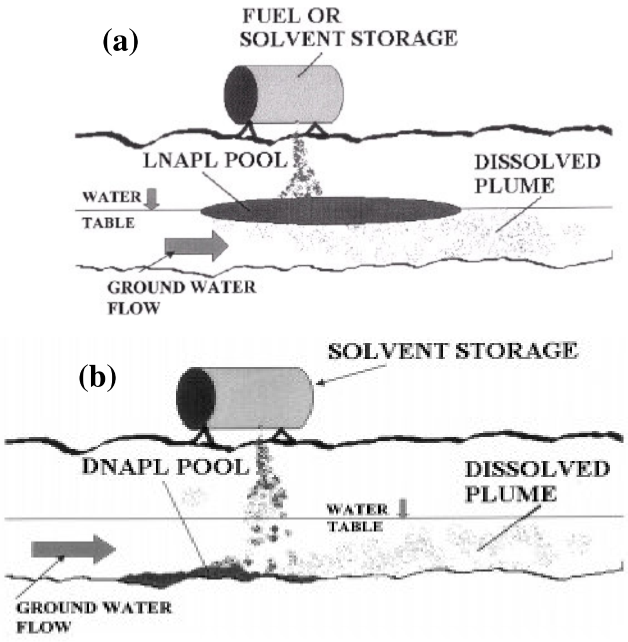


Fig. 4: Ground water contamination by (a) LNAPL (b) DNAPL [26].

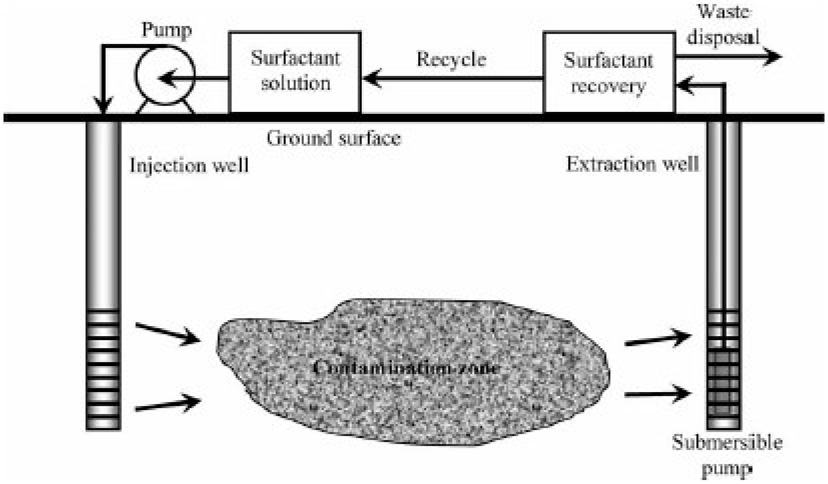


Fig. 5: Schematic illustration of surfactant enhanced aquifer remediation [33].

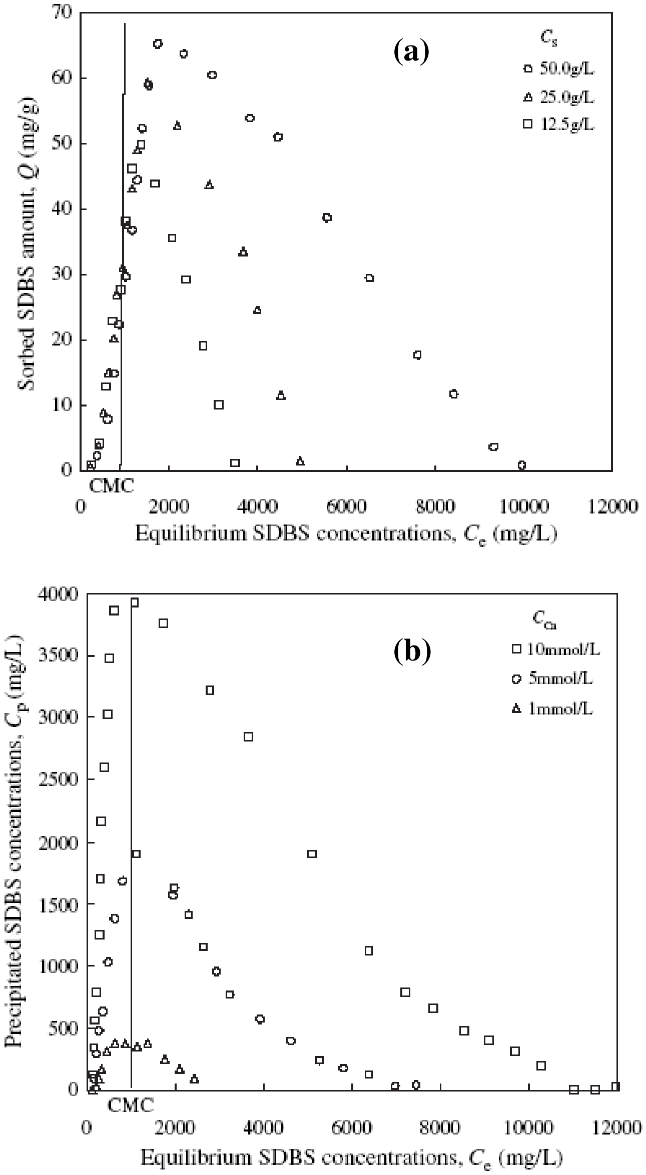
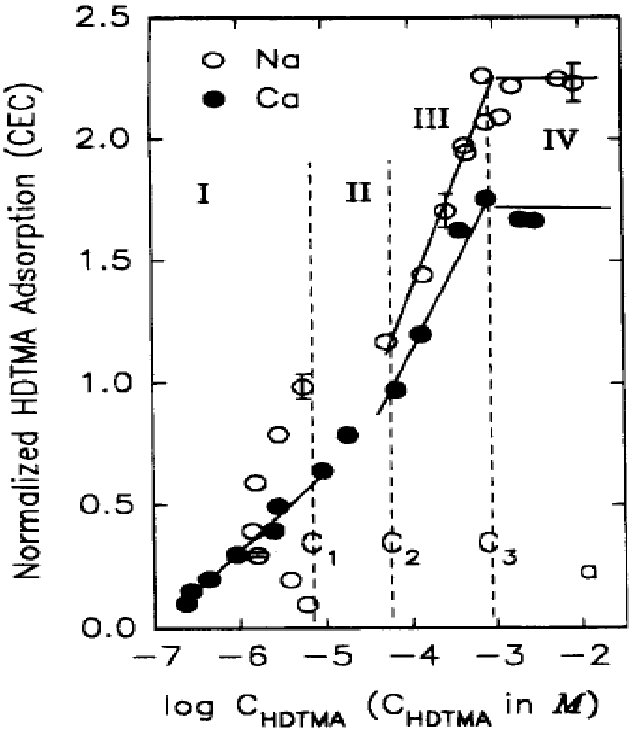


Fig. 6: (a) Sorption isotherm of SDBS by Ca^{2+} – montmorillonite at different concentration of Ca^{2+} – montmorillonite (C_s, g/L). (b) Precipitation between SDBS and $CaCl_2$ at different concentrations of $CaCl_2$ solution (C_{Ca}, mmol/L) [58].



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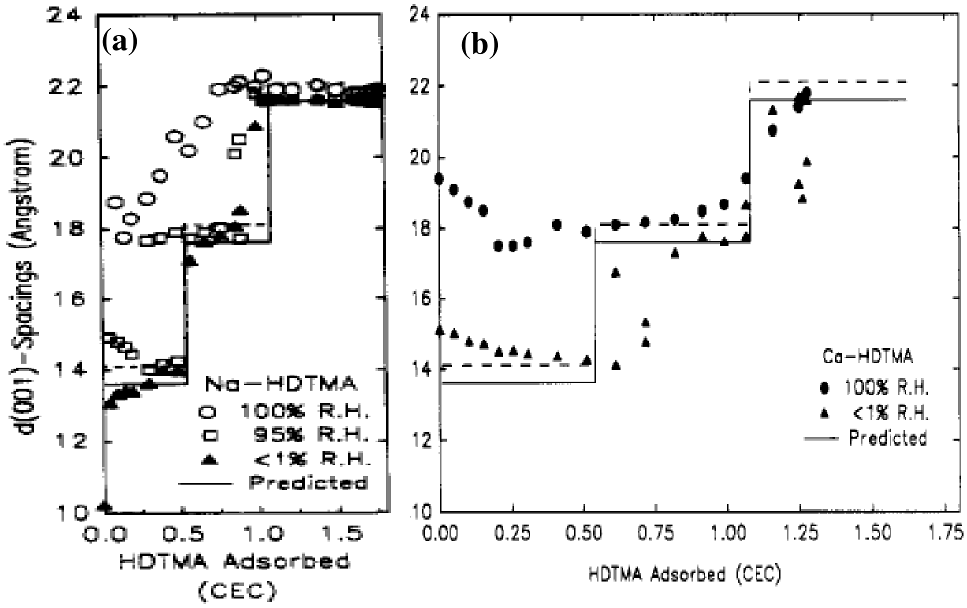

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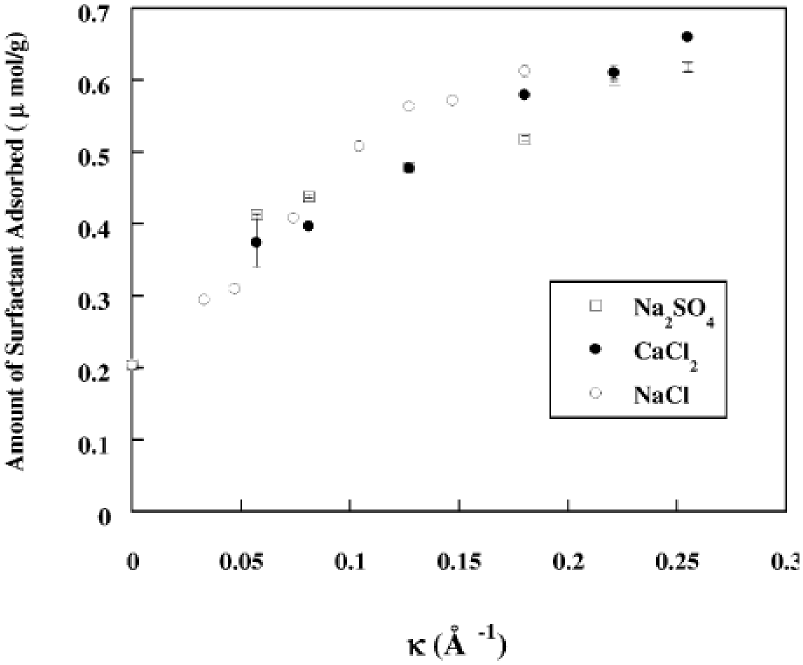

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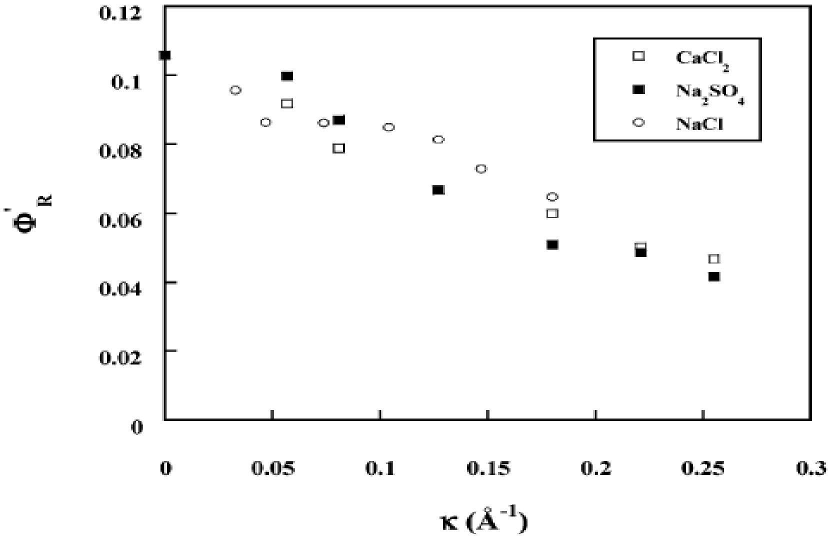

Fig. 10: Variation of reduced potential energy ($\Phi_R^{'}$) of C_{14}PB as a function of Debye-Hückel parameter (κ). The initial concentrations of C_{14}PB were 0.5 mM, and the equilibrium time was taken for 1 hr. at 25 °C [43].

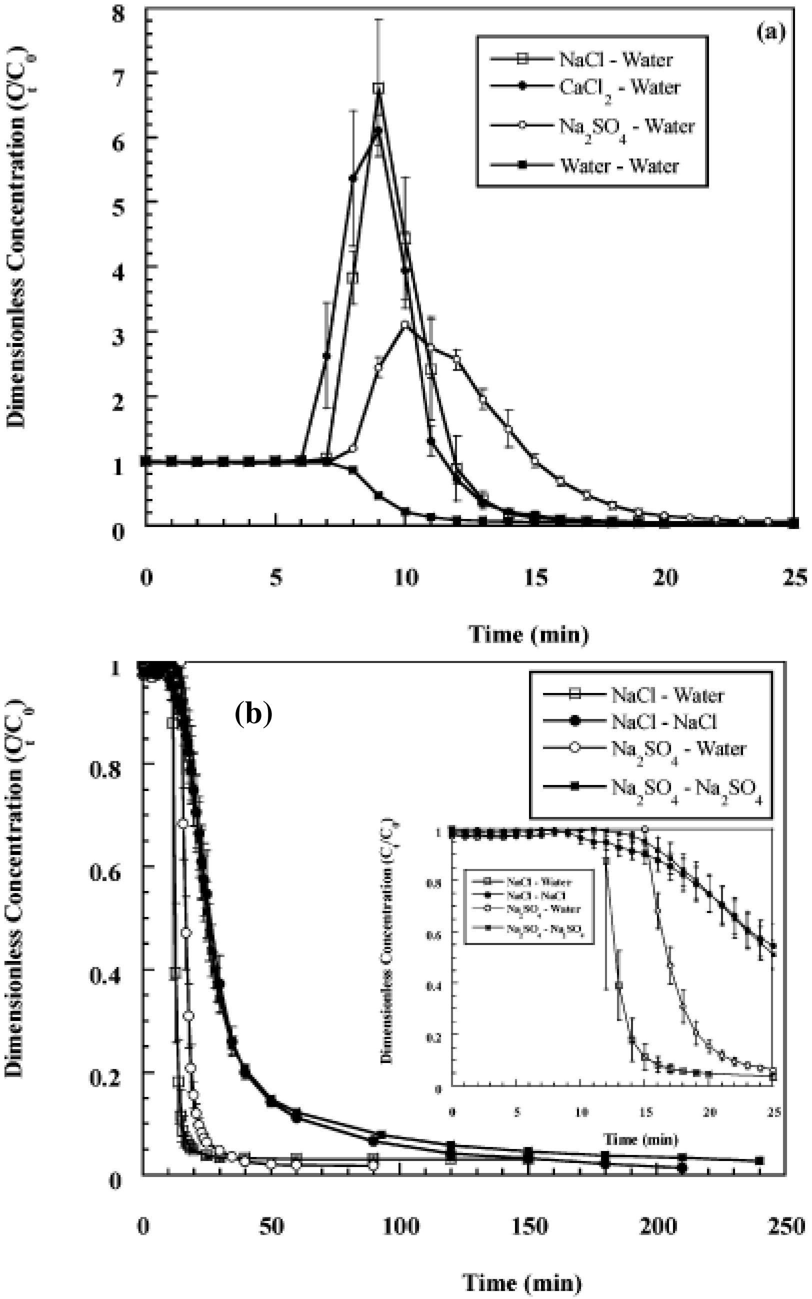

Fig. 11: (a) Desorption of C_{14}PB when eluted with pure water after adsorption at 0.5 mM inlet concentration of C_{14}PB in the presence of electrolytes (The concentrations of NaCl, $CaCl_2$, and Na_2SO_4 used were 100 mM, 50 mM, and 50 mM, respectively). For simplicity, the data are labeled by the solutions used in the adsorption-desorption sequence. (b) Desorption of C_{14}PB when eluted with pure water and in the presence of electrolytes (excluding the peak). Inset shows the same plot at a smaller time scale. Experiments were carried out at 25 °C [43].

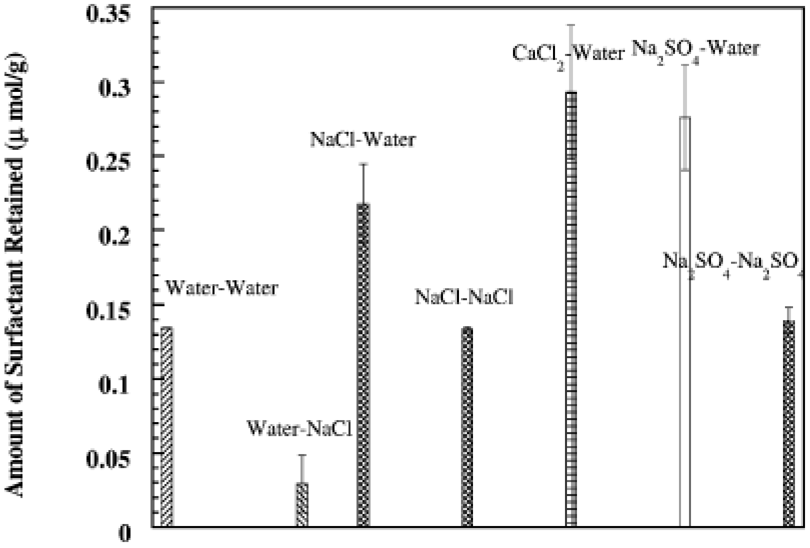

Fig. 12: Amount of $C_{14}PB$ retained in the sand column after desorption under different electrolyte conditions at 25 °C. The adsorption was performed at 0.5 mM inlet concentration of $C_{14}PB$ in the presence and absence of electrolytes [43].

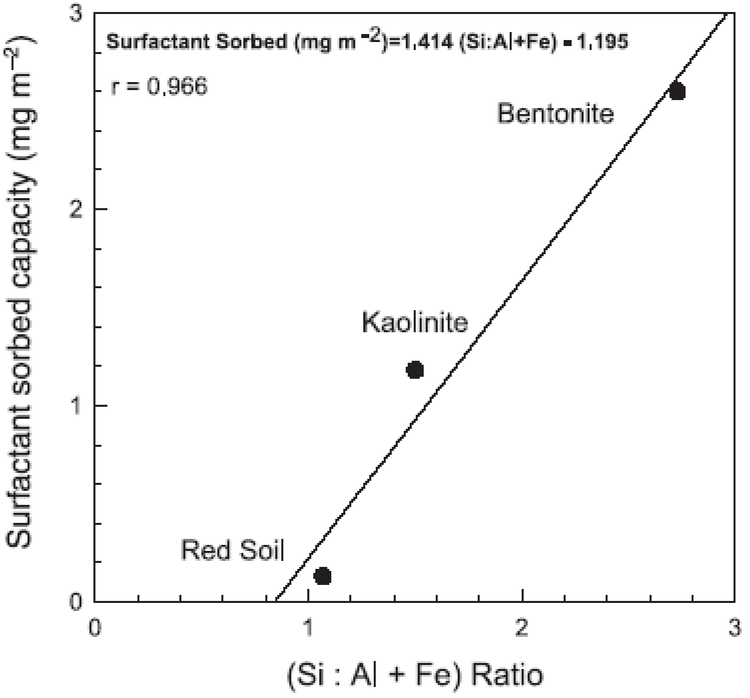

Fig. 13: Correlation between Si:(Al + Fe) ratio and A_9PE_{10} sorption capacity [71].

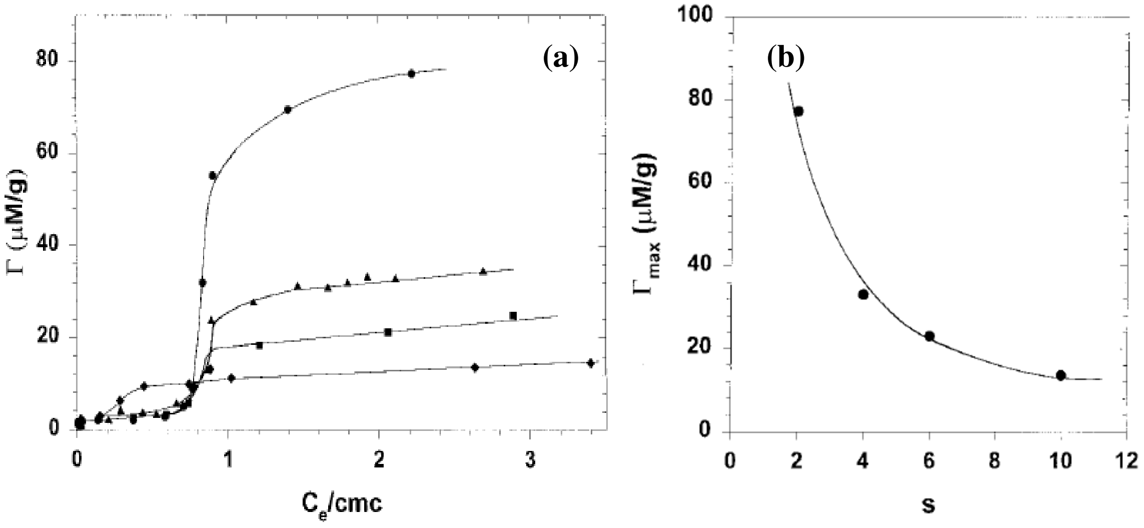

Fig. 14: (a) Adsorption isotherms of 12–2–12 (●); 12–4–12 (▲); 12–6–12 (■); and 12–10–12 (◆) on silica at 25 C. (b) Variation of the maximum amount of adsorbed surfactant with the spacer carbon number *s* [112].

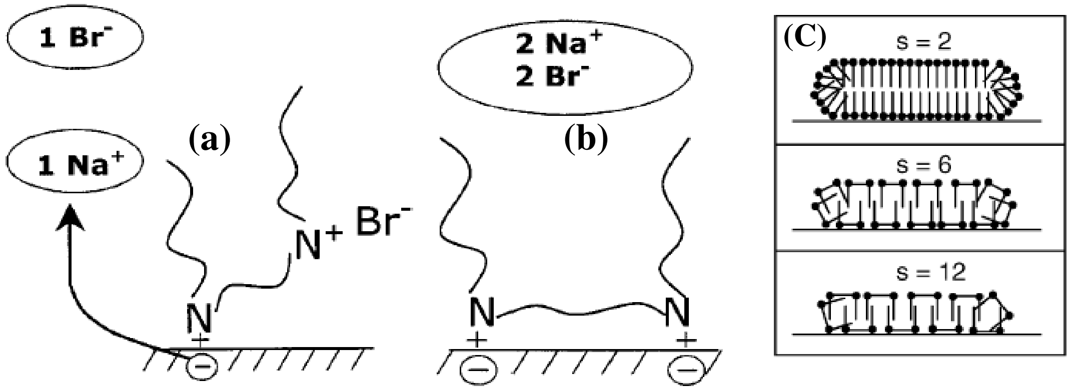

Fig. 15: Schematic presentation of the adsorption of (a) 12-2-12, (b) 12-10-12 dimeric surfactants onto silica during the ion-exchange adsorption step [115], and (c) variation in the adsorbed surfactant layer as the spacer size is increased [111].

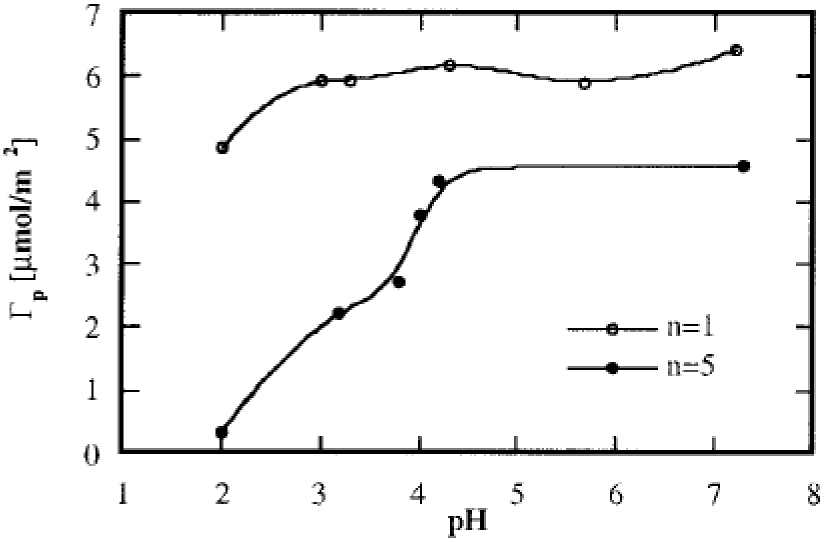

Fig. 16: Plateau surface excess (Γ_p) of $C_{12}N_1CO_2$ and $C_{12}N_5CO_2$ as a function of pH. The measurements were performed at a bulk concentration of 4 CMC (pH ≈ 7) [123].

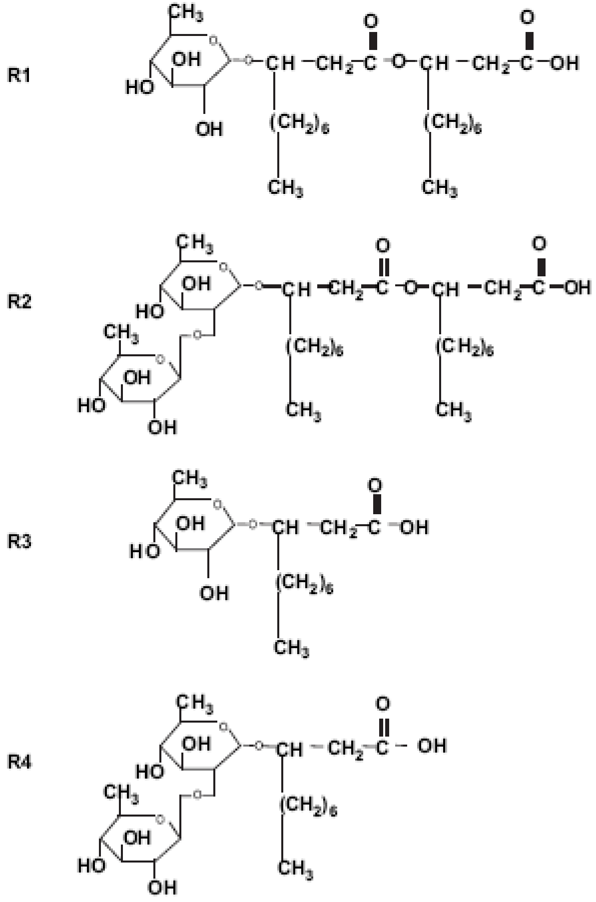

Fig. 17: Structure of four different rhamnolipids produced by *Pseudomonas aeruginosa* [20].

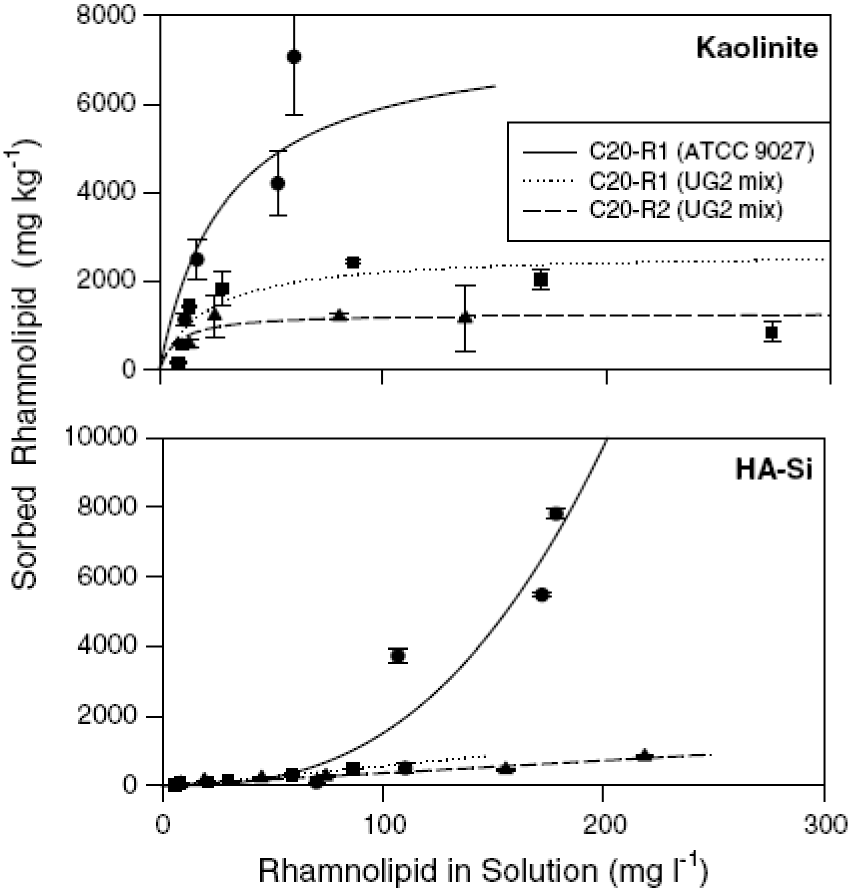

Fig. 18: A comparison of the sorption of R_1 alone (from ATCC 9027) with R_1 when it is in a R_1/R_2 mixture (from UG2) by kaolinite, and humic acid-coated silica (HA-Si). For ATCC 9027, the C20-R_1 form comprises 80% of the rhamnolipids. For UG2 mixture, the C20-R_1 and C20-R_2 forms comprises 25% and 55% respectively [132].

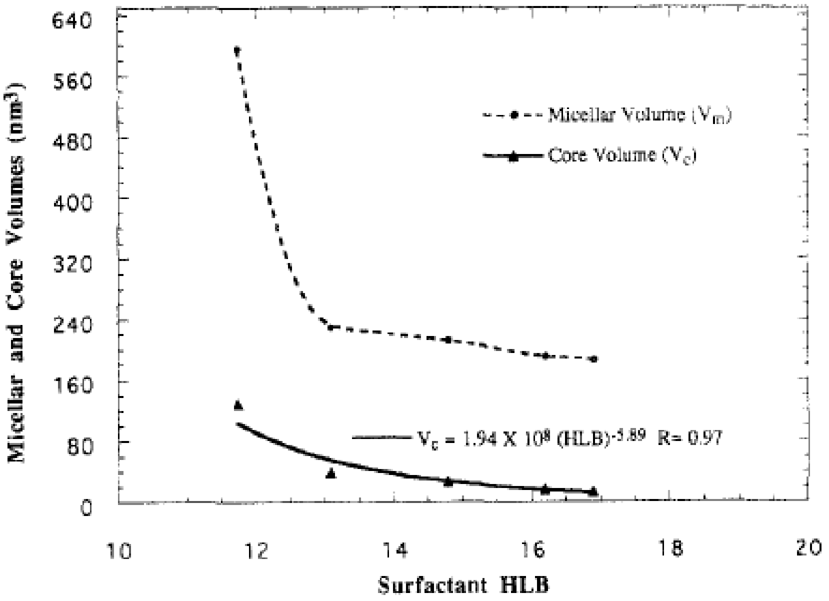

Fig. 19: Effect of surfactant HLB on total and core volumes of dodecyl alcohol ethoxylate micelles in dilute solutions at 25 ° C [145].

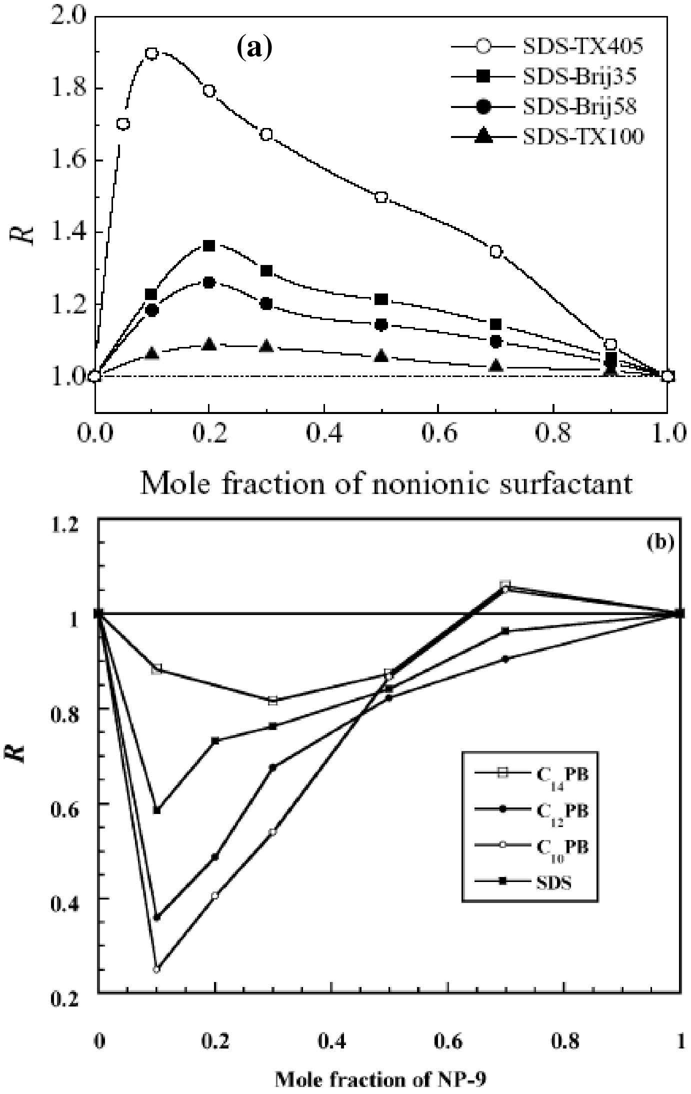

Fig. 20: Deviation ratios (*R*) as a function of the solution composition of nonionic surfactants in different mixed surfactants (a) solubilization of pyrene [161], (b) Solubilization of naphthalene [105].

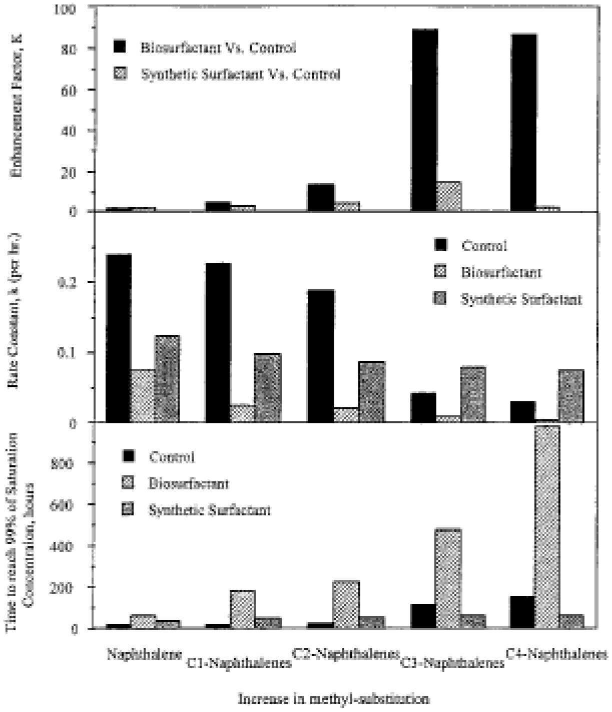

Fig. 21: Aqueous solubility-enhancement factor (*K*), first-order rate coefficient (*k*), and time to reach 99% of the saturation concentration for the naphthalenes family, as calculated by optimizing the first-order saturation model [193].

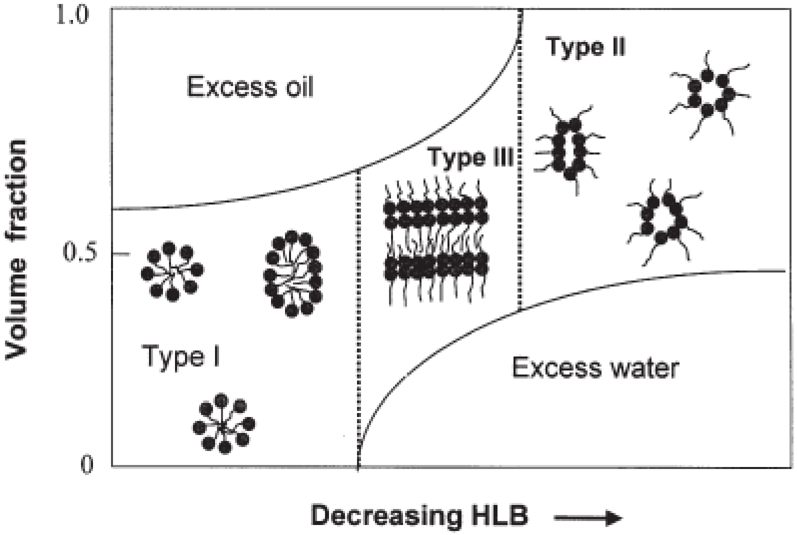

Fig. 22: Typical phase behavior of microemulsion showing the transition from oil in water (type I) to bicontinuous structure (type III) and water in oil structure (type II); initial volume ratio of oil to water = 1:1 [197].

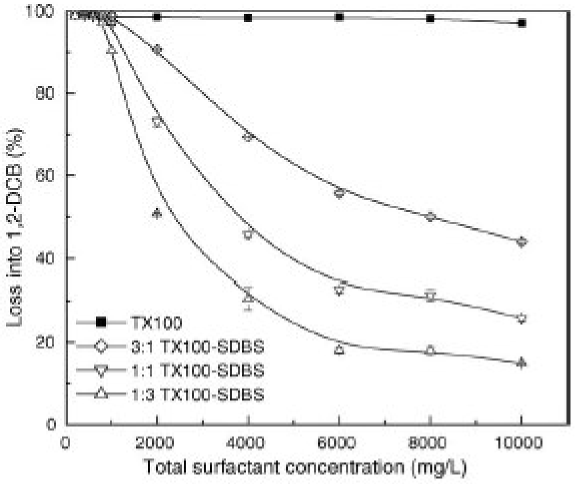

Fig. 23: TX100 losses into 1,2-DCB organic phases vs. total surfactant concentration at 1:40 phase ratio of 1,2-DCB: water (v/v) [164].

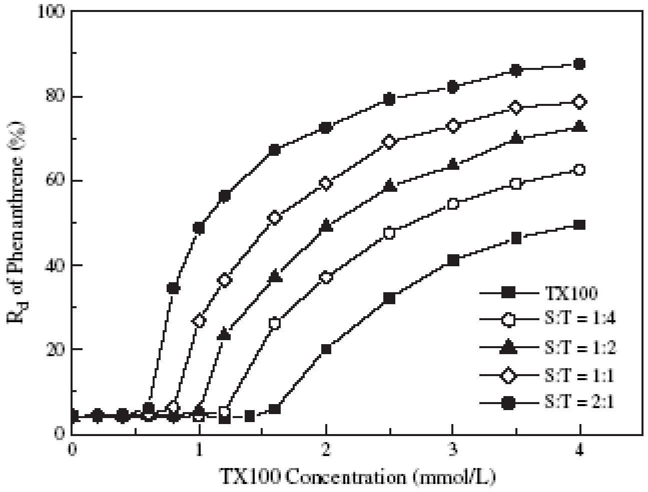

Fig. 24: The desorption percentage (R_d) of phenanthrene by different surfactant systems with various mole ratios of SDS (S) to TX100 (T) [265].

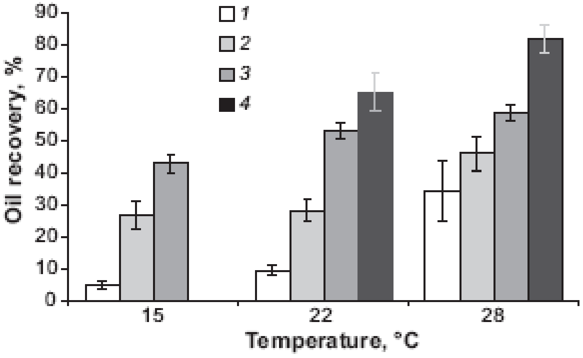

Fig. 25: Biosurfactant-enhanced oil recovery from the model soil at different temperatures. Surfactants used: (1) water (Control); (2) Tween 60 (synthetic surfactant); (3) Rhodococcus biosurfactant produced on ndodecane; (4) Rhodococcus biosurfactant produced on n-hexadecane [268].

Fig. 26: In situ flushing system at the pilot site [278].