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Chapter

Surfactants and Their Applications for Remediation of Hydrophobic Organic Contaminants in Soils

Roger Saint-Fort

Abstract

Soil contaminated with ubiquitous hydrophobic organic contaminants (HOCs) is a worldwide recurring concern arising from their indiscriminate disposal, improper management, and accidental spills. A wide range of traditional remedial strategies have been the common practice. However, these treatment methods have become cost prohibitive, not environmental friendly, and less accepted by society. Surfactant-enhanced remediation technology represents a cost-effective and green technology alternative to remediate such contaminated sites. Surfactant remediation technologies are conducted in-situ or ex-situ as two broad categories, or in combination. Among these technologies are soil flushing, washing, phytoremediation, and bioremediation. More applied research continues to quantify the efficiency of surfactant-enhanced mass transfer phase using a single surfactant solution while their binary blends to remove mixed HOCs in soils are also a focus of interest for research. There is a great potential to develop novel synthetic and biosurfactants that will exhibit higher biodegradability, less toxicity, higher removal efficiency, more economical and more recyclable. This work thus provides a review of the applications and importance of surfactant-enhanced remediation of soil contaminated with HOCs. Relevant environmental factors, soil properties, surfactant chemistry, mechanisms, mass transfer phase, and field designs are summarized and discussed with purposes of providing greater context and understanding of surfactant-enhanced remediation systems.

Keywords: Remediation, surfactants, soil, hydrophobic, contaminants

1. Introduction

A major environmental concern around the world is soil contamination by ubiquitous hydrophobic organic contaminants (HOCs) due to their improper management. Such contaminants pose serious environmental and health risks to the public, and can be difficult to remediate due their intrinsic complexity and their weathering. Soils contaminated with HOCs not only can be deleterious to the ecosystem, it can lead to increasing economic loss and ecological insecurity. HOCs which are largely organic in nature, are characterized by relatively low solubility, a specific density that can be greater or less than 1, nonpolar compounds and have been shown to be toxic, mutagenic and/or carcinogenic even at trace concentrations in the soils. Example of HOCs include aromatic compounds in petroleum and fuel residue, chlorinated compounds in commercial solvents, pharmaceutical chemical

wastes like trichlorophenol, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane (DDT) etc. Furthermore, many HOCs in the soil can be volatile and their behavior may engender vapor intrusions in various structures [1]. As previously reported [2] their availability for biochemical transformations is significantly affected by their large octanol–water partition coefficients ($\log K_{ow} > 2$). Even at very low concentrations, HOCs have shown to enter the food chain through various pathways and as bioaccumulating compounds, may ultimately threaten human life and other ecological receptors. Removal of HOC in soils can represent a significant challenge because such efforts can be site specific, costly, and often with limited success for its associated plumes [3]. Particular attentions to the ubiquitous deployment of surfactant-based remedial technologies indicate their ability to provide the means of great practical importance for implementing environmentally friendly remedial solutions, at low cost, and in a scientifically and engineering sound manner. Traditional framework in using surfactant remediation technologies are in-situ or ex-situ as two broad categories, or in combination. Among these technologies are soil flushing, washing, and bioremediation.

The in-situ remedial method involves remediation of the contaminated soil matrix without excavating the contaminated soil. This approach is generally considered less disruptive to the land ecosystem, may require multi-stage of operation, highly affected by soil physical properties and characteristics, and the time required to achieve the remediation effect may be substantial. The long treatment time associated with in-situ remediation may make the site unusable during the remediation period. Several in-situ remediation techniques have been developed which include surfactant aided flushing techniques. In conducting in-situ soil flushing (i.e., soil washing) remediation, a low concentration of surfactant solution is passed through an in-place contaminated soil using a vertical injection or infiltration process. The surfactant solution entrains the dissolved contaminants to an area where it can be collected and removed for treatment or disposal. However, the groundwater beneath the contaminated soil may serve as the discharge point for the extraction fluids. In such instance, the groundwater needs to be treated to adhere to environmental standards and maintain strict environmental quality at the site to protect public health and ecological receptors. Following HOCs in-situ surfactant-enhanced mass transfer phase into the soil solution, phytoremediation has been applied to extract, sequester, and detoxify the contaminants [4]. Since phytoremediation capacity is species specific, using a combination of plants as remedial agents will increase the efficacy of the remedial process. A notable advantage of phytoremediation, it is scientifically referred to as green technology and low cost. However, the time required to achieve the remedial target is typically longer compared to the other in-situ remedial approaches. Surfactants are also used in performing in-situ bioremediation of HOCs. The intended goal is to increase the bioavailability of the organic contaminants through mass transfer dissolution into the soil solution matrix and direct aqueous solubility. In this review, bioremediation is defined as a process, which relies on biological mechanisms to degrade, detoxify, mineralize or transform concentration of organic contaminants to an innocuous state. Often, nitrogen and phosphorous are limited as key soil nutrients and need to be added to biostimulate the soil natural microbial biodegraders. Both phytoremediation and bioremediation in-situ techniques will be affected by climatic conditions at the site.

The ex-situ approach can be conducted on-site or off-site. It involves excavating, storing and pre-treating the contaminated soil. Then, followed by treatment and redisposition of the clean soil. Treatment aided surfactant may take place in a variety of ways. Most common approaches involve biopile, windrow, and

bioreactor. Such ex-situ practices are more preferable compared to the popular dig and dump method in which the contaminated soil is excavated and dumped in an industrial landfill. Under this widely practiced conventional approach, the contaminants are not mineralized nor destroyed and represent long term threat to human health and ecological systems [5]. Environmentally friendly and cost saving features are among the major advantages of surfactant-enhanced bioremediation offer compared to landfilling, chemical and physical methods of remediation. However, the higher costs associated with transportation and associated liabilities of moving hazardous soil, and destruction of the soil ecosystem associated with excavation summarize the main disadvantages of soil ex-situ remediation over in-situ. In some instances, ex-situ treatment is preferred as a treatment as it offers more redelopment options of the land, treatment endpoint occurs faster and often the feasibility of being used with other treatment methods.

In their common form, surfactants are a group of amphiphilic chemicals constituted by both a hydrophobic moiety (chain) and a hydrophilic moiety (head) in the molecular structure of varying length in various surfactants. In fact, the unusual properties of aqueous surfactant solutions are best ascribed to the presence of the polar or ionic head group that interacts with an aqueous environment which leads to the solvation of the surfactant via ion-dipole or dipole–dipole interactions. Surfactants (short for "surface active agents" represent a unique class of compounds with distinct chemical and physical properties. Surfactants unique molecular structure give them the ability to dramatically alter interfacial and surface properties as well as to self-associate and solubilize themselves in micelles [6].

Surfactants manufactured by petrochemical plants are known as synthetic or chemical surfactants. Those produced from biological organisms are known as natural or biosurfactants. These lead to a vast array of their practical applications in terms of health, care products, food, petroleum processing etc. Irrespective of their source, the hydrophilic head group in the surfactant molecule is considered to be the main factor responsible for their special chemistry [7]. Historically, the costs of synthetic surfactants production remain comparatively less than biosurfactants. Several health and environmental concerns arise from using petroleum-based surfactants. In this regard, they are marginally biodegradable, can pollute soil and water, may bioaccumulate in the environment, and disruption of the endocrine system. On the other hand, biosurfactants being derived from biotechnology processes, are more environmentally friendly substance and often referred to as green technology. However, like petroleum-based surfactants, natural surfactants are associated with skin irritation and allergies. Considering the vast array of surfactants molecular structure and properties, one can anticipate an increase use in a myriad of environmental application for decontamination of soil matrices. This entails that surfactants with different properties and molecular structures can be strategically selected for different soil decontamination purposes. Importantly, particular consideration should be given to determine combining various surface agents for achieving greater remedial efficiency. This work provides an examination of surfactant-enhanced remediation of soil contaminated with hydrophobic organic contaminants as well as practical and general considerations involved in their implementation.

2. Classification of surfactants

Surface active compounds are the most commonly used chemicals in everyday life. The number of different molecules of surfactants that have been manufactured must be in in the thousands and many have found practical use in society.

Unfortunately, it is somewhat surprising that surfactants, until only very recently, been explored for environmental remediation applications. Architecturally, a surfactant molecule contains a chain, the hydrophobic moiety, that can be linear or branched while the head is the polar or ionic moiety [1] (**Figure 1**). The hydrophobic is typically a hydrocarbon chain of an average of length of 12 to 18 carbon atoms and may involve an aromatic ring. For the purpose of this review, surfactants are divided into four main categories depending on the nature of the polar moiety as depicted in **Table 1** [1]. An in-depth discussions of surfactants chemistry and structure are presented elsewhere [6–8]. Furthermore, there are a number of review of publications available for surfactants use in specific industries [9]. A summary of basic information of various surfactants that have been used for the remediation of soil contaminated with HOCs is depicted in **Table 2**.

Biosurfactants are a group of surface active agent biomolecules produced by microorganisms. It has been suggested that surface active biomolecules can be best divided into low-molecular mass molecules or higher-molecular mass polymers. An adaptation of their classification is depicted in **Table 3**.

In recent years, scientists have been working diligently at evaluating the effectiveness of various types of surfactants to degrade organic contaminants in soils. In

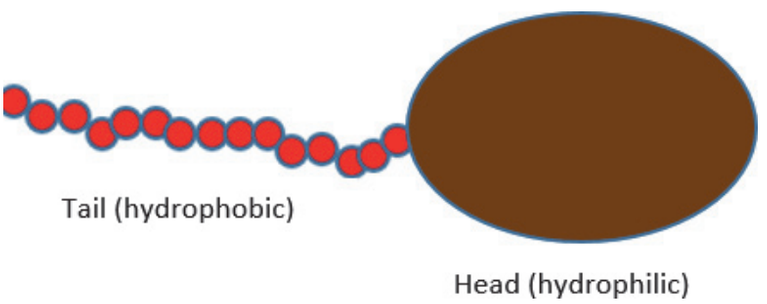


Figure 1.
Structural parts of conventional surfactant molecule.

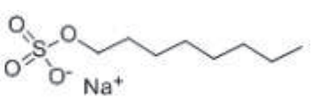
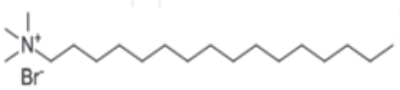
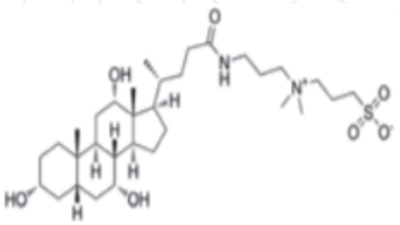
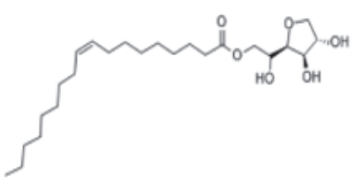
Head charge/chemical structure example	Group class
 sodium octyl sulfate	Anionic
 Cetrimonium bromide	Cationic
 3-[(3- cholamidopropyl) dimethylammonio]-1-propanesulfonate.	Zwitterionic or Ampholytic
 Span 80	Nonionic

Table 1.
Category of surfactants classification [1].

Surfactant	Name/components	Type	Molecular formula	MM (g/mol)
TX100	P-tertiary-octylphenoxy polyethyl alcohol	Noninionic surfactant	$C_{14}H_{22}O(C_2H_4O)_n(_{n\ =\ 9–10})$	625
CAPB	Cocoanut amide propyl betaine	Zwitterionic surfactant	$C_{19}H_{38}N_2O_3$	342.52
SDS	Sodium dodecyl sulfate	Anionic surfactant	$NaC_{12}H_{25}SO_4$	288.372
AOS	Alpha olefin sulfonate	Anionic surfactant	C_nH_{2n}-$1SO_3Na$ (n = 14–16)	324
SLES	Sodium laureth ether sulfate	Anionic surfactant	$CH_3(CH_2)_{10}CH_2(OCH_2CH_2)_nOSO_3Na$	288.38
Tween 80	Polyoxyethylene sorbitan monooleate	Nonionic surfactant	$C_{64}H_{124}O_{26}$	1310
Surfactin	Cyclic lipopeptide	Zwitterionic biosurfactant	$C_{53}H_{93}N_7O_{13}$	1036.3
Brij 35	Poly(oxyethylene)$_{23}$ dodecyl ether	Nonionic surfactant	$C_{12}H_{25}(OC_2H_4)_{23}OH$	1198
Saponin	Pentacyclic triterperne saponin	Nonionic biosurfactant	$C_{58}H_{94}O_{27}$	1223.3
Sophorolipid	Sophorolipid	Nonionic biosurfactant	$C_{34}H_{58}O_{15}$	706.8
Tergitol NP-10	Polyethylene, mono (p-nonylphenyl) ether	Nonionic surfactant	C_{15}-H_{24}-$O(C_2$-H_4-$O)n$	642 (average)
Calfax 16 L-35; Dowfax 8390	Sodium heaxadecyldiphenyl ether disulfonate	Anionic gemini surfactant	$C_{28}H_{40}Na_2O_7S_2$	598.72
CAHS	Cocamydopropyl hydroxysultaine	Zwitterionic surfactant	$C_{20}H_{42}N_2O_5S$	422.62
APG	Alkyl polyglucosides	Nonionic biosurfactant	$C_nH_{2n}O_6$	320–370

Table 2.
Basic information of surfactants used in soil remediation of HOCs.

this section, the classification and discussion of surfactants will be more specifically focused on surfactants that have practical relevance in the remediation of soil contaminated with HOCs.

2.1 Ionic surfactants

The family of ionic surfactants is comprised of cationic, anionic and zwitterionic surfactants. They have been applied successfully for the mass transfer solubilization and removal of a variety of HOCs such as PCBs, dense nonaqueous phase liquid (DNAPLs), light NAPLs, BTEX in different soil types. Many literature documents their success in laboratory scale testing and from site-specific soils at pilot or full scale [8–12]. Interest in developing more effective (higher performance/cost ratio) and less toxic surfactants formulation has led to the emergence of Gemini surfactants. It has been reported that the surface active of Gemini surfactants could be of a several order of magnitude greater than conventional surfactants [13]. They are

Biosurfactants class		
Microorganisms origin		**Photogenic origin**
Low molecular mass	**High molecular mass**	
Glycolypids: Conjugates of fatty acids and carbohydrates. Most common biosurfactants: trehalopids, Sophorolipids, rhamnolipids. *Burkholderia plantarii.* Producing microorganisms: *Mycobacterrium, Arthrobacter spp, Pseudomonas aeruginosa*	**Polymeric biosurfactants:** Typically consists of three to four Repeating sugars with fatty acids attached to them. Most common biosurfactants: emulsan, liposan, alasan Producing microorganisms: *acinethobacter calcoaceticus, candida lipolytica*	Saponins, lecithins, soyprotein, lactonic, soybean oil, glycolipid, Sunflower seed
Lipopeptides and lipoproteins: Consist of a lipid attached to a polypeptide chain. Most common biosurfactants: surfactin and lichensyn Producing microorganisms: *Bacillus sp.*	**Particulate biosurfactants:** Can be extracellular vesicles and whole microbial cell. Most common biosurfactants: vesicles, whole microbial cells. Producing microorganisms: *acinetobacter calcoaceticus, pseudomonas marginalis, cyanobacteria*	
Phospholipids, fatty acids and neutral lipids: Length of hydrocarbon chain in their structures determines the hydrophilic and hydrophobic balance. Most common biosurfactants: corynomycolic acid, phosphatidylethanolamine Producing microorganisms: *Rhodococcus erythropolis, corynebacterium lepus*		

Table 3.
Biosurfactants classification (adapted with permission from [1]).

used to describe dimeric surfactants which are surfactants that have two hydrophilic (chiefly ionic) polar groups and two hydrophobic chains on each surfactant molecule (**Figure 2**). These twin parts of the surfactant are linked through a spacer of varying link [14]. Gemini surfactants offer a number of superior properties when compared to conventional ionic surfactants. These advantages can be best

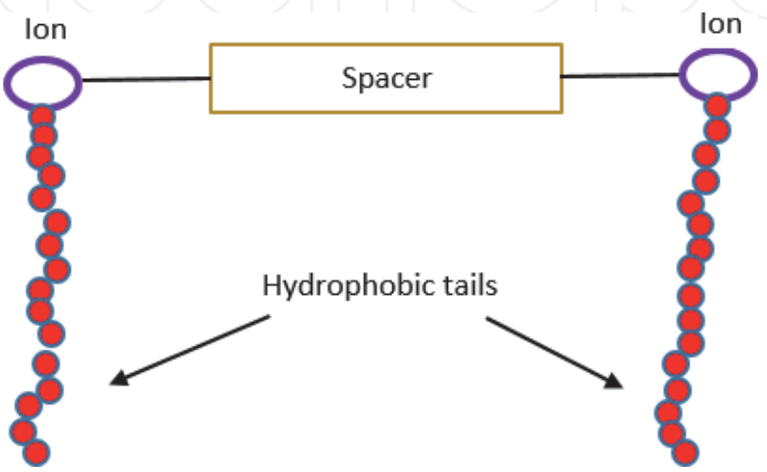


Figure 2.
Illustration of a gemini surfactant.

summarized as lower concentration requirement for solubilizing HOCs, higher aggregation at significantly lower concentration, superior wetting agent, surmount hard-water tolerance effect on mass transfer into soil solution and increased surface activity (C_{20}).

2.2 Nonionic surfactants

Nonionic surfactants are a group of surfactants that hardly dissolve in water, are neutral, and do not have any charge on their hydrophilic end. Their polar portions are typically made up of oxygen-containing groups. Nonionic surfactants solubilize in aqueous phase through hydrogen bonds formation of hydrophilic moieties with water. As the temperature is raised, it reaches the point at which large aggregates of the nonionic surfactant separate out into a distinct phase. There are several properties of nonionic surfactants that make them more suitable candidates to use in soil remediation of HOCs compared to ionic surfactants. Nonionic surfactants tend to have low toxcity, more biodegradable, more cost-effectiveness, low susceptibility to aggregate clay minerals, and low CMC. In the context of this review, toxicity is the measurable adverse effect that a surfactant will have on the soil microorganisms, while biodegradability refers to the ability of the soil microorganisms to destroy the surfactant. The literature abounds with scientific reports that document the wide application of nonionic surfactants for site-specific contaminated by a variety of HOCs [15–18].

2.3 Biosurfactants

Recently, there has been significant research interest in developing and investigating cost-effectiveness production of biosurfactants with unique properties and potential wide applications. One germane challenge that environmental scientists faces in the application of synthetic surfactants-enhanced soil remediation is their toxicity and biodegradability in the environment. It is noted that the environmental applications of biosurfactants has been gaining rapid interest and acceptance in the field of surfactant-enhanced soil remediation. This is due to their attractive physicochemical properties, low toxicity, high biodegradability and relative ease of preparation make these surface active biomolecules suitable candidates for soil remediation.

3. Classification of soil matrices

3.1 Laboratory method

Investigation of contaminated soils requires determining their physical properties for their classification. To this effect, soil classification can be approached from the perspective of the soil texture and organic matter content. The co-influence of both characteristics will have significant impact on the behavior of contaminants and surfactants when performing surfactant-enhanced soil remediation. Such impact is demonstrated through sorption and desorption, bioavailability, mechanism of interactions, contaminants leaching and fate in the soil. Most soils consist of a combination of sand, silt and clay and their range in size is reported in **Table 4**. Depending how much clay, sand, and silt that are present, the soil is given a name. The textural class of a soil is determined by the percentage of sand, silt, and clay. Soil texture determination begins by segregating the fine earth from the rock fragments. Fine earth refers to soil fraction that passes through a #10 sieve. It includes

Particles name	Particle diameter (mm)
Very coarse sand	2.0 to 1.0
Coarse sand	1.0 to 0.50
Medium sand	0.50 to 0.25
Fine sand	0.25 to 0.10
Very fine sand	0.10 to 0.05
Silt	0.05 to 0.002
Clay	< 0.002

Table 4.
Size range of soil particles.

all particles smaller than 2 mm in diameter. Sand, silt, and clay particles are components of fine earth. These three are called the separates of the fine earth. The soil textural triangle (**Figure 3**) is a representation of the mineral content of a soil in various combinations of clay, silt, and sand. The most common method for determining soil texture is the hydrometer method. According to this method, the soil separates are dispersed with solution of sodium metaphosphate (Calgon), blended and the density of the suspension measured at various time intervals. After dispersion, the amount of each particle group (sand, silt, clay) are determined by using a hydrometer. Once these percentages have been determined by the hydrometer method, the triangle can then be used to determine the soil textural class name.

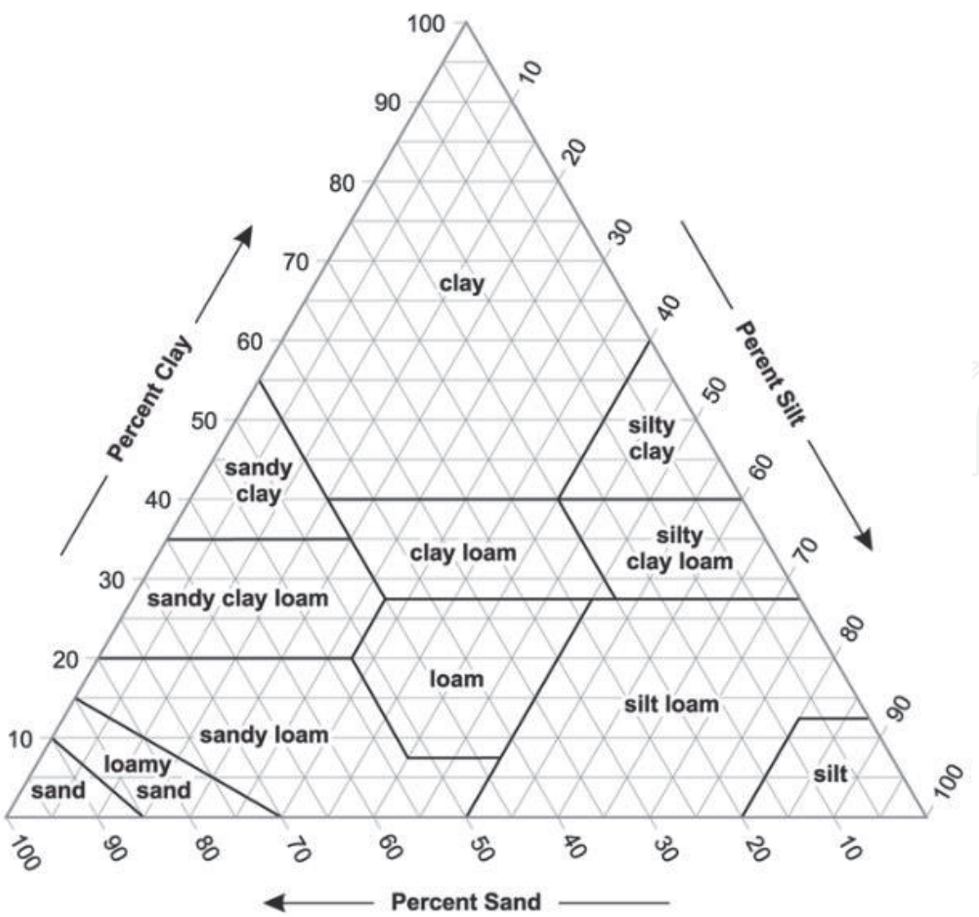


Figure 3.
USDA triangle representation of textural soil classes.

3.2 Field estimate assessment

A rough estimate of a soil textural class can be obtained by the method of feel. This method is used by environmental scientists and engineers in preliminary site reconnaissance, detailed site and contaminant characterization, sampling for transport and fate modeling, risk assessment, and in remediation selection and design. Development and execution of textural field program is relatively simple and inexpensive. In conjunction, overall project costs may be reduced as field method provides a more efficient alternative to other more complex and expensive methods. However, when dealing with a contaminated site, safety requires that one should wear gloves and avoid direct contact with contaminated soil material being assessed.

The method of feel is based on visual and tactile observations. This technique involves working a wet soil sample between the thumb and fingers to estimate the amount of sand, silt, and clay. Rarely, if ever, does a particular soil consists wholly of one soil separate or size fraction. General properties of the three major soil separates are reported in **Table 5**. The method by feel requires some practice to acquire a high level of proficiency.

Soil separate	Diameter of particles	General characteristics
Sand	2–0.05 mm	Individual particles feel gritty when the soil is rubbed between fingers. Not plastic or sticky when moist. Moist sample collapses after squeezing.
Silt	0.05–0.002 mm	Feels smooth like flour or corn starch and powdery when rubbed between the fingers. Not plastic or sticky when moist.
Clay	Less than 0.002 mm	Feels smooth, sticky, and plastic when moist. Forms very hard clods when dry. Particles may remain suspended in water for a very long period of time.

Table 5.
Basic characteristics of soil separates.

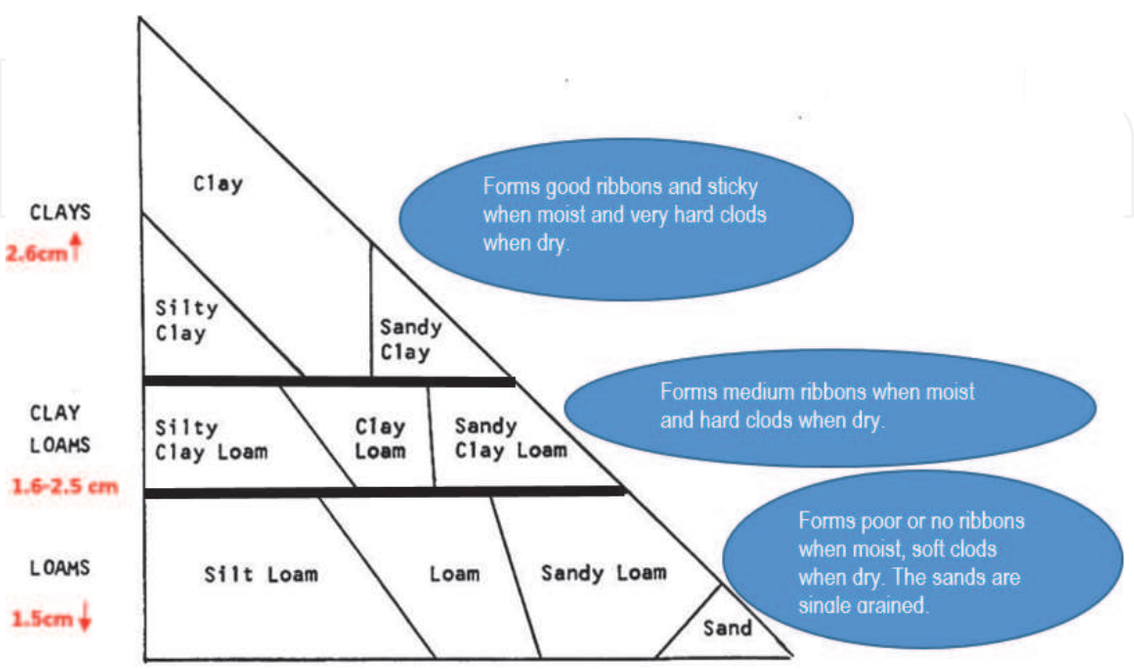


Figure 4.
Modified textural triangle for determining soil texture by the feel method.

3.2.1 Modified textural triangle

It can be used on contaminated soils when the conditions and context favor its use. Clay content is estimated by the length of the soil ribbon formed and is referred in **Figure 4**. Both, **Figure 4** and **Table 5** can be used to estimate the textural class name for a contaminated soil.

3.2.2 The unified soil classification system

The Unified Soil Classification System (USCS) established in 1942 is also commonly used in contaminated site environmental investigation. Each type of soil is given a two-letter designation based on its texture, atterberg limit and organic matter content (**Table 6**). Since every soil contains a blend of soil separates, the

USDA modified textural triangle	**USCS letter symbols**
Loam:	**ML:**
• Has a good blend of silt and clay, moderate looseness • Forms short ribbons • Sand is noticeably felt but does not dominate	As per Loam clues
Sandy loam:	**SM:**
• Forms very poor ribbons, good looseness • Enough silt and clay to give the sample body • Sand presence dominates • Moist soil does not crumble entirely after squeezing	As per Sandy Loam clues
Silt loam:	**ML:**
• Forms short, broken ribbons, average to moderate looseness • Not sticky when moist • Fells smooth, powdery	As per Silt Loam clues
Clay loam:	**CL:**
• Forms medium, broken ribbons, poor looseness • Noticeably plastic and sticky • A great amount of girt • Relatively hard to work between thumb and forefinger	As per Clay Loam clues
Sandy clay loam:	**SC:**
• Forms short medium, broken ribbons, moderate looseness • Feels gritty and sticky	As per Sandy Clay Loam clues
Silty clay loam:	**MH:**
• Forms high to medium, broken ribbons, moderate looseness • Feels smooth and sticky • Does not feel very gritty	As per Silty Clay Loam clues
Sandy clay:	**MH or CH:**
• Forms relatively long, broken ribbons, poor to average looseness • Feels unequivocally sandy and vary gritty • Sample very hard to work between thumb and forefinger • A lot of water is needed to wet a dry sample before it can be worked	As per Sandy Clay clues
Silty clay:	**CH:**
• Forms relatively long, broken ribbons, poor looseness • Feels very velvet smooth, very sticky, hard to break • Dry sample takes a lot of water to wet	As per Silty Clay clues

Table 6.
Tactile and observational clues related to textural classes for USCS and USDA.

possibility of soil that contains only sand or clay is not realistic. For additional information on soil classification by feel, the reader is referred elsewhere [19, 20].

4. Behavior of surfactants at soil/liquid interface

Surfactants at very low concentration can solubilize HOCs by reducing surface and interfacial tensions of the soil water solution. Surfactants will typically consist of a strongly hydrophobic group (water hating) referred to as the tail of the molecule and a strongly hydrophilic group (water loving), which is the head. Owing to the hydrophilic portion, surfactants can exhibit high solubility in water, while the hydrophobic portion causes part of the molecule to reside in an insoluble phase. Hydrogen bonding property and Van deer Waals forces between water molecules are the main reasons for preventing HOCs to form aqueous solutions in a soil system. Therefore, their mass distribution is primarily confined to the solid phase of the contaminated soil. However, at a specific, higher concentration of surfactant, commonly known as the critical micelle concentration (CMC), molecular aggregates are formed. The CMC is a specific property of a surfactant. In technical term, the CMC value represents the concentration of maximum solubility of a surfactant at 25°C in a particular aqueous soil solution. It should be noted that the effectiveness of CMC at a contaminated site may be affected by temporal and seasonal variations exhibited by the soil solution properties. It is through micellar solubilization, the process by which aggregations of surfactant monomers form micelles that HOCs canbecome solubilized. The solubilization process dictates the suitable approach in relation to remedial options and site-specific characteristics. The presence of surfactants in the soil solution will be accompanied by an interplay between the soil solution and concentration of surfactant. An adaptation of the interplay is depicted in **Figure 5**. Therefore, surface activity of surfactants should be viewed as a dynamic phenomenon. The solubilization of HOCs in the soil solution is accompanied by an increase in the Gibbs energy transfer which results in a decrease in entropy. This thermodynamic process is believed to to be the result of the breakdown of hydrogen bonding in the water molecule. Generally, the lower the CMC of a surfactant molecule in a soil system, the more stable will be the micelles and correspondingly the mass transfer process. The most commonly held view of key

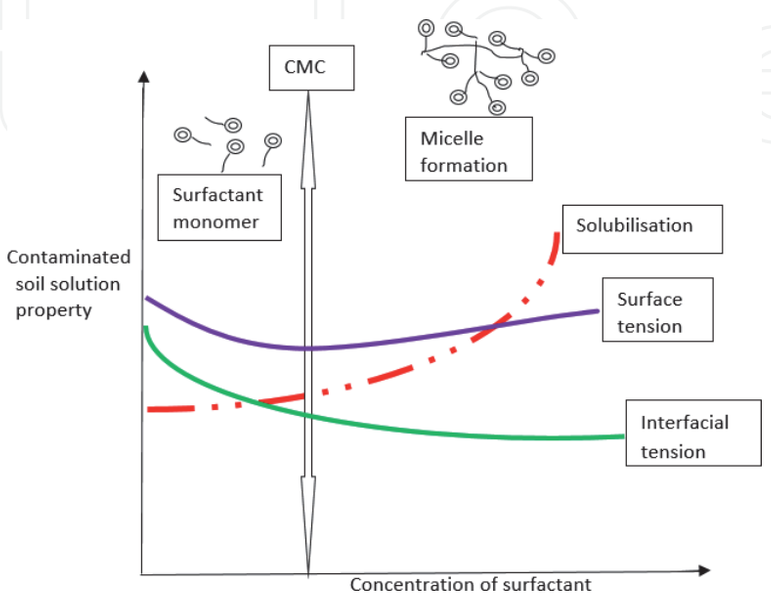


Figure 5.
Illustration of various interplays at the soil water-interface and HOCs. (Reproduced with permission from [1].)

factors affecting micellar solubilization of HOCs in soil by nonionic, ionic, and biosurfactants are the following: soil moisture, sorption, soil moisture, salinity, surfactant hydrophobic properties, texture, organic carbon, pH, and interfacial energy [1].

The effectiveness of a particular surfactant in solubilizing a specific HOC can be determined through the molar solubilization ratio (MSR) and micelle-water partition coefficient (K_{mc}). The MSR is the number of solute molecules solubilized per surfactant molecule. Namely the MSR can be calculated according to Eq. (1):

$$MSR = (S–S_{CMC})/(C_s–CMC) \quad (1)$$

where

MSR = moles of organic contaminant solubilized per mole of surfactant added to the aqueous phase

S = apparent solubility of organic contaminant at a given surfactant concentration.

S_{CMC} = CMC point of surfactant.

C_s = apparent solubility of organic contaminant at CMC (i.e., C_s > CMC).

CMC = critical micelle concentration

Studies on mixed surfactant systems competitive effects on hydrophobic contaminants solubilization has been investigated and reported elsewhere [21–23]. In mixed surfactants, the MSR for the HOC can be estimated using the MSR obtained in single-surfactant solutions assuming the ideal mixing rule [24] and can be represented by Eq. (2):

$$MSR_m = Y_1MSR_1 + Y_2MSR_2 \quad (2)$$

where

MSR_m = moles of surfactant solubilized in mixed surfactants

Y_1 and Y_2 = molar fractions of the two surfactants

MSR_1 and MSR_2 = molar solubilization ratios for the HOC

A plot of the aqueous HOC concentration solubility versus surfactant concentration, MSR and K_{mc} can be determined from the slope of the linearly fitted regression equation, respectively.

The K_{mc} can be obtained from Eq. (3):

$$K_{mc} = \frac{MSR}{(1 + MSR)V_w\, S_{CMC}} \quad (3)$$

where the variables are as previously defined.

It is suggested that the greater the values of MSR and K_{mc} the larger the solubilization capacity of the surfactant in the soil micellar solution.

The micelle-aqueous phase partition coefficient (K_m) is often used as another approach to quantify the solubilization capacity of a single surfactant [14]. Eq. (4) can be used to obtain K_m:

$$K_m = X_m/X_a \quad (4)$$

where

X_m = the mole fraction of hydrophobic compounds encapsulated in the micellar phase given by {MSR / (1+ MSR)}.

X_a = the mole fraction of hydrophobic compounds in the aqueous phase

The soil-water partition coefficient K_d is a parameter commonly used to determine the relative affinity of a contaminant for the solid phase, C_s, and aqueous

phase, C_w. The greater the K_d value means that a contaminant tends to accumulate onto the soil matrix. K_d can be obtained from Eq. (5):

$$K_d = \frac{C_s}{C_w} \tag{5}$$

The apparent soil-water partition,, K'_d, can be determined from adsorption equilibrium and we get Eq. (6):

$$K'_d = \frac{K_d + C_{sorbed}\, K_{psf}}{1 + C_{micelle}\, k_{mc}} \tag{6}$$

where

C_{sorbed} = the amount of surfactant sorbed onto the soil

K_{psf} = the partition coefficient of the HOCs in the sorbed surfactant

$C_{micelle}$ = concentration of micelle in soil solution

K_{mc} = micelle-water partition coefficient

For in-situ soil washing and surfactant-enhanced bioremediation, the solubilization potential of the HOC should be optimized. Basic information on the soil properties regarding range and distribution pattern of pH, texture, organic carbon, and salinity should be determined. Strategic adjustments in the delivery and concentration of the surfactant solution can be made.

5. Environmental risks and toxicity of surfactants

Surfactants are economically important and vital to our economy. They are a diverse group of chemicals, widely used by society and continue to be part of our daily life. However, as new surfactants are synthesized annually and surfactants production overall continue to rise, concerns about their impact on the environment and human health have been raised and studied [25–27]. Achieving high contaminant removal and mass transfer without causing any negative effects on the soil system are the primary considerations in the application of surfactants. Toxicity and biodegradability of surfactants are typically tested under different environmental conditions based on the intended application. Typically, most surfactants are not considered acutely toxic to organisms at concentrations typically encountered in the environment. Toxicity is measured in terms of effective concentration (EC_{50}) or lethal concentration (LC_{50}). EC_{50} represents the surfactant concentration (mg L^{-1}) that results in a 50% reduction in a microbial population or a biological community. LC_{50} refers to the concentration of a surfactant that causes the death of the microbial soil community or living organisms after 96 hours of exposure. Surfactants, including their metabolites, that have a toxic effect on a soil microbial community is referred to as xenobiotic surfactants. The harmful effects of xenobiotic surfactants occur through the rupture and penetration of the cellular membrane by interacting with lipids and proteins [28]. Nonetheless, the relationship between surfactants chemical structure, physicochemical parameters, biological activity and environmental impact is still ambiguous. Even less studied and understood are the comingling effects of multiple surfactants on the soil ecosystem. It can be hypothesized while a single surfactant may have minimal adverse impact on the environment. In the presence of other surfactants, it may have antagonistic effects in the soil and other terrestrial ecosystems.

In general, the two main challenges related to surfactant-enhanced soil remediation are their toxicity and biodegradability. Surfactants are considered to be

biodegradable if its molecular structure can be mineralized by the soil natural microbes through metabolic activities. On the other hand, toxicity reflects the adverse impact created by surfactants on the soil biota. Generally, the order of surfactants toxicity are biosurfactants < nonionic < anionic < cationic. Toxicity effects of surfactants may occur when a surfactant coats, sorbs onto soil particles and accumulate to toxic level. This leads to the formation of a hydrophobic layer around the soil aggregates which modifies the soil hydrophobicity. The effects are destruction of soil ability to absorb water, reduction of water infiltration into the soil. If surfactants accumulate in soils to toxic level around the plants rhizosphere, the phytotoxicity effects of the surfactant will lead to growth reduction and crops yield or death of vegetation. Most synthetic surfactants used in soil remediation are not readily biodegraded by the soil microbes and can result in toxic adverse effects on the soil ecosystem [29]. Ionic surfactants such as SDS and CATB are highly biodegradable, but exhibits high toxicity. In contrast, the nonionic surfactant Tween [30] and the biosurfactant Rhamnolipid [31] are highly biodegradable and has low toxic. Surfactants used in soil remediation and their degradation products may leach into the aquifer or enter other components of the terrestrial system. The endocrine system is a network of glands and organs that produce, store, and secrete hormones. If exposed to these substances, they would have the potential to disrupt the normal functioning of endocrine system in wildlife and human beings [32].

6. Mechanisms of surfactant-enhanced solubilization

The typical soil system will consist of five distinct phases represented by solid, solution, organic, and gaseous. When HOCs are released in a soil system, the natural dynamic processes of immobilization and demobilization, and mobilization processes occur without solubilization enhancement (**Figure 6A**). Immobilization or sorption is the dominant process and implies the removal of HOCs from the soil solution and the soil gaseous phase leading to retention on the soil solid phase. When the system becomes surfactant-enhanced, demobilization or desorption dominates and as a result, the HOC is released from the solid phase into the solution phase (**Figure 6B**). Mobilization or migration which refers to transport of HOCs in the soil porous media is also significantly enhanced by increasing solubilization HOC. These processes interact to influence surfactant-enhanced soil remediation. Studies have shown that mobilization or emulsification and solubilization are the two main mechanisms by which surfactants enhance the mass transfer solubilization of hydrophobic organic contaminants sorbed onto the soil organic matter and sediments in the soil aqueous phase. Mobilization takes place at concentrations of surfactant below CMC, whereas emulsification allows for dispersion of one phase into the other. Surfactant monomers accumulate at the soil-HOC and soil-water interfaces. This has for effect to change the wettability of the soil system by maximizing the contact angle between the HOC and the soil. A repulsion effect between the hydrophobic groups of the surfactant moiety and the rest of the surfactant molecule is caused by surfactant molecules retained on the surface of the HOC, thereby further enhancing the desorption of the contaminant from the soil particles [33]. The solubilization process occurs at concentrations above the surfactant CMC. At the same time, more sorbed HOCs are partitioned in the soil solution phase leading to more contaminant being solubilized and bioavailable. It is inevitable that a certain amount of surfactant will be sorbed onto the soil system and will be ineffective. Sorbed surfactant does not contribute to the mobilization and solubilization dynamism. Mobilization effect results in enhancing soil flushing remediation through transport and leaching of the HOC in the soil porous media and increased

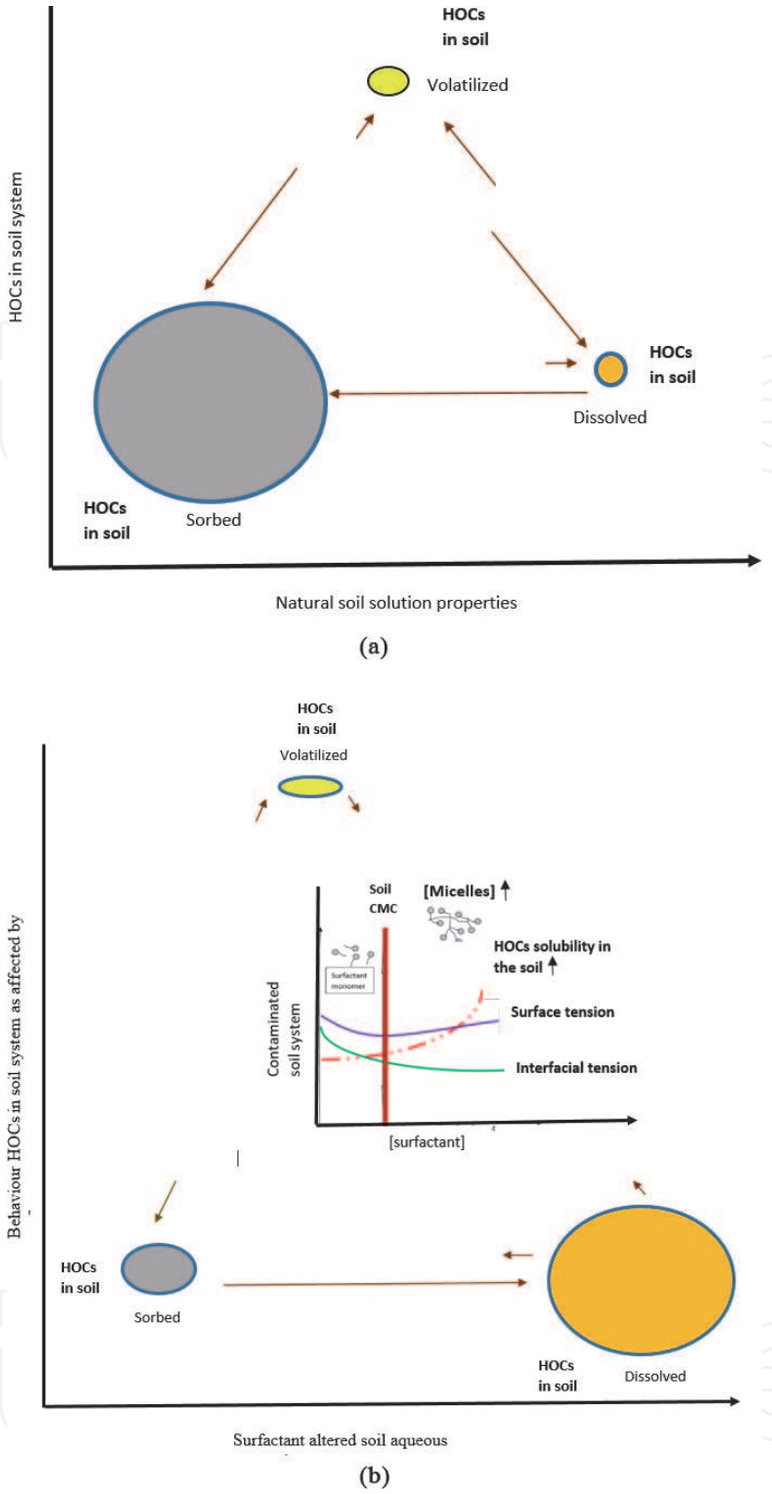


Figure 6.
Illustration of the enhancement effects of surfactant on the solubility of HOCs in a soil system: (A) no surfactant-enhancement, (B) surfactant-enhancement effects. (Arrows indicate intensity of equilibrium between HOC phases).

bioavailability for biodegradation. Basically, solubilization effect of surfactant increases the apparent solubility of HOCs in a contaminated soil.

7. Field strategy and design of surfactant-enhanced remediation

It is important to characterize and delineate the HOC in the soil in order to successfully implement a surfactant-enhanced remedial program. In this review, a

simplified overview of the main components at a specific contaminated site investigation approach is illustrated in **Figure 7**. The site investigation will begin with a site reconnaissance and inspection. Then, representative intrusive judgmental sampling as the primary approach, field screening, borehole logging as per USCS, sample collection, and analysis. A variety of field testing methods are often used by field investigators to aid in the preliminary site assessment delineation program and to facilitate selection of samples. Soil gas surveys are frequently used in the field as a means of detecting the presence of volatile organics (VOCs) in the soil. Headspace vapor analysis, this field testing method is commonly used for assessing conditions of the soil samples during a drilling and sampling program. The last stage of the soil

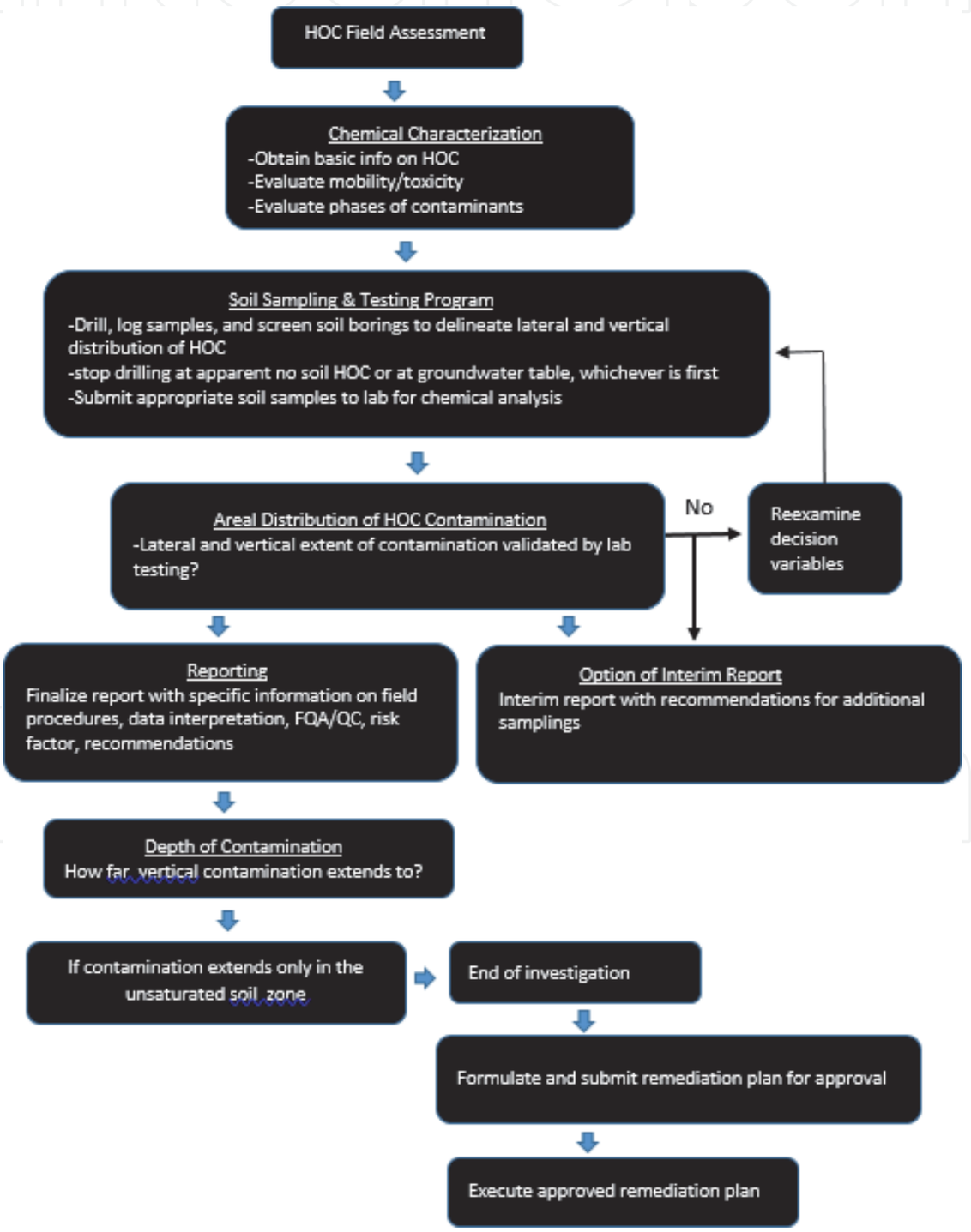


Figure 7.
General procedure of investigating HOC in soils.

investigation and surfactant-enhanced remediation program is the collection of confirmatory samples to determine whether or not the target clean-up goal has been achieved.

The mostly widely remedial methods for surfactant-enhanced remediation are in-situ flushing (washing), phytoremediation, ex-situ soil washing and ex situ bio-remediation. All methods require solubilization of the contaminant to be effective. However, in situ flushing solubilization must be accompanied with migration of the contaminant in the soil porous medium for collection, removal, and treatment. Each of these aforementioned methods is briefly discussed in the next sections.

7.1 In-situ flushing

In-situ soil flushing remediation method is a process that uses a flushing aqueous solution of surfactant to extract HOC by flooding the surface of a contaminated site or injection through vertical wells into a contaminated zone. Through continuous injection of the surfactant solution via the injection wells, contaminants partition into the flushing solution and leached into the soil. The mobilized contaminant-leaching solution flows through the contaminated zone and is extracted by downgradient extraction wells (**Figure 8**). The contaminant-flushing solution mixture is separated and treated or disposed of, or the treated effluent is reinjected. The physical and chemical properties of a soil, and the amount and type of surfactant solution are key factors in determining the efficiency of soil flushing [34]. However, some nonscientific factors including the cost of surfactant, dosage of surfactant solution, and the size of the contaminated site should be considered in order to ensure the economy of the remediation project.

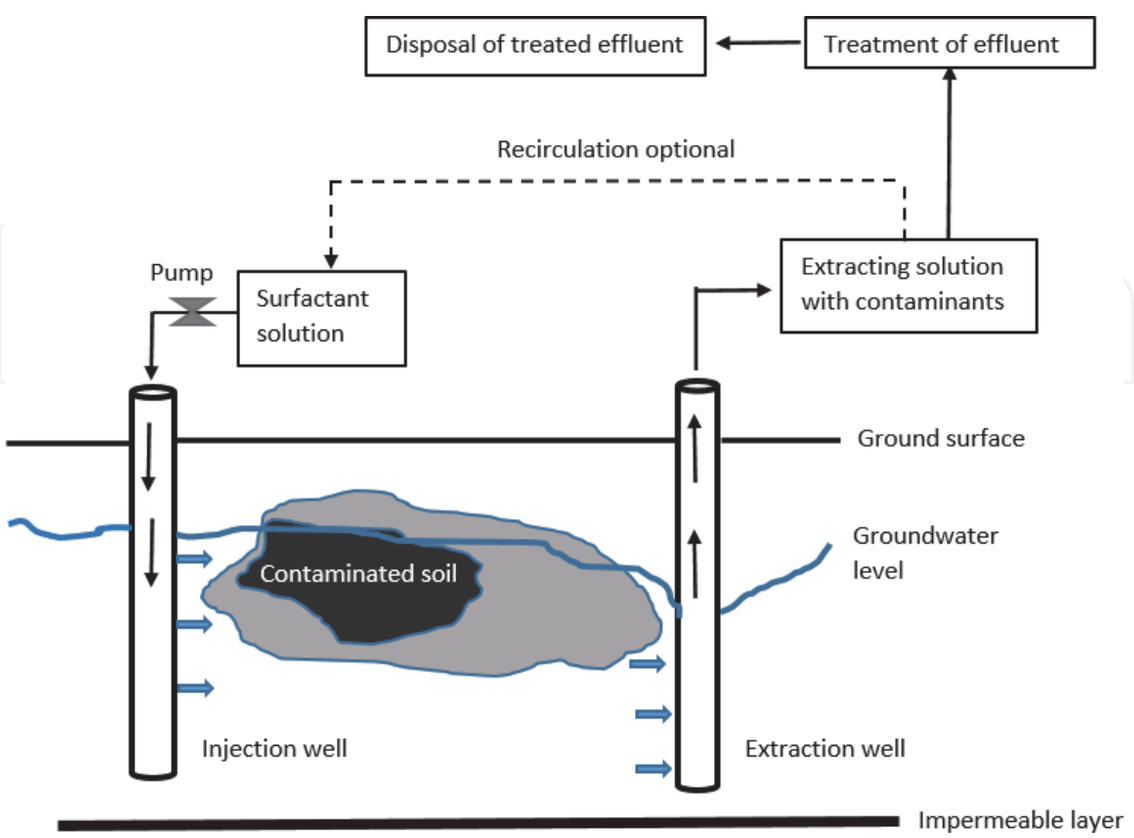


Figure 8.
Schematic of an in-situ flushing system for soil remediation.

7.2 In-situ phytoremediation

Phytoremediation remediation is a green technology technique that makes the use of plants as natural agents to absorb, degrade and/or sequester HOC over time in a contaminated soil. However, it can be slow and strategically should be used in a treatment train approach with in-situ flushing when feasible. Plants take up chemicals when their roots take dissolved chemicals and nutrients from the soil aqueous solution and additionally, HOC can be biodegraded by micro-organisms found in the plants rhizosphere. Efficacy of phytoremediation will depend on a combination multiple mechanisms in relation to specific plant species. The mechanisms may involve phytoremediation capacity, phytoaccumulation, phytovolatilization, rhyzodegradation, and phytodegradation. Crucial is optimizing surfactant-enhanced mass transfer of sorbed HOC in the aqueous soil solution particularly in the presence of multiple contaminants. Various contaminants may have different affinity for the soil sorbing sites which in return will affect the strength and mechanism of retention. When choosing plant species for a phytoremediation project, several relevant factors should be examined including type of plant root system, above ground biomass, depth of roots penetration, toxicity tolerance to the contaminants and surfactant, plant hardiness, depth of vertical contamination, adaptability to prevailing climatic conditions, resistance to diseases and pests, plant growth rate, nutrients requirement, and time required to achieve the desired level of cleanliness.

7.3 Ex-situ soil washing

Ex-situ soil washing is a mechanical process that involves delineating the areal extent of contamination, excavating the contaminated soil, pretreat it as necessary and then treat it with a surfactant solution. The soil washing can be performed in batch or continuous modes. The main steps are schematically depicted in **Figure 9**.

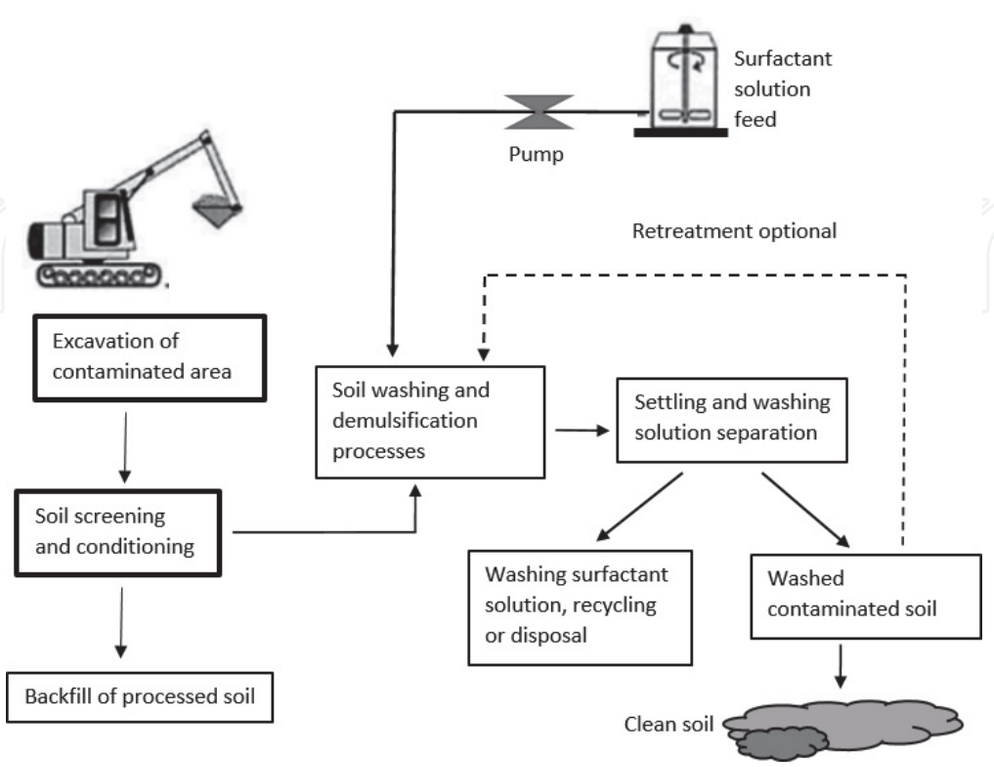


Figure 9.
Schematic diagram of ex-situ soil washing.

In practical term, ex-situ soil washing is considered a time-efficient and all-around technique, and a media transfer technology. It allows to treat a broad range of contaminant types and concentrations. Removal of coarse fractions is a key step and they can be reused on site as clean fill. However, there is a general held view that this technique is only cost efficient for coarse and granular soils where the clay and silt content make up less than 30% of the soil matrix. Factors that may limit the effectiveness and applicability of this method include effective removal of HOC sorbed onto clay-size particles by a surfactant, high soil humic content, and ambient temperature at treatment time.

7.4 Ex-situ surfactant enhanced bioremediation

Ex-situ surfactant enhanced bioremediation method refers to the biostimulation of soil natural biodegraders and increasing contaminant bioavailability. Two main prerequisites for biodegradation to take place are carbon source as electron donors and nutrients, as amendment. HOC contaminants in soils exhibit no or very low solubility at all and thermodynamically tend to partition to the soil solid phase. The concomitant effect is the level of hydrophobicity displays limits dissolved mass transfer phase and bioavailability, thereby limiting its biotic degradation in the soil system. Optimizing nitrogen and phosphorous status in the contaminated soil can have direct impact on contaminants biodegradation and microbial activity. This technique can be performed in various configurations which include windrow and various types of bioreactors. The general procedure of an ex-situ soil bioremediation is illustrated in **Figure 10**. Regardless of the system configuration and design emphasized, the treatment process must be optimized. Aqueous slurry conditions range from 20 to 40% w/v and should be not toxic to the soil microbial population. The slurry bioreactor sometimes may operate in sequencing batch reactors to achieve a desired treatment train objective (**Figure 10**). In this regard, dehalogenation conducted under anaerobic conditions is a prerequisite prior to

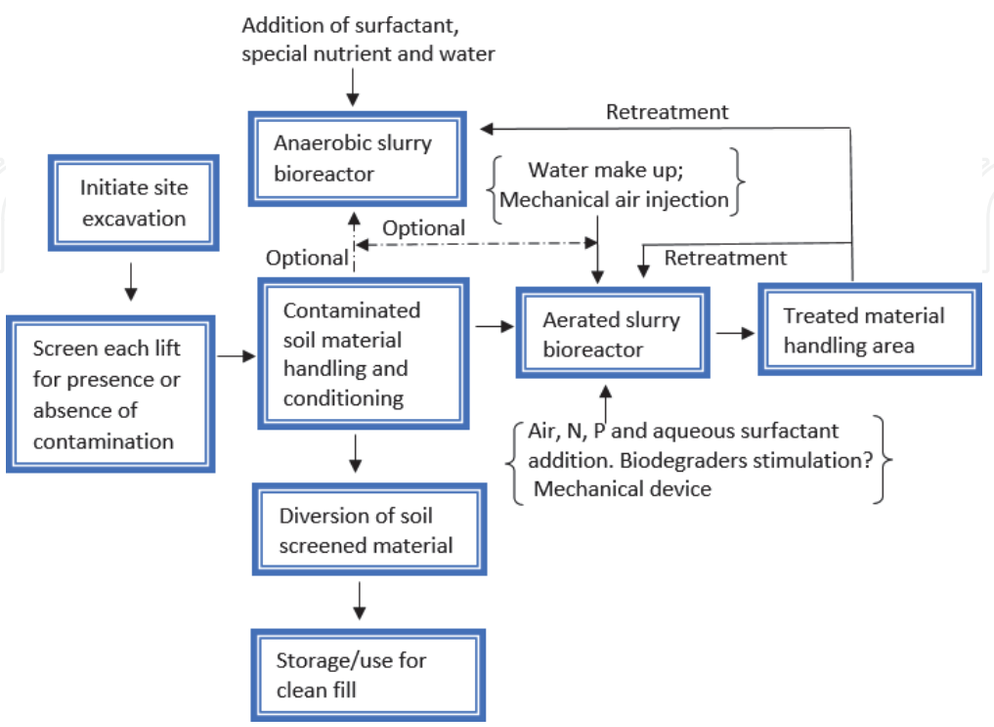


Figure 10.
Illustration of a typical batch sequencing slurry bioreactor (adapted with permission from [1]).

aerobic treatment. If dehalogenation is not required, the biodegradation treatment process can be performed under aerobic conditions only. Aerobism can be maintained during treatment by performing slurry mixing with mechanical or pneumatic devices in a rather intermittent than continuous mode. Mechanical mixing homogenizes the contaminant in the slurry bioreactor. A matrix summary of critical success factors for ex-situ surfactant enhanced bioremediation can be found elsewhere [1].

8. Mixing surfactants for their enhancement effect

Remediation of contaminated with mixed HOCs is generally very challenging and compounded due sorption on the soil matrix and different solubility properties. The strategy of mixing different classes of surfactants is to achieve a synergistic solubilization effect for the extracting solution. For example, when ionic and non-ionic surfactants are combined, the mixed surfactants solution results in a stronger solubilization effect than single surfactant solution. The reason is that nonionic surfactants diffuse the ionic surfactants and to some degree, reduce the influence of electrostatic repulsion between affecting the ionic surfactant molecules [35]. It has been reported that appropriate combination of several surfactants could inhibit the respective sorption of individual surfactant onto the soil. So, the loss of surfactant resulting from sorption is reduced and thereby increases the capability of mixed surfactants for HOC desorption in soils [36–39]. Synergistic effects of mixed surfactants in the binary blends can be best attributed to a decrease of CMC of the surfactant solutions, larger amount of available micelles formation, increase of MSR, lower polarity and higher aggregation of number of the mixture micelles.

9. The future of surfactants application for site clean-up

The potential adverse impact of HOC in soil has been a significant concern around the world for the public, policy makers, environmental regulators, and scientists. Even at very low concentrations and low solubility, these contaminants are generally considered highly toxic, mutagenic as well as carcinogenic, or can pose some other harm to humans and other ecological receptors. Costly site-specific remediation strategies have often been employed and too often with limited success. In many instances, site-specific remediation strategies are designed towards partial mass removal, plumes containment, source zone stabilization, relative to a formulated acceptable risk-management objective. The use of surfactants-aided soil remediation represents a technically attractive, cost-effective, and promising technology for reclaiming and rehabilitating contaminated sites. As a remediation technology, it is becoming well established because of its effectiveness and its promising results to retain the original nature of soil. Ideally, the primary goal of surfactant-aided remediation is to achieve 100% bioavailability and removal of contaminants with minimal xenobiotic effects and toxicity. Current research activities are very promising in this regard and continue to make more efficient synthetic and biosurfactants. However, there is an urgent need for both theoretical and empirical research on tertiary blends of surfactants-aided soil remediation and with additives mixed. More elaborative research works is also needed to elucidate the potential fate, characterization of soil and environmental interaction properties, health and ecological risks that may arise from surfactants entering the environment.

10. Conclusions

Surfactants-enhanced soil remediation represents an effective alternative to traditional remedial framework and has been successfully incorporated into various ex-situ and in-situ remediation technologies. There is a great potential to develop novel synthetic and biosurfactants that will exhibit higher biodegradability, less toxic, higher removal efficiency, more economical and more recyclable. Noteworthy are the prospects of the development and commercial production of mixed surfactants with low CMC containing additives mixed that will reduce remediation cost and increase remedial performance.

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References

[1] Saint-Fort R. Ex-situ surfactant enhanced bioremediation of NAPL impacted vadose zone. In: Larramendy, L.M., Soloneski, S., editors. Soil Contamination: Current Consequences and Further Solutions. InTech; December 2016. p. 307-327.

[2] Yang Y, Tao S, Zhang N, Zhang DY, Li XQ. The effect of soil organic matter on fate of polycyclic aromatic hydrocarbons in soil: a microcosm study. (2010) Environmental Pollution (5):1768-1774.

[3] Kohn N P, Evans N R. 2002. Phase I Source Investigation, Heckathorn Superfund Site, Richmond, California. PNNL-14088. Prepared for the U. S. Environmental Protection Agency by Battelle Marine Sciences Laboratory, Sequim, Washington; published by Pacific Northwest National Laboratory, Richland, Washington.

[4] Ashraf S, Ali Q, Zahir Z A, Ashraf S, Asghar H N. Phytoremediation: environmentally sustainable way for reclamation of heavy metal polluted soils. (2019) *Ecotox.* Environ. Safe. 174: 714–727.

[5] Song Y, Hou D, Zhang J, O'Connor D, Li G, Gu Q, Li S, Liu P. Environmental and socio-economic sustainability appraisal of contaminated land remediation strategies: A case study at a mega-site in China. (2018) Sci. Total Environ. 610-611:391-401.

[6] Rosen M J. Surfactants and Interfacial Phenomena, Wiley, New York, NY, 2nd Edition, 1989.

[7] Roy W R, Griffin R A. Surfactant-and-chelate-induced decontamination of soil materials: current status. Environmental Institute for Water Management Studies. Open File Report 21. The University of Alabama, AL, USA, 35487 (1988).

[8] Eljack M D, Hussam A. Extraction and solubilisation of crude oil and volatile petroleum hydrocarbons by purified humic and fulvic acids and sodium dodecylbenzenesulfonate. (2014) J. Environ. Sc. Health. A. 49: 1623-1630.

[9] Tang C F, Lian X J. Removal of diesel from soil using Rhamnolipid and sodium dodecyl sulfolane. (2013) Appl. Mech. Mater. 361-363:875-878.

[10] Peng S, Wu w, Chen J. Removal of PAHs with surfactant-enhanced soil washing: Influencing factorsand removal effitiveness. (2011) Chemosphere 82:1173-1177.

[11] Gitipour S, Narenjkar N, Farvash E S, Asghari H. Soil flushing of cresols contaminated soil: application of nonionic and ionic surfactants under different pH and concentrations. Journal of Environmental Health Science and Engineering 12:47.

[12] Liu F, Wang C, Liu X, Liang X, Wang Q. Effects of alkyl polyglucoside (APG) on phytoremediation of PAH-contaminated soilby an aquatic plant in the Yangtze Estuarine Wetland. (2013) Water, Air, Soil Pollut. 224:1633.

[13] Rosen M J. Geminis: A new Generation of Surfactants. (1993) Chemtech 23:30-33

[14] Menger F M, Littau C A. Gemini-surfactants: synthesis and properties. (1991) J. Am Chem. Soc. 113:1451.

[15] Villa R D, Trovo A G, Nogueira R F P. Soil remediation using a coupled process soil washing with surfactant followed by photo-Fenton oxidation. (2010) J. hazard Mater. 174:770-775.

[16] Zheng G, Selvam A, Wong J W C. Enhanced solubilisation and desorption of organochlorine pesticides (OCPs)

from soil by oil-swollen micelles formed with a nonionic surfactant. (2012) Environ. Sci. Technol. 46:12062-12068.

[17] Pei G, Zhu Y, Cai X, Shi W, Li H. Surfactant flushing remediation of o-dichlorobenzene and p-dichlorobenzene contaminated soil. (2017) Chemosphere 185:1112-1121.

[18] Ivey G A, Beaudoin M. Case study: In-situ surfactant enhanced DNAPL recovery pilot project, Refinery site. Montreal Canada. In: FCS 2010: Federal Contaminated Sites National workshop, Montreal, Quebec, Canada.

[19] *Thien* S J. A flow diagram for teaching texture by feel analysis. (*1979*) Journal of Agronomic Education 8: 54-55.

[20] Soil Texture, on the Web, [access online] http://www.fao.org/fishery/docs/CDrom/ FAO_Training/FAO_Training/General/x6706e/ x6706e06.htm. [accessed August 20, 2021].

[21] Zhentian S., Jiajun C., Jianfei L., Ning W., Zheng S. Anionic-nonionic mixed-surfactant-enhanced remediation of PAH-contaminated soil. (2015) Envron. Sci Pollut Res. 22(16): 12769-12774.

[22] Parekh P., Varade D., Parikh J., Bahadura P. Anionic-cationic mixed surfactant systems: micellar interaction of sodium dodecyl trioxyethylene sulfate with cationic Gemini surfactants. (2011) Colloids Surface A: Physicochem Eng Asp 385(1):111-120.

[23] Mohamed A., Mafoodh, A.M. Solubilisation of naphthalene and pyrene by sodium dodecylsulfate (SDS) and polyoxyeethylenesorbitan monooleate (Tween 80) mixed micelles. (2006) Colloids Surface A: Physicochem Eng Asp 287(1):44-50.

[24] Mohamed A, Mafoodh A M. Solubilisation of naphthalene and pyrene by socdium dodecylsulfate (SDS) and polyoxyethylenesorbitan monooleate (Tween 80) mixed micelles. (2006) Colloida and Surfaces A: Physicochemical and Engineering Aspects 287:44-50.

[25] Jackson M, Eadsforth C, Schowanek D, Delfosse T, Riddle A, Budgen N. Comprehensive review of several surfactants in marine environments: Fate and ecotoxicity. (2016) Environ Toxicol Chem. 35 (5): 1077-1086.

[26] Ying G G. Fate, behavior and effects of surfactants and their degradation products in the environment. (2006) Environ Int. 32 (3): 417-431.

[27] Cowan-Ellsberry C, Belanger S, Dorn P, Dyer S, McAvoy D, Sanderson H, Ersteeg D, Ferrer D, Stanton K. **Environmental Safety of the Use of Major Surfactant Classes in North America.** Critical reviews in Environmental Science and Technology. (2014) 44 (17): 1893-1993.

[28] Volkering F, Breure AM, Rulkens WH. Microbial aspects of surfactant use for biological soil remediation. (1997) Biodegradation 8: 401-417.

[29] Ishiguro L, Koopal, L K. Surfactants adsorption to soils component and soils. (2016) Adv Colloid Interface 231:59-102.

[30] Franzetti A, Di Gennaro P, Bevillacqua A, Papacchini M, Bestetti G. Environmental features of two commercial surfactants widely used in soil remediation. (2006) Chemosphere 62:1474-1480

[31] Bodarenko O, Rahman PKSM, Rahman TJ, Kharu A, Ivask A. Effects of rhamnolipids from *Pseudomonas aeruginosa* DS10-129 on luminescent bacteria: toxicity and modulation of cadmium bioavailability. (2010) Microb. Ecol.59:588-600.

[32] Yin G G, Kookana R S. Endocrine disruption: an Australian perspective. (2002) AWA J Water 29 (6):53-57.

[33] Deshpandle S, Shiau B J, Wade D, Sabatini D A, Harwell J H. Surfactant selection for enhancing ex situ soil washing. (1999) Water Res. 33:351-360.

[34] Zhou Q X, Sun F H, Liu R. Joint chemical flushing of soils contaminated with petroleum hydrocarbons. (2005) Environ Intl. 31:835-839.

[35] Lee J, Yang J S, Kim H J, Baek K, Yang J W. Simultaneous removal of organic and inorganic contaminants by micellar enhanced ultrafiltration with mixed surfactant. (2005) Desalination 184:395-407.

[36] Yang K, Zhu L Z, Xing B S. Enhanced soil washing of phenanthrene by mixed solutions of TX100 and SDBS. (2006) Environ. Sci. 40:4274-4280.

[37] Zhou W, Zhu L. Enhanced soil flushing of phenanthrene by anionic-nonionic mixed surfactants. (2008) Water Res. 42:101-108.

[38] Yu H, Zhu L, Zhou W. Enhanced desorption and biodegrdation of phenanthrene in soil-water systems with with the presence of anionic-nonionic mixed surfactants. (2007) J. Hazard. Mater. 142:354-36].

[39] Liu J, Chen W. Remediation of phenanthrene contaminated soils by nonionic–anionic surfactant washing coupled with activated carbon adsorption. (2015) Water Sci Technol 72 (9):1552-1560.