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Ex Situ Surfactant-Enhanced Bioremediation of NAPL-Impacted Vadose Zone

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Additional information is available at the end of the chapter

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Abstract

This work presents a review of surfactant-enhanced bioremediation of hydrophobic organic contaminants in the soil with a focus on ex situ method. Conventional strategies of disposal methods in secure landfill and incineration have become cost prohibitive and environmentally risky and do not restore the contaminated soil, whereas chemical and physical methods have shown very limited success and can also be expensive. Traditional bioremediation pertaining to remedial technology of hydrophobic organic contaminants in soil has empirically demonstrated limited success due to their low aqueous solubility. Addition of single synthetic surfactant or biosurfactant, or in combination, has the potential to increase their mass transfer phase, hence their bioavailability. Surfactant-enhanced biodegradation represents a promising costeffective alternative to complete mineralization of hydrophobic organic contaminants in soil. In this work, the potential of surfactants on the remediation of contaminated soil in an *ex situ* approach is reviewed with considerations given to the practical aspects of field components. Surfactant-enhanced biodegradation represents a promising costeffective alternative to complete mineralization of hydrophobic organic contaminants in soil. In this work, the potential of surfactants on the remediation of contaminated soil in an ex situ approach is reviewed with considerations given to the practical aspects of field components.

Keywords: surfactant, NAPL, vadose zone, bioremediation, bioreactors, CMC, hydrophobic, soil



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1. Introduction

In recent years, improper management of non-aqueous phase liquid (NAPL) hydrocarbons such as polyaromatic hydrocarbons, petroleum hydrocarbons, as well as other hazardous substances such as creosote and coal tar, has resulted in the formation of source zone plumes, virtually recalcitrant, in the vadose zone. The impacted vadose zone containing pooled NAPL and its residual are commonly referred to as the source zone. Generally, NAPLs are hydrophobic, low water-soluble liquids with a specific density that can be greater or less than 1. Nonetheless, NAPL chemical constituents that are soluble enough in the vadose source zone architecture may travel downward because of gravitational and capillary forces to contaminate the groundwater [1]. Many NAPL compounds are volatile and their behavior in the vadose zone may cause vapor intrusion concerns. The potential adverse impact of NAPL contamination has engendered significant concerns among the public, policymakers, environmental regulators, and scientists. Even at very low concentrations, NAPL constituents are considered highly toxic, mutagenic, and/or carcinogenic or can pose some other harm to humans and other environmental receptors [2]. Costly site-specific remediation strategies are often warranted and sometimes with limited success for the NAPL source zone and its associated plumes. In many instances, remediation strategies are designed towards partial mass removal, plumes containment, source zone stabilization, relative to a formulated acceptable riskmanagement objective. Surfactant-enhanced soil bioremediation has been proven as a promising technology through both empirical studies and field applications as a result of its low cost and the lack of toxic metabolites. Traditional framework of bioremediating NAPLimpacted soil is a very difficult process because of the mass transfer dissolution limit into the soil solution matrix, sorption onto the soil matrix, toxicity of constituents to soil biota, alteration in soil matrix physical properties. These factors have made the traditional bioremediation design approach at contaminated sites ineffective. Increasing dissolved mass transfer phase is a vital prerequisite towards achieving successful biodegradation of NAPL-impacted soil. Surfactants or surface active agents represent a class of chemicals that has the ability to increase the bioavailability of NAPL constituents by acting as solubilizing agents in the source zone. An ex situ remediation design properly strategized will allow exponential optimization of biotreatment process by enhancing the native capability of the soil microorganisms and risk mitigation. This work provides a fundamental review and approach of ex situ surfactantenhanced bioremediation of NAPL-contaminated vadose zone as it pertains to an ex situ design program.

2. Architecture of NAPL in the vadose zone

Once accidentally released in the vadose zone, a NAPL will begin to create a dynamic source zone as it is contacting the soil matrix. A simplified conceptual site model (CSM) of a NAPL release in the vadose zone is shown in **Figure 1.** A NAPL heavier than water is defined as a dense NAPL (DNAPL), and if the NAPL has a density less than water, it is referred to as a light NAPL (LNAPL). In some cases, the source release may be single or a mixture of both types of



Figure 1. Simplified CSM of a NAPL release in the vadose zone.

NAPL. Irrespective, the NAPL will typically consist of multi-component of chemical compounds with varying degree of solubility. **Table 1** provides examples of characteristics for DNAPL and LNAPL compounds commonly encountered at contaminated sites. When released in significant quantity, the presence of air in soil pores in the vadose zone allows a NAPL to move downward under the force of gravity expressed in the capillary and bond number without overcoming a displacement pressure [3]. Soil NAPL saturation [4] is defined as Eq. (1):

$$S_s = NAPL Volume released/Volume of Open Pore Space$$
 (1)

Fraction of the NAPL is held in place by capillary forces in the soil open pores space through which it flows. This immobile fraction under static conditions is termed residual saturation or globules. As a result, this creates a persistent source of contamination for groundwater. The relative fraction of a NAPL fluid immobilized and a continuous NAPL becomes discontinuous in a given volume of soil is termed residual saturation, R_s, which is expressed as Eq. (2):

$$R_s = (Volume of NAPL/Volume of voids)100$$
 (2)

In addition, retention capacity (R_c) [5] has also been used to describe residual saturation of the non-wetting phase in the vadose zone as in Eq. (3):

$$R_c = R_s \times \text{soil porosity}$$
 (3)

Compounds	NAPL type (D or L)*	Molecular formula	Molecular weight (g/mole)	Aqueous solubility (mg/L)	Density (kg/m³)	Vapor pressure (mmHg) @ 25°C	Viscosity (cP)
Chloroform	D	CHCl ₃	119.38	8000	1483	160	0.58
Perchloroethylene	D	C_2Cl_4	165.83	1100	1623	14	0.89
Aroclor 1254	D	C ₁₂ H ₅ Cl ₁₅	326.43	0.057	1540	7.71E ⁻⁰⁵	1800
Aroclor 1242	D	C ₁₂ H ₆ C ₁₄	261	0.200	1381	1.00 E ⁻⁰³	1350
Carbon tetrachloride	D	CCl ₄	153.82	8000	1590	90	0.91
Methylene chloride	D	CH_2Cl_2	84.93	13,000	1330	435	0.44
Naphthalene	D	$C_{10}H_{8}$	128.17	30	1140	9.44E ⁻⁰²	0.9684 @80°C
Nitrobenzene	D	$C_6H_5NO_2$	123.11	2090	1204	0.245	1.863
Anthracene	D	$C1_4H_{10}$	178.23	1.29	1250	6.56E ⁻⁰⁶	3.00-01
Nitrobenzene	D	$C_6H_5NO_2$	123.11	2090	1204	0.245	1.863
Benzene	L	C_6H_6	78.11	1840	876	95	0.75
Ethylbenzene	L	$C_6H_5CH_2CH_3$	106.17	152	866	9.998	0.669
Toluene	L	C_7H_8	92.14	520	862	21	0.59
Xylenes:	L	C ₈ H ₁₀	106.16	178	880	7	0.812
0-Xylenes				161	860	8.29	0.62
m-Xylene				162	860	9	0.61
p-Xylene							
MTBE	L	$C_{5}H_{12}O$	88.15	55,000	740	250	0.35 @15°C
Phenol	L	C_6H_6O	94.11	82,800	1060	0.40	9.7 @20 oC

Source: PubChem, Properties are typically at 20°C;

*D =Dense; *L = Light.

Table 1. Properties of select NAPL common pollutants.

Depending on the vadose zone NAPL-related characteristics and volume released, several distinct plumes may emerge. As the system strives to maintain a locale-scale equilibrium, contaminants may be transferred between phase media as environmental conditions change in accordance with equilibrium constants (**Figure 2**). In the vadose zone, the vapor and dissolved phases are significant in terms of mass transfer and transport as well as further spreading of contamination. Under most conditions in low conductivity areas into which diffusion and migration of a NAPL plume have occurred, these migration pathways can become intermittent sources of low-level contamination after the NAPL source mass has disappeared [4]. If the source zone and/or pooled NAPL is not timely and effectively risk managed, downward migration of NAPL constituents will eventually enter the phreatic zone resulting to further spreading of contamination at the site and significant additional remediation costs. The presence of moisture in the soil as well as infiltrating precipitation is required

for downward movement of dissolved NAPL contaminants. The fundamental mass transport equation for the vadose zone can be applied according to Eq. (4):

$$R (\partial C/\partial t) = D_s (\partial^2 C/\partial z^2) - V (\partial C/\partial z) - \eta C + \zeta$$
(4)

where

- 1. C = solute concentration in the aqueous solution at time t
- 2. D_s = soil moisture diffusion coefficient
- **3.** $\partial C/\partial z =$ concentration gradient
- 4. η = rate decay



Figure 2. Dynamic of chemical phases in mass distribution of NAPL in the vadose zone.

NAPL movement once it reaches the saturated zone will be a function of its density. Evidence suggests that Darcy's equation used to describe fluid movement through a permeable bed can be equally applied. Numerical models have been used to predict movement of NAPLs in porous media [5–7]. In a one-dimensional model, hydraulic conductivity variable, K, is replaced by intrinsic permeability, κ to take into consideration the varying hydraulic characteristics pertaining to a NAPL fluid [8]. The negative sign in Eq. (5) is to indicate that flow is in the direction of decreasing head:

$$V = -(\kappa \, pg \,/\, \omega) \, dh \,/\, dL \tag{5}$$

where

V = Darcy velocity (cm/s)

 κ = intrinsic permeability (1 darcy = 1 × 10⁻⁸ cm²)

 $p = density of NAPL (g/cm^3)$

g = force of gravity (980 cm/s²)

 ω = dynamic viscosity (cp) of NAPL

dh/dL = hydraulic gradient of NAPL mass

in Eq. (5), the hydraulic gradient is derived as described in Eq. (4), then Eq. (6) is expressed as:

$$dh/dI = (\beta + Q/pg) dL$$
(6)

where

 β = reference elevation

Q = atmospheric pressure.

3. Solubilization of NAPLs by surfactants

Chemical surfactants and natural surfactants (biosurfactants) are surface active agents. The first ones are manufactured by petrochemical plants, whereas the latter are produced by biological organisms. However, the majority of surfactants produced and utilized are chemicals because of economic factors. In their common form, surfactants are amphipathic molecules constituted by both a hydrophobic moiety (chain) and a polar or ionic moiety (head) of varying length in different surfactants. The chain can be linear or branched:



They tend to partition preferentially at the interface between fluid phases of different degrees of polarity and water bonding, consequently, making them the most versatile chemicals. Roy and Griffin [9] reported that the hydrophilic head group is the main factor responsible for the special chemistry of surfactants. Surfactants that are generated chemically are referred to as synthetic surfactants. They are generally grouped into various categories depending on the nature of the polar moiety (**Table 2**). The hydrophobic portion of these molecules are alkylbenzenes, alcohols, olefins, paraffin, or alkyl phenols, while the polar moiety will consist of either a sulfonate, sulfate, or a carboxylate group in the case of anionic surfactants. A quaternary ammonium group is found in cationic surfactants. The hydrophilic moiety of non-ionic surfactants is represented by sucrose, polypeptides, or polyoxyethylene groups. In contrast, biosurfactants are grouped according to the chemical composition of the different molecules representing the hydrophobic and hydrophilic moieties as well as microbial origin. Alternatives to petrochemicals and microbial generated surfactants are plant-based classified surfactants. As a natural solution for environmental remediation and daily common applications, plant-based surfactants offer the same very qualities and effectiveness that are found in a synthetic or biosurfactants.



 Table 2. Summary of chemical surfactants classification.

It has also been suggested that biosurfactants can be conveniently divided into low-molecular mass molecules or high-molecular mass polymers. An adaptation of their classification is provided in **Table 3** [10, 11].

Class type biosurfactants					
Microorganisms group		Phytogenic group			
Low mass	High mass				
Glycolipids:	Polymeric biosurfactants:	Saponins, lecithins, soy protein,			
Conjugates of fatty acids and carbohydrates.	Typically consists of three to four	lactonic, soybean oil, glycolipid,			
Most common biosurfactants:	repeating Sunflower seed				
trehalopids, Sophorolipids, rhamnolipids.	sugars with fatty acids attached to				
Burkholderia plantarii,	them.				
Producing microorganisms:	Most common biosurfactants:				
Mycobacterrium, Arthrobacter spp, Pseudomonas	emulsan, liposan, alasan				
aeruginosa	Producing microorganisms:				
	acinetobacter calcoaceticus, candida				
	lipolytica				
Lipopeptides and lipoproteins:	Particulate biosurfactants:				
Consist of a lipid attached to a polypeptide	Can be extracellular vesicles and				
chain.	whole microbial cell.				
Most common biosurfactants:	Most common biosurfactants:				
surfactin and lichenysin	vesicles, whole microbial cells.				
Producing microorganisms:	Producing microorganisms:				
Bacillus sp.	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, phosphatidylethanolami	ne				

Producing microorganisms:

 $Rhodococcus\ erythropolis,\ corynebacterium\ lepus$

Table 3. Summary of biosurfactants classification (Adapted with permission from [10, 11]).

Hydrogen bonding property between water molecules is the primary factor responsible for NAPL insolubility in water. Surfactants can solubilize NAPL constituents by reducing surface and interfacial tensions of water (**Figure 3**). Reduction in the surface tension of water may range from 70 mN m⁻¹ to less than 30 mN m⁻¹ [12], thereby increasing the wetting ability of

water. Surfactant molecule that is unable to form hydrogen bonding in an aqueous phase leads to an increase in the free energy of the system. This leads to an increase in NAPL solubilization in the water phase achieved through the formation of micelles. It has been reported that the aggregation number to form micelles is between 50 and 100 surfactant molecules [12]. Increasing surfactant concentration to above a critical micelle concentration (CMC) will lead to the formation of dynamic micelles by incorporating the hydrophobic solubilizates into the hydrophobic cores of the micelles [12]. Surfactant molecules that exist as monomers below the surfactant's CMC have minimal effects in the aqueous solubility of the system. As surfactant concentrations above the CMC threshold increase, the solubilization process of hydrophobic contaminants increases linearly with surfactant concentration. Invariably, micelle formation allows increased mobilization and partitioning of sorbed NAPL contaminants into the soil solution by lowering capillary forces. The lower the CMC value of a given surfactant in a system, the more stable will be the micelles and therefore the mass transfer process.



Figure 3. Interplay between hydrophobic contaminant solubility, surface tension, interfacial tension and micelle in the case of a specific surfactant at the core-water interface.

The capacity of surfactants to affect micellar solubilization of hydrophobic organic compounds is affected by the following factors:

• Temperature: CMC's typically increases with increase above a certain temperature as micelle formation is opposed by thermal agitation, termed the Krafft point. However, non-ionic surfactants do not show Krafft points. Consequently, increasing temperature tends to decrease their solubility. The temperature at which non-ionic surfactants begins to exhibit surface active properties loss is termed the cloud point.

- Salinity: presence of electrolytes tends to reduce repulsion forces between charged groups of the micelle and consequently inhibit CMC formation.
- Surfactant hydrophobic property: As the hydrophobicity portion of a surfactant increases, this results in a decrease in the formation of CMC. Above C₁₈. CMC appears constant. This is ascribed to coiling of the long hydrophobic moiety in the aqueous phase.
- Soil moisture content: Soil moisture level must be high enough to allow mass-transfer. Heavy soils relative to a coarse soil type will require a higher level of moisture in the system to enhance contaminant solubilization by a specific surfactant.
- Presence of other organic molecules: May affect water structuring such as to create a shift in CMC. Structure makers such as sugars are known to lower CMC, while structure breakers like urea and formamide typically will increase surfactant solubility. In a mixed surfactant mixture system, CMC may synergistically occur at a lower level than any of the CMC's of the single pure surfactants.
- Sorption: It reduces the concentration of surfactant monomers in the aqueous phase. Under such conditions will not aggregate to form micelles of colloidal-size until the sorption process is overcome through addition of more surfactant. CMC becomes more appreciable.
- pH: Depending on the nature of the surfactant and the degree of humification of the soil organic matter, CMC may be affected. Enhanced solubility of organic chemical may be observed at pH values at which soil humus and surfactant are found mostly ionized and at opposite charged.
- Interfacial energy: The interfacial tension of a given surfactant solution decreases with correspondingly increase in the surfactant monomers in a system. This leads to an attainment of a minimum free energy state. Enhanced micellar solubilization of hydrophobic organic compounds is favored.

The effectiveness of a particular surfactant in solubilizing a NAPL constituent may be represented by the molar solubilization ratio (MSR) [13] defined as expressed in Eq. (7):

(7)

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

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

CMC = critical micelle concentration

By plotting solute concentration as a function of surfactant concentration, MSR can be determined from the slope of the linearly fitted regression equation. The micelle aqueous-phase partition coefficient (K_m) is often used as another approach to quantify the solubilization capacity of a single surfactant [14]. K_m can be defined according to Eq. (8):



by $\{MSR/(1 + MSR)\}$

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

Studies on mixed surfactant systems competitive effects on hydrophobic contaminants solubilization has been investigated and reported elsewhere [15–18].

4. Mineralization of NAPL

The most widely applied soil bioremediation approach to organic contaminants involved the biostimulation of natural microbial biodegraders. Biodegradation requires a source of carbon (organic contaminant) and nutrients, as amendment. The hydrophobic organic contaminants represent the carbon source as electron donors, while nitrogen and phosphorous are essential for microbial growth for cellular metabolism. Addition of nitrogen particularly is often necessary due to heavy demands by the biodegradation process. Phosphorous is usually amended in lower concentration. Optimizing nutrient status of a contaminated soil can have direct impact on microbial activity and contaminants biodegradation. In some instances, the negative effects of high nutrients amendment with NPK on soil biodegradation especially on aromatics have been reported [19–21].

The ultimate microbial aerobic degradation process of converting bioavailable NAPL constituents in a contaminated soil matrix:



This process is commonly referred to as mineralization. The degradation process is brought about under aerobic conditions. NAPL constituents are hydrophobic organic chemicals that exhibit limited or no solubility in contaminated soils and thermodynamically tend to partition to the soil solid phase. Sorption may account for more than 95% of the total contaminant mass. As a consequence, the hydrophobic contaminant exhibits limited dissolved mass transfer phase and bioavailability, which limits its biotic degradation in the soil. Therefore, in a contaminated soil environment, biodegradation of an organic hydrophobic compound should be envisioned as a stepwise process involving contaminants bioavailability and species of biodegraders.

The use of surfactants represents a cost-effective and promising method that can enhance bioremediation of organic hydrophobic contaminants in soils. Many studies have shown that surfactants can solubilize and mobilize hydrophobic organic contaminants sorbed onto soil matrices [22–24]. Adding surfactant to a contaminated soil matrix is expected to enhance microbial degradation through mobilization or emulsification. Mobilization takes place at concentrations below CMC and the solubilization process above the surfactant CMC, whereas emulsification allows for dispersion of one phase into the other. A certain amount of surfactant in the slurry system will inevitably be sorbed onto the soil particles. Sorbed surfactant does not contribute to the solubilization and bioavailability of contaminants during treatment. The more surfactant is sorbed, the less effective will be the surfactant. Furthermore, soil hydrophobicity may increase as more surfactant becomes sorbed onto the contaminated soil matrix.

Considerations	Remarks			
Environmental factors				
Acclimation	Proper biodegraders; enzymatic adjustment for metabolic process			
Temperature	Mesophiles 15–45°C			
Oxygen	Aerobes; DO > 0.30 mg/L			
pН	Optimum range 5–9			
Nutrients	Sufficient N, P not limiting biodegraders growth; C:N:P ratio of 100:50:1			
Redox potential	Greater than 70 mV; promote aerobes			
System slurry	Optimized to promote mass transfer; 50-80% of soil water intrinsic saturation			
Metabolites	Non-toxic			
Salinity	Low inhibition of CMC formation			
Surfactant properties				
Environmental risk	Pose no risk to the environment			
Toxicity	No inhibitory effects; not toxic to any receptors			
Substrate source	Not a preferential growth substrate			
Sorption behavior	Low sorption onto soil constituents			
Effective concentration	Efficient in increasing aqueous solubility of organic compounds at			
	low concentration			
Recalcitrancy	Non-persistent; biodegradable and mineralizable			
CMC	Effective below CMC; partial micelle encapsulation of contaminant; low sequestration vis-à-vis target contaminant			

Table 4. Relevant environmental and surfactant considerations for ex situ surfactant-enhanced bioremediation.

Surfactants can enhance metabolic degradation and thereby, contaminants mineralization in the soil by two main mechanisms [25]. One mechanism involves the increase in the contaminant bioavailability for microorganisms. The second mechanism is due to interaction with cell surface resulting in the hydrophobicity increases in the cell surface allowing hydrophobic organic chemicals to interact with bacterial cells. Environmental factors and surfactant properties affecting the metabolic capability of biodegraders in the soil vis-à-vis hydrophobic organic contaminants are summarized in **Table 4**.

The role of treatability studies for *ex situ* surfactant-enhanced bioremediation of hydrophobic organic contaminants contaminated soil is vital. It will allow to derive crucial information that will serve as blueprint to optimize field operation. Typically, a treatability study will be conducted in laboratory microcosms to inform (a) on the dosage of surfactant required to optimize contaminant mass transfer, (b) on the effect of temperature on contaminant bioavail-ability as temperature may affect surfactant efficiency and microbial activity, (c) on optimum biostimulation through the addition of appropriate nutrient amendments such as N, P and other elements, (d) optimum moisture level as it will vary with soil type, (e) selection of appropriate surfactant, (f) modeling rate of contaminants degradation under varying environmental factors, (g) rate of oxygen and nutrients consumption under different environmental conditions, (h) implement bioaugmentation utilization by inoculation with acclimated bacteria strains, (i) the complimentary effects of combined bioaugmentation and biostimulation, (j) determine whether targeted level of cleanup is attainable, (k) formulation of an efficient and effective monitoring program for field treatment operation, (l) the engineering design, (m) potential surfactant toxicity and means to reduce it, (n) sorption behavior of a surfactant.

The two main strategies can be highlighted for assessing a bioremediation system performance. A material balance approach consists of extracting and quantifying residual parent compounds and monitoring partitioning in the headspace phase. The other strategy involves monitoring the system for CO_2 production. A direct correlation occurs between mineralization of the parent compound and CO_2 production.

The biodegradation during the treatability assessment may be modeled through either a firstor zero-order power rate model [26]. A zero-order reaction indicates the biodegradation of a parent contaminant in the microcosm occurs at a constant rate and independent of concentration and time. If the parent compound C is mineralized to CO_2 , the rate of disappearance of C is given by Eq. (9):

$$dC/dt = -k \tag{9}$$

integration yields Eq. (10):

$$C_t = C_o - kt \tag{10}$$

where

 C_t = parent compound present at time t

C_o = initial concentration of parent compound

k = zero-order reaction rate constant

t = corresponding sampling time.

First-order reactions have rates that depend on mass transfer of parent compound concurrent to its biodegradation, Eq. (11):



where

C = parent compound concentration

t = corresponding sampling time

k = first-order reaction rate constant integration yields Eq. (12):

$$\operatorname{Ln}(C_{t}) - \operatorname{Ln}(C_{o}) = \operatorname{Ln}(C_{t}/C_{o}) = -kt$$
(12)

where

 C_t = parent compound present at time t

C_o = initial concentration of parent compound

k = first-order reaction rate constant (time⁻¹)

t = corresponding sampling time.

Solving for concentration yields Eq. (13):

$$C = C_o e^{-kt}$$
(13)

and parameters are as defined above.

Biosurfactants may be the strategic choice for increasing contaminant bioavailability in bioreactors while minimizing toxicity to biodegraders. An examination of the literature indicates that synthetic surfactants while effective for increasing contaminant mass transfers at the recommended concentration may show inhibitorial effects on the microorganisms in the bioreactor [27, 28]. In such case, this will inhibit cell proliferation and thus the biodegradation of organic contaminants. According to empirical evidence, surfactant toxicity was found to be primarily dependent on its molecular structure, in order of toxicity, generally non-ionic <anionic < cationic [28]. Several practical approaches may be implemented to reduce surfactant

cytotoxicity in a bioreactor by considering a suitable biosurfactant as an alternative to a synthetic surfactant, adding a surfactant at concentration below CMC, using a suitable nonionic surfactants, using a suitable combination of biosurfactant and synthetic surfactant, in some instances, strategically increasing the surfactant concentration to decrease contact of biodegraders with the contaminant, prescreening for a suitable additive such as Ca and Mg as they were found to stabilize the cell membrane, thereby decreasing surfactant toxicity [29].

5. Field implementation

First and foremost, site access should be restricted to minimize human and wildlife exposure to contamination. As a contaminated site, safety should be implemented and followed at all



Figure 4. Approach to main components of implementing a field bioremediation program.

time. A site assessment and site characterization program should be conducted prior to excavating and bioremediating the contaminated soil. A site characterization will involve a more rigorous and field testing program (i.e., drilling and installing groundwater monitoring wells, chemical parametrization of soil samples, soil gas sampling). A good site assessment program should provide basic and qualitative information such as how much? When? What types of contaminants was released? It should also allow to generate site-specific information pertaining to soil physical, chemical, and biological properties critical in the success of the bioremediation program. **Figure 4** provides a simplified overview of environmental site assessment approach. The site characterization should be conducted in a phased approach. Each evolutionary phase should be designed to assess the CSM. As such, this will increase the investigation capacity to perform risk analysis.

Once the areal extent of vadose contamination has been delineated and staked out, excavation can safely proceed ahead. The excavation process should be managed to prevent any additional pollution and protect the environment and human health. Common equipment used to excavate and move soils around the site includes but not limited to: a bulldozer or dozer pushes soil with a hydraulically controlled blade. A backhoe uses a toothed bucket attached to a loom or dipper stick. Front-end-loaders are tractors equipped with buckets that can be used for excavation, lifting, hauling and dumping soil material, hydraulic excavator with primary function for digging, and articulated trucks are used as versatile hauling units.



Figure 5. Flow diagram of a typical batch sequencing slurry bioreactor.

Several bioremediation option processes can be contemplated for on-site and off-site treatment of the excavated contaminated soil material. Irrespective of the system configuration and design, process fundamentals of a surfactant-enhanced-bioremediation efficiency requirements must be optimized prior and during project implementation. Aqueous slurry conditions typically ranging from 20 to 40% w/v are one of the most important types of *ex situ* technique [30–32]. A slurry bioreactor may consist of a vessel or a lined lagoon, which is typically run in

a batch or semi-continuous operation mode. Sometimes, they may be operated in sequencing batch reactors to achieve a desired treatment train objective as illustrated in **Figure 5**. Dehalogenation under anaerobic conditions of chlorinated contaminants is initially necessary prior to aerobic treatment. When dehalogenation is not required, the treatment process can be carried out aerobically only. During treatment, slurry mixing may be performed with mechanical or pneumatic devices in a rather intermittent than continuous mode.

CSE koy yariables	Rotter suggess
Site access	Bestricted
Cite cofety	Followed at all time
Equipment	
Season	Summer, spring, fall
Volume of soil	No restriction
Working area	Sufficient for footprint needed
Characterization	All contaminants of concern
Contaminant types	Organic hydrophobic
Contaminants	Non-toxic level
Acclimation	System time-dependent
Contaminant phase	Liquid or sorbed
Anaerobic bioreactors	Critically ≤ -10 mV for dehalogenation
Redox	Critically \geq + 5 mV for mineralization
C:N:P	100:50:1
Surfactant cost	Low
Remediation cost	Competitive
Surfactant sorption	Low
Timeframe	Fast
CMC	Low
Surfactant availability	Readily
Surfactant toxicity	Non-toxic
Surfactant persistence	Biodegradability balanced with effectiveness
Encapsulation effects	Minimal on bioavailability
Mixed surfactants	Synergistic effects
Soil:liquid ratio	Optimize slurry consistency as per soil type
Public perception	Positive
Regulatory perception	Positive
Surfactant metabolite	Non-toxic
Environmental compatibility	Very good

Table 5. Matrix of CSF for *ex situ* surfactant enhanced bioremediation.

Mixing will play a critical role by increasing mass transfer rates and bioavailability of contaminants as enhanced by the presence of surfactant, provide slurry homogenization, keep solid particles in suspension, and help achieving oxygen transfer in aerobic bioreactor. In its simple design, a SB construction will consist of soil handling and conditioning area, aeration device, the bioreactor (anaerobic/aerobic) itself, drying and storage area of treated material, off-gas treatment, and chemical storage area. Air quality monitoring should be conducted at and around the site.

A matrix summary of critical success factors (CSFs) for *ex situ* surfactant enhanced bioremediation has been best summarized in **Table 5**.

6. Summary

Vadose zone contamination by NAPL hydrocarbons through either natural or industrial processes represents a worldwide concern due to its potential hazard to the environment and health impact to biological receptors. Several scientific and engineering remediation strategies have been researched, developed, field-tested, and subsequently implemented to restore these contaminated sites. For a successful risk management of a contaminated vadose, the contamination must be prevented from spreading and be removed as economically as possible in a time-efficient and practical method. In these capacities, ex situ surfactant enhanced bioremediation has been attracting increasing attentions in recent years. Biosurfactants and chemically synthesized surfactants are relatively low-cost production industrial process. They have been playing an increasing and pivotal role in *ex situ* remediation of contaminated soil due to their unique desorption function capability, strong solubilizing power of hydrophobic organic chemicals, and considerable enhancement of contaminants bioavailability. Several critical issues have, however, to be vigorously researched. However, the data current available indicate some research gap areas. Therefore, a concerted research endeavor is currently needed to better elucidate the fate and behavior of synthetic surfactants in natural ecosystems, mechanism of soil biota toxicity and regulation, hysteresis effect on treated soil properties, metabolites production during biodegradation, soil hydrophobicity increase, synergistic properties of mixed surfactants, combined use of surfactants with additives on enhancing bioreactors performance. Furthermore, the prospects of future development and industrial production of mixed surfactant systems combined with low CMC are very promising alternatives to either biosurfactants or chemically synthesized surfactants. This new generation of surfactants will offer the possibility of removing the large-scale remediation impediments associated with current ex situ surfactant-based soil remediation technology.

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