Chapter 2

Literature Review

2. Literature Review

The proposed objectives are accomplished by carrying out a thorough literature review. The following sections focus on the literature review of techniques available to remediate contaminated soil by the surfactant solution mediated process. Then, the application of surfactant foam and nanoparticle stabilized surfactant foam in the remediation of petroleum contaminated soil is also reviewed for a better understanding of the improved techniques for petroleum oil contaminated soil remediation. Furthermore, the optimization of the petroleum-contaminated soil treatment process by RSM is discussed. The literature review on the importance of analyzing the foaming behavior of laundry detergent is studied further.

2.1 Remediation of petroleum contaminated soil by surfactant systems

2.1.1 Application of surfactant solution in remediation of petroleum contaminated soil

Application of surfactant solution to solubilize petroleum hydrocarbon and to treat contamination such as diesel, petrol, and crude oil is more than 50 years old phenomena (Rogers et al., 1963). Li et al. (2016) report the application of surfactants for the solubilization of petroleum hydrocarbons from contaminated soil. Several parameters, both extrinsic and intrinsic, have been taken into consideration to achieve the desired level of contaminant removal.

The intrinsic factors include the nature of the soil to be assessed (mineral components, biological and physicochemical property), nature of contaminant (source and age), and nature of surfactant. The soil constitutes of mineral particles, organic matter which acts as effective sorbents of contaminant and mainly accumulates the hydrophobic contaminant easily on its surface. These, as a whole, determine the amount of contaminants for the remediation process. Higher the clay content of the soil, higher is the sorption of contaminant and surfactant to the soil. Removal of the strongly bound contaminant from clay soil depends on the availability of the surface for the surfactant to interact with the contaminant. Properties of soil such as porosity, pore size, and shape affect the binding of contaminants and their removal from soil by any treatment method. Soil with macroscopic pore (diameter > 0.08 mm) structure responds better to remediation than that of soil with a microscopic pore (< 0.08 mm) structure. Soil with macroscopic pore prevents clogging and readily allows the movement of water and other agents in the soil. Soil with regular spherical pore shape shows faster transportation of water and contaminant into the subsurface than the soil with irregular pore shape. The porosity of soil varies based on the soil type and its particle size. Soil (like clay) with smaller particle size, higher pore volume, and larger surface area has a large holding capacity (Dexter, 2004). That is the reason why clay binds a larger amount of contaminants stronger than the sandy soil with larger particle size (Abdel-Moghny et al., 2012b). As the contaminant penetrate deeper in clay soil and bind strongly to it, it becomes difficult to remove these strongly adhered contaminants from clay soil by surfactant mediated method (Fogden, 2012). The clay soil has a high swelling tendency in contact with the organophilic phase of the contaminants and blocks the pores available for surfactant interaction. Thus, sandy soil is easier to remediate by surfactant than clayey soil (Zuo et al., 2015).

Petroleum contaminant present in any environment (soil/water) is mostly characterized by the hydrocarbon composition; alkanes, alkenes, and aromatic chains. Depending on the petroleum product, it may contain trace amounts of heavy metals such as lead (Pb) and copper (Cu) (Abu-Elgheit et al., 1981; Akpoveta et al., 2018). Surfactants reduce the interfacial tension at the oil-water interface thereby increasing the transport of hydrocarbons from the oil phase, helping in mobilization and micellar solubilization. Micellar solubilization is dependent on the concentration of the surfactant above CMC. Below CMC, the surfactant has a negligible impact on the aqueous solubility of hydrocarbons. The effectiveness of a surfactant in the solubilization of different organic contaminants is described by its molar solubilization ratio (MSR). For contaminant Naphthalene, the nonionic surfactants Triton X-100 and Brij-35, show higher MSR value compared to ionic surfactants Sodium Dodecyl Sulfate (SDS) and Sodium Dodecylbenzenesulfonate (SDBS). The solubilization of hydrocarbons in aqueous solution also depends on the hydrophobic chain length of the surfactant. It has been found that the values of MSR increase with an increase in the hydrophobic chain length of the surfactant. Solubilization tendencies of contaminants like benzene, n-hexane increase with the increase in chain length of an ionic surfactant. With the same hydrophobic chain length, nonionic surfactants tend to solubilize hydrocarbon contaminants more compared to ionic surfactants. This typically leads to higher removal efficiency of hydrocarbon contaminants from the soil. Branched hydrophobic chain surfactants have less solubilization tendencies for hydrocarbons compared to the isomeric straight-chain surfactants due to their shorter chain length.

The hydrophile-lipophile balance (HLB) number varies for different types of surfactants like ionic, nonionic. Nonionic surfactants have HLB numbers from 0 to 20. Ionic surfactants, however, tend to have HLB values up to 50. The core volume of a micelle decreases with an increase in the HLB value of the surfactant, thus leading to a reduction in solubilization of petroleum hydrocarbon contaminants. This is true for the solubilization of contaminants like dodecane, decane, and hexane. Also, the solubilization of petroleum hydrocarbon contaminants tends to increase with the rise in temperature for both ionic and nonionic surfactants, thus leading to improved contaminant removal efficacy.

In lab scale, the research works are found to be carried out as a combination of chosen intrinsic and extrinsic factors. Extrinsic factors include the concentration of surfactant and contaminants, solvent, flow rate, time and design of the reactor for surfactant-contaminant interaction, the rate of mechanical stirring, etc. Researchers decide single or multiple surfactants, contaminant(s), and then the remediation related experiments are carried out based on the variable extrinsic factors.

In contrast with the anionic surfactants, the major properties that make nonionic surfactants suitable candidates for the removal of petroleum contaminants from the soil include biodegradability, cost-effectiveness, and low susceptibility to aggregate clay minerals in the soil (Franzetti et al., 2006). Petroleum contaminants, including NAPLs such as gasoline, kerosene, diesel, and dense non-aqueous phase liquid (DNAPL) such as phenanthrene are reported to be treated by the Tween surfactant. Ahn et al. (2008) report the use of a surfactant solution of Tween 80 at a concentration of 2000 mgL^{-1} to remove 72% of phenanthrene from a sandy soil contaminated with 1000 mgL^{-1} of phenanthrene by the mechanical stirring process at 160 rpm for 48 h. Zhao et al. (2016a) investigate the effect of Tween 80 on the removal of phenanthrene from contaminated sandy soil to a level of 100 $mgkg^{-1}$. Tween 80 at the concentration of 4000 mgL^{-1} result in 99% removal efficiency of phenanthrene with 2 h of treatment by mechanically stirring the surfactant solution. Tween 80 is also used for the extraction of the heaviest fractions of the petroleum hydrocarbon from contaminated soil (Huguenot et al., 2015). Other heavily studied nonionic surfactants include Triton X-100, Brij and Alkylpolyglucoside.

The other contaminants, such as fuel oil and crude oil, are shown to be effectively removed from the contaminated soil by Tween surfactant. Li et al. (2015) achieve 91% removal by washing the crude oil contaminated clayey soil (20000 mgL^{-1}) with aqueous Tween 20 solution at 30 mgL^{-1}, by the mechanical stirring process at 160 rpm for 3600s.

Triton X-100 is another effective nonionic surfactant. Villa et al. (2010) achieve 100% removal of diesel oil from silty soil contaminated at a level of 5000 mgL^{-1} by washing it for three cycles with an aqueous solution of Triton X-100 at a concentration 12 times higher of its effective CMC. Ceschia et al. (2014) report 94% removal of crude oil by using a Triton X-100 aqueous solution at a concentration of 5 mgL^{-1} from Ottawa sand contaminated at 31000 mgL^{-1} level, by a mechanical stirring process at 470 rpm for 3600 s.

Brij is another commonly used nonionic surfactant for the treatment of petroleum-contaminated soil. Ahn et al. (2008) study the efficiency of 2000 mgL^{-1} Brij 30 solution in solubilizing phenanthrene by the mechanical stirring process at 160 rpm. Their results indicate a final removal efficiency of 84% from sandy soil contaminated with 1000 mgL^{-1} of Phenanthrene. Ramamurthy et al. (2009) treat a fine sandy soil contaminated with engine oil (0.1 $mgkg^{-1}$) by aqueous Brij 35 solution of concentration 1600 mgL^{-1}, at a flow rate of 0.16 mLs^{-1} and have achieved 46.8% maximum removal efficiency.

Alkylpolyglucoside (APG), another nonionic surfactant, shows high biodegradability and can be used to treat soils contaminated with crude oil, diesel, and dichlorobenzene (DCB). Han et al. (2009) study the surfactant washing process to treat sandy soil, contaminated with 12300 $mgkg^{-1}$ of crude oil, by mechanical agitation process using an aqueous solution of APG. They have reported a maximum contaminant removal efficiency of 97% by combining 600 mgL^{-1} APG and an inorganic salt, such as $Na_5P_3O_{10}$ and Na_2CO_3. Pei et al. (2017) compare the effect of APG aqueous solution with aqueous Tween 80 surfactant solution in the removal of DCB from quartz sand contaminated with 589 $mgkg^{-1}$ of DCB. At a concentration ~ 4000 mgL^{-1} and flow rate of 0.01 mLs^{-1}, APG exhibited 80% degradation of DCB, whereas Tween 80 showed 76% removal at the same application conditions.

The other nonionic surfactants reported in the literature for the treatment of contaminated soil include nonylphenols and ethoxylated surfactants (Hernández-Espriú et al., 2013; Vreysen and Maes, 2005). Polyethylene glycol nonyl phenyl ether aqueous solution at a concentration of 7000 mgL^{-1} is shown to remove 99% of lubricating oil from coarse sandy soil, contaminated with 50000 $mgkg^{-1}$ of lubricating oil (Abdel-Moghny et al., 2012a). Mędrzycka et al. (2015) report 95% removal of polyalfaolefin oil from the sandy soil by utilizing the ethoxylated surfactant. Everett et al. (1994) report 85% removal of diesel from soil having a particle size below 70 microns by using a super nonionic surfactant polyakylene in their patent. Some researchers demonstrate the application of nonionic surfactants for efficient contaminant removal in industrial scale treatment sites. Ivey-sol, a formulation consisting of various nonionic surfactants marketed by Ivey international Inc., shows the capacity to remove petroleum hydrocarbons from contaminated soil subsurface. When utilized at a contaminated refinery site in Montreal, Canada, covering eight-acres of land, Ivey-sol results in huge mass recovery of DNAPL and BTEX within two weeks treatment period. The Ivey-sol surfactant formulation works better because it improves the contaminant's miscibility in the aqueous phase and thereby enhances their desorption from the soil surface (Ivey and Beaudoin, 2010). Ivey sol surfactant formulation is also effectively used in treating petroleum contaminated sites and has resulted in 97% removal of petroleum hydrocarbon contaminants from the site (Zhang et al., 2014).

The anionic surfactants remain the most widely used surfactants in the soil washing process (Peng et al., 2017). Many literature document the solubilization of contaminants by anionic surfactants. An anionic surfactant, such as SDS and SDBS, tends to solubilize the crude oil, petroleum hydrocarbons, etc. (Eljack and Hussam, 2014; Rahal et al., 2016). Khalladi et al. (2009) have applied SDS solution at a flow rate of 0.05 mLs^{-1} to soil comprised of 94% silt, contaminated with 3450 $mgkg^{-1}$ diesel, and found the removal of diesel from soil to be as high as 97%. Salehian et al. (2012) have treated the diesel-contaminated sandy soil (20000 mgL^{-1}) with 20 mgL^{-1} aqueous solutions of SDS, which resulted in maximum removal efficiency of 45%. SDS is known to be used for the removal of hydrophobic organic compounds such as toluene, benzene, and xylene. Similarly, Tang and Lian (2013) report 59% of diesel removal from riverside soil using a 2500 mgL^{-1} SDS aqueous solution by a mechanical stirring process at 200 rpm and 25°C. Vincent et al. (2012) utilize an aqueous solution of SDS at a concentration of 10^4 mgL^{-1} to treat crude oil-contaminated sandy soil (level 10000 mgL^{-1}) and report 76% of removal efficiency. Ceschia et al. (2014) are able to achieve 86% crude oil removal from Ottawa sand (contamination level of 31000 mgL^{-1}), by treating the soil with 5 mgL^{-1} of aqueous SDS solution. The study involves mechanical stirring of the surfactant solution at 470 rpm for 3600 s. Long et al. (2013) investigate the correlation between the concentration of SDS and flushing time in the removal of toluene from the sandy soil by the surfactant flushing process. For any flushing process, the concentration of surfactant and time of flushing process determines the efficiency and cost-effectiveness of the operation (Guerin, 2015). Liang et al. (2016) report 90% removal of a blend of hydrocarbons, Benzene, Toluene, Ethylbenzene, and Xylene (BTEX) from sandy loam soil, contaminated at the level of 1000 $mgkg^{-1}$, utilizing aqueous SDS solution at a concentration of 5000 mgL^{-1} and a flow rate of 0.2 mLs^{-1}. Gitipour et al. (2014) use aqueous SDS solution at a concentration of 5000 mgL^{-1} to treat sandy soil contaminated with 9000 mgL^{-1} cresols. The surfactant solution with a flow rate of 0.005 mLs^{-1} results in 78% of maximum removal.

Tien et al. (2000) report 90% solubilization of oil contaminants from sandy loam soil by using a combination of anionic surfactant SDBS, at a concentration of 20000 mgL^{-1}, with alcohol such as n-decane and n-pentanol. Zacarias-Salinas et al. (2013) depict that SDBS could be used for soil washing in the in-situ treatment of motor oil-contaminated industrial sites. Notably, they could achieve 68% of contaminant removal from a site, comprising of clayey soil, contaminated with motor oil. This is done by treatment with 1000 mgL^{-1} of the surfactant solution by a rotary shaker method at 200 rpm. Svab et al. (2009) treat polychlorinated biphenyl (PCB) contaminated (contamination level of 78 $mgkg^{-1}$) sandy silt soil with an alpha-olefin sulfate surfactant solution at a concentration of 3500 mgL^{-1} and reported 90% removal efficiency.

Shiau (2008) combines sodium dioctyl sulfosuccinate with a cosurfactant, calfax, to treat industrial site contaminated with light non-aqueous phase liquid (LNAPL) and report 93% removal efficiency in the patent. It has been reported that a blend of anionic surfactants consisting of sodium monosulfonates, dialkyl monosulfonates, and dialkyl disulfonates has high biodegradability and results in enhanced recovery of jet fuel (JP-8) from contaminated soil at a fuel point site (area 463.6 m^2) in New York by mobilization. This blend requires ten times less volume of surfactant than that is required by the traditional surfactant flushing process (Hayward et al., 2010). Martel et al. (2005) report treatment of PCB contaminated building sites using anionic surfactant sulfonates along with alcohol and achieve 22% removal of PCB from the soil.

Comparatively, very few studies report the utilization of cationic surfactants in the treatment of contaminated soil. Generally, strong sorption of positively charged surfactant to the negatively charged soil surface results in less availability for contaminant removal (Zhu et al., 2005). Also, cationic surfactants are highly toxic to the environment and hence could not be considered as a suitable surfactant during the flushing process (Wang et al., 2012). Li et al. (2016) report maximum 50% removal of the pollutant from a clayey soil, initially contaminated with 20000 mgL^{-1} crude oil, by treatment with 300 mgL^{-1} of Cetrimonium bromide (CTAB) surfactant solution. Cationic surfactants can be utilized for efficient contaminant removal process when combined with other technologies such as electrokinetic treatment process, microbial degradation process, etc., (Chaprão et al., 2015; Cheng et al., 2017; Sri Ranjan et al., 2006). López-Vizcaíno et al. (2011) utilize cationic surfactant alkylbenzyldimethylammonium chloride at a concentration of 10000 mgL^{-1} to increase the mobility of flushing aqueous solution between the electrodes during electrokinetic remediation.

Few studies also report the use of mixed surfactants for remediation of contaminated soil (Sales and Fernández, 2016; Shi et al., 2015). The removal efficiency of the contaminant from soil has been found to improve in some cases by utilizing mixed surfactant systems (Shi et al., 2013). The combination of anionic and nonionic surfactants is also of practical interest, as it facilitates application for a wide range of conditions such as pH, salinity, temperature of soil (Gandhi et al., 2001).

2.1.2 Application of surfactant foam in remediation of petroleum contaminated soil

Reported studies on the utilization of nanoparticle stabilized surfactant foam for the efficient treatment of soil contaminated with petroleum oil are limited when compared with surfactant foam and surfactant solution. In the past decade, extensive works have been carried out on the surfactant foam whereas; very few work has been reported on the nanoparticle stabilized foam for the removal of contaminant from soil. Various reported work on the effective use of surfactant foam and nanoparticle stabilized surfactant foam in the literature will be discussed in the following section.

Huang and Chang, (2000) report good homogeneity of foam flow for the nonionic surfactant Triton X-100 at a concentration of 2000 mgL^{-1} and simultaneously result in 85% removal of pentadecane from a column packed with glass beads. Whereas, only 26% removal efficiency is obtained for the surfactant solution. Shi and Chen, (2012) investigate the effect of antifoaming agents such as dodecanol, siloxane oil, and kieselguhr on Triton X-100 foam created by mechanically stirring the 5000 mgL^{-1} of surfactant solution at 3000 rpm. Siloxane oil is reported to control the foam height during flushing and resulted in 75.9% of removal efficiency for a soil contaminated with PAH to a level of 220 $mgkg^{-1}$. Mulligan and Eftekhari, (2003) produce a 99% stable Triton X-100 foam, using aqueous surfactant solution at a concentration of 5000 mgL^{-1}, by injecting air at a flow rate of 0.58 mLs^{-1}. It achieves 85% removal efficiency for fine sand, contaminated with 1000 $mgkg^{-1}$ of pentachlorophenol. Parnian and Ayatollah, (2008) compare the effectivity of Triton X-100 surfactant solution and foam at a concentration of 100 mgL^{-1} on diesel contaminated clayey loam soil. As evident from their column study, the surfactant foam aided remediation results in a 90% maximum removal efficiency, whereas, the surfactant solution shows only 87%. Wang and Chen, (2014) report a 94% removal of transformer oil from quartz sand contaminated with 110 $mgkg^{-1}$ of pollutants using Triton X-100 foam created from an aqueous solution of concentration 10000 mgL^{-1} and by injecting nitrogen gas at a flow rate of 0.1 mLs^{-1}. Similarly, (Wang and Chen, 2014) produce a 99% stable Triton X-100 foam from an aqueous solution of concentration 5000 mgL^{-1} by using nitrogen gas at a flow rate of 0.1 mLs^{-1}. This results in 85% removal of PCB from coarse sand, contaminated with transformer oil at a concentration of 110 $mgkg^{-1}$. Lee et al. (2013) prepare Tween 80 foam of 7 cm height by Ross-Miles method, which shows 87% of diesel oil removal from the sandy soil contaminated at a concentration of 2692 mgL^{-1}. This process of treating the contaminated soil with low foam quantity is economically feasible in comparison with the surfactant solution flushing process. Jeong et al. (2015) demonstrate the surface foam treatment process for removal of diesel from sandy soil, contaminated to a concentration of 100 $mLkg^{-1}$. 73% of final diesel removal is accomplished by spraying aqueous Tween 80 foam, created at a concentration of 6.6 mgL^{-1}, on the surface of the contaminated soil. Also, the foam, sprayed on the soil, maintained the temperature effective for biodegradation of contaminants by microbes. Maire et al. (2015) attempt to measure the solubility of DNAPL contaminants from soil at a level of 80000 mgL^{-1} by surfactant foam. They report a maximum 93% DNAPL removal from the soil by injecting CO_2 gas at a flow rate of 0.1 mLs^{-1} in the aqueous surfactant solution of Tergitol of concentration 50000 mgL^{-1}. The amount of surfactant required by surfactant foam to achieve a removal efficiency of 90% of DNAPL from soil is found to be lesser than that required for surfactant solution flushing in many folds.

Rothmel et al. (1998) and Szafranski et al. (1998) demonstrate the effect of foam, created by stirring the aqueous solution of surfactants SDS and Steol at a concentration of 500 mgL^{-1}, for the removal of trichloroethylene (TCE). The foam flushing process is carried out at two different pressures; 3 and 10 psi, which produce 60 and 75% removal of TCE from the soil, respectively. Couto et al. (2009) claim that surfactant foam, created by injecting air at a flow rate of 0.6 mLs^{-1}, is more effective than the surfactant solution for remediation of sandy soil contaminated with 80000 mgkg^{-1} of diesel oil. The foam created with anionic surfactant SDS at a concentration of 11700 mgL^{-1} shows 99% removal efficiency. The surfactant solution, on the other hand, shows only 20% removal efficiency. Jeong et al. (2015) treat sandy soil, contaminated with 100 mLkg^{-1} of diesel, by foam generated using the surfactant SDS at 6.6 mgL^{-1}. They have shown a maximum removal efficiency of 73.7%. da Rosa et al. (2015) report 62% contaminant removal from sandy soil tainted with 5000 mgkg^{-1} of diesel oil by using surfactant SDS (of concentration 2300 mgL^{-1}) microfoam produced by a high-speed homogenizer at 15000 rpm. Zhong et al. (2011) achieve 68% TCE removal from soil sediment using foam of Sodium Lauryl Ether Sulfate at 5000 mgL^{-1} produced by injecting nitrogen gas at a flow rate of 0.16 mLs^{-1}. Wang and

Chen, (2012) utilize SDS foam, created by passing air at a flow rate of 0.1 mLs^{-1} (air-liquid ratio of 100:5), to remove transformer oil from quartz sand contaminated at a rate of 110 mgkg^{-1}. Maximum 75% contaminant removal efficiency is achieved.

Many reports have been published with specific insight into the remediation of petroleum contaminated soil by surfactant foam. Effects of surfactant structure on foam-oil interactions have been studied (Vikingstad et al., 2006). Stern, (1991) report a method for the removal of hazardous contaminants from soil by applying surfactant foam prepared with polyhydroxy polymers in their patent. Some industrial case studies on the application of surfactant foam to treat petroleum-contaminated sites (Unit 2, Hill Air Force Base, Utah, USA) have been reported. Foam prepared from a surfactant solution with air is continuously inoculated into the contaminated zone through an injection well. Surfactant stabilized foam is proven to enhance transport in the soil layer and results in a 95% removal efficiency (Ward, 2000).

2.1.3 Application of nanoparticle stabilized surfactant foam in remediation of petroleum contaminated soil

Stabilization of aqueous foam by using colloidal particles has been discussed since 1958 (Shearer and Akers, 1958). Nanoparticle, such as iron, started to be used to treat PCB contamination since 1997 (Wang and Zhang, 1997). Nanoparticles along with surfactant solutions have been applied for enhancing the oil recovery in early 2000. The tendency of nanoparticles to increase the stability of aqueous foam has been utilized both in oil recovery and remediation of oil-contaminated soil. Thus it has been proved to be an effective alternative approach to overcome the limitation in the existing methods (Otto et al., 2008; Vikingstad et al., 2005). Ju et al. (2006) experimentally investigate the enhancement of the oil recovery by the addition of hydrophilic nanoparticles. Worthen et al. (2013) show that the presence of nanoparticles at the interface can provide long-term stability to the foam. Silica nanoparticle of size ranging from 5.5-165 nm is studied to enhance foam stability. Foams prepared with 50% silica nanoparticles remain stable for long 23h. Lv et al. (2015) depict that the increase in foam stability, in the presence of silica nanoparticle, occurs as the silica nanoparticle attach to interface and leads to a stronger viscoelastic layer to prevent the collapse of the bubble. The foam generated by surfactant SDBS along with silica nanoparticle has a half-life of 65 min, whereas, the foam produced only with SDBS exhibits a half-life of only 35 min. Zheng and Jang, (2016) report a reduced hydraulic conductivity of foam stabilized by silica nanoparticles in the range of 5-50 nm in a sand column. This helps in improving the isolation of contaminants from the soil barrier. A foam column generated by the cationic surfactant CTAB along with silica nanoparticles retained 80% of the original foam height even after 17 days.

Aqueous surfactant foam has been utilized as an effective vehicle to deliver Nano zero-valent Iron nanoparticles (Fe^0 nanoparticles) for remediation of soil subsurface. The Fe^0 nanoparticle, in the form of foam dispersion, effectively facilitates its gravitational flow rather than aiding in lateral flow in the soil layer. This, as a whole, affects the retention of Fe^0 nanoparticle in the soil surface and the removal of the contaminant from the soil. Noticeably, 100% delivery of Fe^0 nanoparticle in the deep vadose zone of soil is achieved by using foam, produced by 1% of the surfactant Sodium Lauryl Ether Sulfate, as a vehicle (Ding et al., 2013). Shen et al. (2011) show that foam stabilized by common surfactants such as SDS, Tween-80, Tween-20, and Triton X-100 are readily able to deliver Fe^0 nanoparticle in the soil subsurface. The presence of Fe^0 in foam aids in overcoming the film breakage of foam and improves the transport of microsphere in the soil environment. Jamei et al. (2012) achieve ~99% of degradation of hydrocarbons from contaminated soil by utilizing Fe^0 of 40 to 80 nm. The contaminated soil is treated with 4000

mgL^{-1} of Fe^0 along with ultrasonic waves. (Su et al., 2014) study the stability of foam in the presence of Fe^0 particles. The foam stability remains unaffected even at a very high nanoparticle concentration of 2800 mgL^{-1}.

2.1.4 Optimization of petroleum contaminated soil treatment process by RSM

Spencer et al. (1996) analyses the degradation of diesel from contaminated soil by oxidation of hydrogen peroxide (H_2O_2) using central composite rotatable design (CCD). The optimization of H_2O_2 concentration with process variables concentration of the contaminant and the soil organic carbon content resulted in enhanced removal of diesel from the soil. The result suggests that the soil treatment process is strongly affected by the initial diesel concentration in the soil but unaffected by the varying carbon content in the soil. The optimum condition of diesel degradation was reported at low volume/high concentration of H_2O_2 at an initial diesel concentration of 2000 mg/kg of soil. Overall the contaminant degradation process required 83 moles of H_2O_2 to degrade one mole of diesel. The optimization of diesel degradation by response surface process also leads to the design of the cost-effectiveness of the process. At the optimized condition, a total of 1200 mg of 2000 mg of initial diesel concentration was degraded thus requiring 282000 mgL^{-1} of H_2O_2. The cost of operation at this optimized condition amounts to 38 USD per 909 kg of soil. However, increasing the degradation level to 1600 mg from 1200 mg of diesel from soil would require 300000 mgL^{-1} of H_2O_2 which would require 285 USD for treating 909 kg of soil.

Joshi and Lee, (1996) experimentally evaluate the optimal condition of using nonionic surfactants to achieve better removal efficiency from contaminated soil. The process parameters including surfactant concentration, the ratio of surfactant solution volume to soil weight, and temperature of washing solution are selected to be optimized as these parameters are most significant to achieve the target contaminant. For the soil washing conditions understudy, an optimal contaminant removal of 70% is obtained at the surfactant concentration of 4% (v/v) and temperature of 60ºC. The optimization of process parameters experimentally involves varying each parameter and fixing all other conditions at one level. Thus experimental optimization consumes time, as well as the degree of achieving an accurate optimum condition, is limited. Optimization methods such as RSM provides a true optimum of a response with fewer experimental trials than the experimental optimization approaches where the one variable is optimized at a time by fixing all other process parameter constant (Yusri et al., 2018).

Kalali et al. (2011) investigate the surfactant mediated treatment of soil contaminated with crude oil using nonionic surfactant Brij35. They utilize CCD to optimize the removal efficiency percentage by studying the effect of interactive process variables including concentration and volume of surfactant solution, washing time and the number of the washing cycle, pollution age. The optimum surfactant concentration of 8 gL^{-1} supplied for 75 min thrice resulted in maximum removal efficiency of 80%. The study reveals a quadratic model result from RSM with produces low p- high R^2 values (0.987). Though their research is useful in estimating the optimum contaminant removal efficiency, it fails during the validation process. The primary reason behind this lies in the fact that the contaminant removal by a surfactant is affected by the physicochemical properties of the soil. Thus it is significant to consider the property of soil during the optimization of the treatment process. Long et al. (2013) utilize BBD to analyze the experimental variable affecting the toluene removal efficiency from contaminated soil by the surfactant flushing process. The experimental variables including the treatment time, surfactant concentration and flow velocity are considered as the variables affecting the final removal efficiency of toluene. Optimum surfactant concentration results in maximum toluene removal efficiency; it reports as 1.8 wt% after 472 min of optimum washing time at a flow velocity of 0.8 mL/s. Gharibzadeh et al. (2018) apply the BBD to optimize the parameters influencing the phenanthrene removal from soil using RSM. The factors including surfactant concentration, washing time, humic acid concentration and liquid soil ratio are considered for the optimization study. The maximum removal efficiency of 70.69 % is reported at the optimum surfactant concentration of 5000 mgL^{-1}, liquid soil ratio of 30 v/w, the humic acid concentration of 9.88 mgL^{-1}, after 2 h of washing time. Mirzaee et al. (2017) develop the optimum condition for the treatment of soil contaminated with petroleum hydrocarbons using magnetite nanoparticles using RSM. The quadratic model result from RSM produces low p-value (0.0057) and high R^2 values (0.976). The maximum removal of petroleum hydrocarbon 74.2 % is reported at 17.5:1 molar ratio of H_2O_2 and magnetite nanoparticle. The optimization of the surfactant foam and surfactant foam stabilized by Fe^0 in remediation of petroleum contaminated soil is not much reported in the literature. There is a need to study the effect of various parameters influencing the stabilization of surfactant foam by nanoparticle to achieve optimum diesel contaminant removal efficiency from the different soil.

2.2 Formulation of liquid laundry detergent

Various developments have occurred in the laundry washing and detergent preparation. Many works of literature report the production of better detergent formulation for enhancing the washing efficiency. Kharkate et al. (2005) prepare liquid detergent by using anionic surfactant sodium lauryl sulfate (SLS) as a key ingredient. The clear solution of liquid detergent produced by them results in better detergency compared to commercially available liquid detergents. The prepared liquid detergent has a surface tension value of 31 dynes cm^{-1}, whereas the commercially available detergent has a higher surface tension value of 33.9 dynes cm^{-1}. Similarly, the foam volume of the prepared liquid detergent (30.74 mL) was higher compared to that of commercially available detergent (28.8 mL). Also, they achieve a better detergency value as high as 94% with the prepared detergent, but the commercial detergent is reported to show only 66% of detergency. Owing to its easier preparation the liquid detergent can be easily adapted in any existing manufacturing plant. Choi et al. (2016) investigate the washing of fabrics using ultrasonic waves. Their results demonstrate that the bubbles produced by ultrasonic waves are capable of removing dirt from the soiled fabrics. They have reported improved performance of textile washing by 15% compared with conventional machine washing.

Wang et al. (2014) demonstrate that the mixed surfactant system has better foaming properties than that of individual surfactants and this, in turn, increases detergency of the surfactant system. The foamability of the mixed surfactants Alcohol ether sulfates (AES)/ Dodecyltrimethylammonium Chloride (DTAC) and Dodecyl-(2-hydroxyethyl)-dimethylammonium chloride (DHDAC)/ Dodecyl-di(2-hydroxyethyl)- methylammonium chloride (DHHAC) at sample concentrations of 2.5 gL^{-1} is measured by Ross-Miles method. In the Ross-Miles method, the foam stability is defined by the foam volume at 30 s of foam generation. Reuter and Mettin, (2016) demonstrate the mechanism of cleaning by foam bubbles produced by the detergent during the domestic washing process. The particles are deposited strongly by the spin coating technique on the glass slide which mimics the surface to be cleaned. The prepared glass slide is then immersed in a container with deionized water where the bubble collapse event is captured by a high-speed camera. The cleaning of the surface is observed from the centre of the bubble in a circular pattern. The removal of particle from the surface occurs at the radius of the bubble as its starts collapsing from its centre. In this manner cleaning efficiency can be measured by the normalized radius of this bubble. During this phase the bubble still does not reach the boundary of the surface. In the next phase of collapse a vortex flow is generated, which swiftly moves towards the solid glass surface and spreads by radial expansion. As the bubble spreads on the surface, the particles adhered to the glass are removed.

The performance of detergent is greatly affected by the hardness of the water. The surfactant molecules react with the calcium and magnesium in the hard water to form insoluble precipitates and also prevents foaming (Noïk et al., 1987). These precipitates settle in the fiber matrix of fabric making the surface rough and stiff leading to damage of fabrics . Gotoh et al. (2016) investigate the effect of water hardness on the detergency using various surfactants. The detergency of the surfactants, such as sodium oleate, sulfonates, sulfate, and oxyethylene are evaluated. The washing process is carried out by immersing one piece of untreated clean cloth and a piece of soiled cloth in the surfactant solution prepared with hardness salts. As the water hardness level increases, the efficiency detergent to remove the soil from the fabric decreased. The precipitate hence formed gets adsorbed strongly on the fabric damaging the cloth. The foaming power of detergent drastically reduced with increasing hardness. At 300 ppm hardness level there is no foaming even at higher concentration of surfactant used. This impetuous reduction in foaming property is due to the insoluble precipitates formed initially and is evident from the decrease in the surface tension values. Amaral et al. (2008) report the foaming behavior of surfactants in different levels of water hardness. They report foam properties such as foam stability in terms of varying agitation speed (8000, 9500 & 13500 rpm). The foam volume produced by 0.5 % of CTAB, Tween 80, and SDS were 13, 11 and 15 mL, respectively. They report that the water salinity, do not affect the foam properties of the surfactant solution without any concrete evidence. The effect of water salinity remains unclear from this study. This result cannot be accepted as such because the foaming property of the detergent solution is not only defined by the surfactant but also greatly influenced by the additives and other factors such as mode of preparation of foam. For instance the foam prepared with stirring may tend to show varying foam property than that of mechanical agitation. Thus, investigation of foaming behavior of complete liquid detergent with various additives in different water hardness is required.

2.3 Research Gaps and novelty

The spilling of petroleum products on the soil surface alters the chemical properties of soil in terms of increased pH and reduced carbon content in the soil (Streche et al., 2018). Due to their large scale use as one of the primary potential fuel, gasoline, petrol and diesel oil are considered the most spilled in the environment (Namkoong et al., 2002). The application of a surfactant solution to solubilize petroleum hydrocarbon and to treat contamination such as diesel is more than 50 years old phenomena (Rogers et al., 1963). As can be seen from the literature survey many studies report the use of surfactant solutions for the treatment of soil contaminated with diesel. The major drawback of a surfactant solution is the process consumes the major volume of surfactant adding further to the cost of operation. However, so far reported very few research works, both theoretical and experimental, can successfully correlate the process determinants such as surfactant concentration, the environmental property of surfactant. Most of the research reported is discrete and case study type in nature. The need of the future is for elaborative research work in this area with thoughtful design and systematic approach, to answer which surfactant foams could be most effective (in terms of removal efficiency, cost, and toxicity issues) for what type of soil(s) and contaminant(s).

Few recent studies have reported the use of surfactant foams for the effective removal of petroleum contaminants from soil. However, these studies lack to report the stabilization of surfactant foam, which is an important parameter considering the realistic contaminated soil subsurface conditions. Aqueous foam can be stabilized by the incorporation of polymer, nanoparticles, etc. along with the surfactant system (Lesov et al., 2014; Zhao et al., 2015). Further, this methodology has an additional advantage; in comparison to the surfactant solution alone, the stabilized surfactant foam typically uses less amount of surfactant. Nanoparticle stabilized surfactant foam appears to be an effective remediation strategy for the removal of petroleum oil from the soil, but further detailed research is still required. It is crucial to understand the potential mechanism of interaction of nanoparticle stabilized foam with the contaminant.

Remediation of contaminated soil with iron nanoparticles has been scarcely studied in the last decade, while reports on examining the effects of iron oxide nanoparticles are truly scarce. Reportedly hydrophilic iron nanoparticle is used to reduce the DNAPL concentration by increasing mass transfer between DNAPL and the aqueous phase (Adusei-Gyamfi and Acha, 2016). These solid particles can withstand the extreme conditions and can migrate in the subsurface to eliminate the contaminant from the soil layer. A few reports have been published regarding the application of iron nanoparticle stabilized surfactant foam in the removal of diesel contaminants from the soil. Ding et al. (2013) mention that delivering Fe^0 nanoparticle, in the form of a dispersion, effectively facilitates gravitational flow rather than aiding in lateral flow in the soil layer, whereas, the foam could be a useful tool to deliver Fe^0 nanoparticle in soil subsurface in all directions. This, as a whole, affects the retention of Fe^0 nanoparticle in the soil surface and thereby influences the removal of the contaminant from the soil. In another study, Shen et al. (2011) discuss the efficacy of the foams produced from commonly available surfactants (such as SDS, Tween-80, Tween-20, and Triton X-100) to deliver Fe^0 nanoparticle in the soil subsurface. The application of surfactant foam stabilized using biodegradable additives ethylene glycol, and allyl alcohol for treating diesel-contaminated soil has not been explored in great depth so far. There is a need to study the effect of various parameters influencing the surfactant foam stabilized by nanoparticle to achieve optimum diesel contaminant removal efficiency from the different soil. Utilization of RSM to optimize the parameters involved in nanoparticle stabilized foam mediated remediation of petroleum contaminated soil is not much reported in the literature.

The aim of the current work is thus to identify the potential of those biodegradable additives to stabilize surfactant foam as well as to treat diesel contaminated soil. The present research work is the first of its kind, reporting the remediation of diesel-contaminated soil with surfactant foams stabilized by hydrophilic/hydrophobic SiO_2, Fe^0, and Fe_3O_4 nanoparticles. Also, diesel removal from different soil types (desert, coastal, and clay soil) is optimized for the first time, using RSM, using alkyl polyglucoside phosphate (APG-Ph) foam, stabilized by Fe^0.

In the current work different combinations of surfactants contaminated soil. Initially, we have selected an anionic and a nonionic surfactant SDS and Tween-80 respectively considering its high biodegradability (Table 2.1) to be stabilized by biodegradable additive allyl alcohol, ethylene glycol. However, lower removal efficiency and foam stabilization are achieved with this combination and additives are used to stabilize foam and utilize it for effective treatment of diesel owing to the higher HLB value (40) of SDS and higher alkyl chain length (C18) of Tween-80.

Table 2.1: Properties of different surfactants applied for remediation of diesel contaminated soil in the present research work

Surfactant	**Type**	**Molecular Weight (g/mol)**	**HLB**	**Alkyl Chain length**	**Biodegradability (%)**	**Toxicity (mg/l)**	**Reference (Biodegradability/ Toxicity)**
SDS	Anionic	288.4	40	C12	92	LC_{50} - 13.9	(Abboud et al., 2007)/ (Bondi et al., 2015)
Tween-20	Nonionic	1226	16.7	C12	90	EC_{50} - 4.5	(Jahan et al., 2008)/ (Bramwell and Laha, 2000)
Tween-80		1310	15	C18	96-99	EC_{50} - 70	(Huguenot et al., 2015)/ (Franzetti et al., 2006)
APG-Ph		>700	11-13	C8	>90	EC_{50} -10.3	(Gamia et al., 1997)/ (Jahan et al., 2008)

Then we selected the nonionic surfactant Tween-20 in combination with SiO_2. Being highly biodegradable and less toxic Tween-20 is expected to produce better diesel removal from soil however; the observation is contradictory due to its higher alkyl chain length (C12) effect. Thus we proceeded with iron nanomaterials such as Fe^0 and Fe_3O_4 to achieve better removal efficiency in combination with highly biodegradable surfactant APG-Ph. Now, APG-Ph (C8) having lower alkyl chain length compared to other selected surfactant produces a better result compared to all other surfactant reported in the work. Also, the silica nanoparticle does not hold the characteristics of the iron nanoparticle to effectively remediate the contaminated soils.

Modern detergents are typically appreciated for their cleaning performance rather than foaming characteristics. Many studies report the formulation of the detergent mixture; also, many detergent products are available commercially in the market. However, there is a need to understand and evaluate the critical properties affecting the detergent. Also, major studies reporting the detergent formulation fail to correlate the detergent performance with foaming behavior. Thus, the current work presents a comparison of foaming capabilities and cleaning performance of detergent formulations containing various combinations of popular nonionic and anionic surfactants. The effect of combinations of the anionic surfactant SLS and the nonionic surfactants such as Tween-20, Tween-80, Triton X-100, and APG on the detergency have been studied and reported for the first time.

2.4 Scope of the present study

Delivery of the nanomaterial in the contaminated soil subsurface requires a suitable vehicle for the effective removal of a contaminant. We have utilized surfactant foam as a vehicle as it has been reported in the literature that foam acts as an effective vehicle and at the same time the nanoparticle stabilizes the foam. To achieve this goal, we have prepared nanodispersion initially by the ultra-sonication method. Then the nanodispersion was used to produce foam by air sparging technique. Surface characterization technique such as surface tension, interfacial tension, zeta potential, viscosity and contact angle measurement was performed. Prior to utilizing nanomaterial, we have used chemical additives such as allyl alcohol, dodecanol, ethanol and butanol to stabilize surfactant foam. The analysis of foam properties of the surfactant along with additives and nanoparticles is required for a better understanding of the surfactant behavior in contaminated soil conditions. The selection of suitable surfactants and additives/nanoparticles for effective remediation of diesel contaminated soil is important. There are very few works of literature, which considers the utilization of nanoparticle along with surfactant foam to treat contaminated soil. Fe^0 stabilized foam can effectively enhance the remediation also foam acts as a suitable vehicle to efficiently deliver Fe^0 in soil subsurface. Fe^0 is a strong reducing agent that donates an electron to the contaminant species and results in the degradation of contaminated soil. Thus, there is a scope for the development of better remediation techniques to treat diesel contaminated soil.