Chapter 1

Introduction

1. Introduction

1.1 Remediation of petroleum-contaminated soil

1.1.1 Environmental impacts of petroleum contaminants

Universally, petroleum is the most consumed fossil fuel in comparison to other sources of energy, such as coal and natural gas. The global rise in demand has led to increased production of fuel to sustain the utility of vehicles produced every year. Oil exploration activities, refining process, and transportation of finished petroleum products result in unavoidable oil spills in the irrigational farmlands, desert and coastal regions (Balba et al., 1998; Becker et al., 2016; Benyahia and Embaby, 2016; Wang et al., 2013). The transportation of crude petroleum products from excavated sites to the refineries and fractionated products from the refineries to the point of distribution is typically done through pipelines, trucks, railways, and ships. However, pipeline still remains the most economical mode of transportation of crude as well as petroleum oil products (Sagers and Green, 1986). In the U.S, 70% of petroleum products are shipped by oil pipeline, in Canada almost 97% of petroleum transport occurs through pipelines. In India, the total length of oil pipeline has seen a 7% increase in the last eight years from 10246 km (2010) to 17753 km (2017). The major advantage of the oil pipeline is the less risk involved in transport than other sources of transportation such as rail and road transport. Also, it aids in cross-border transport of petroleum products between conflict-laden countries (Raballand and Esen, 2007).

Large-scale leakage during transport by rail, ship truck, oil pipeline, fuel storage system, improper management of petroleum waste disposal, etc., constitute the primary sources of petroleum contamination in the soil environment (Bariha et al., 2016; Zheng et al., 2018). Accidents during transport by truck and rail generate abundant chances for hazardous materials to be accidentally released into the environment (Ambituuni et al., 2015). Structural failure leading to leakage of oil arises through corrosion of the metal parts of the pipeline (Hu et al., 2014). The mean lifespan of any oil and gas pipeline made of steel is between 20 to 40 years, but in reality, these oil pipelines are utilized even after it reaches the stipulated lifetime (Afangide et al., 2018). Considering the high cost incurred to lay a new pipeline network 40 % of the worldwide pipeline are still in operation though it has reached its projected life (Azevedo, 2007). The oil pipeline is exposed to internal and external corrosion along its length on the outer surface which is in contact with soil. The pipeline buried in a soil environment with varying levels of oxygen results in differential corrosion of the pipeline (Castaneda and Rosas, 2015). The extended use of pipelines often causes stress to the welded joints and corrodes its physical structure and leads to leakage and contaminates the soil environment (Iturbe et al., 2007). Likewise, the persistent use of the underground storage tank beyond the specified life period causes a high risk of leakage of petroleum oil and leads to severe damage to soil environment and groundwater. The contaminant in soil decreases its permeability thereby preventing water to reach the subsurface (Ayininoula and Kwashima, 2015).

The leakage of crude oil, refined petroleum compounds such as petrol, gasoline, diesel, kerosene and jet fuels from oil pipelines, containers, and storage tanks causes serious threat to the soil fertility, microbial population and leads to various health hazards to human health, agriculture, microbial and marine life (Briggs and Briggs, 2018; Namkoong et al., 2002) (Hemond and Fechner, 2015; Romero et al., 2017; Sepehri and Sarrafzadeh, 2018). Soil microbes play an essential role in conserving the fertility of the soil by degrading organic matter and fixing atmospheric nitrogen (Rashid et al., 2016). The petroleum contaminants adhere intensely to the colloids of organic matter on soil surface and prevent the process of nitrification cause severe damage to this microbial community leading to loss of germination of seeds (Adam and Duncan, 2002; Jan Kucharski et al., 2010; Sutton et al., 2013) and leave the soil unsuitable for cultivation of crops (Conrad, 1996; Tilak et al., 2005). Toxic pollutants in the soil prevent plant growth by disturbing the photosynthetic process (Oyedeji et al., 2012). Obire and Nwaubeta, (2002) report a potential decrease in nitrogen and phosphorus content in soil environment on exposure to refined hydrocarbon.

The worldwide rise in marine transportation of oil over the last decade has caused major oil spills leading to extreme damage to marine and coastal ecosystems (Jiao et al., 2015; Lim et al., 2016). The oil spill during transportation in the sea might eradicate the fisheries and other marine organisms such as oysters, crabs, turtles (Vikas and Dwarakish, 2015). These aquatic animals are essential in maintaining the coastal ecosystem and cultural values of the coastal community (Jernelöv, 2010). The tendency of oil to penetrate soil and sediment over a long period causes instability in the biological community of the beach (Ivshina et al., 2015). For instance, oil washed off by the tide from the sea oil spill disturbs the hatching of sea turtles in the beaches which happens only in the particular period of the year, and this remains as the primary source of income of coastal communities through ecotourism (Kostianoy and Carpenter, 2018; Nayak and Berkes, 2019). Crude oil contaminants could hinder the microalgae growth, which is essential phytoplankton for the thriving of marine fisheries and birds (Essien and Antai, 2005; Venosa et al., 1996).

Assessing the risk of petroleum contaminants to human health is complicated and tedious due to the complex hydrocarbon mixture of petroleum oil. The toxic potential of these hydrocarbons is classified as carcinogenic to humans (Park and Park, 2011; Wang et al., 2015b). Humans are exposed to such contaminants by direct contact of soil through dermal exposure, inhalation and ingestion of contaminated groundwater (Hentati et al., 2013; Park and Park, 2010). The maximum permissible level of petroleum pollutants in groundwater, as described by Yanxun et al. (2011) is 0.3 mgL^{-1}. Effect of polycyclic aromatic hydrocarbon on a human being can either be short term or long term. Short-term effects of dermal exposure include acute skin irritation and inflammation, whereas oral exposure can lead to severe chronic impact and damage of the nervous system. This can also extend to cause jaundice, damaged liver and renal failure (Abdel-Shafy and Mansour, 2016). Inhalation of volatile hydrocarbon can initially cause symptoms of asthma and develop immunological disorders affecting the hematopoiesis, which may lead to reduced production of red blood cells. It is essential to identify suitable remediation techniques to remove this harmful petroleum oil contaminant from the soil.

1.1.2 Various methods to treat petroleum-contaminated soil

Scientists and environmentalists are putting in enormous efforts to develop efficient methods to eliminate harmful contaminants from soil. This, as a whole, leads to the development of numerous technologies for the treatment of contaminated soil. Soil remediation techniques can be classified into in-situ or ex-situ, depending on the approach of carrying out the soil treatment techniques (dos Santos et al., 2017; Maier et al., 2017). Remediation of soil at the contaminated site without the need for excavating the soil states the in-situ technique (Agarwal et al., 2007). The ex-situ approach comprises transferring the soil to a different site for treatment and re-deposition of contaminant-free soil (Caliman et al., 2011). Conventional techniques to treat soil contaminated with diesel compromises of electrokinetic remediation, phytoremediation, solvent extraction, oxidation, thermal treatment, biodegradation and surfactant flushing (Alshawabkeh Akram et al., 1999; Besha et al., 2018; Chen et al., 2001; Gomes et al., 2013; Pavel and Gaverilescu, 2008).

Electrokinetic remediation

Electrokinetic remediation involves the application of direct current at low intensity to remove harmful contaminants from the soil (Acar et al., 1995). In electrokinetic remediation, an electric field is created between two electrodes inserted in the contaminated soil, and the contaminants migrate between the electrodes in the form of ionic products due to the difference in the electrode potential (electro-migration) (Pazos et al., 2011). The application of direct electric current in the soil produces acidic deposits on the electrodes, which gets transported into the soil and notably alters the soil pH and renders it useless for agricultural activities (Ma et al., 2018). The electro-migration between electrodes not only results in a reduction of toxic hydrocarbon levels but also leads to migration of other important species from the soil (Estabragh et al., 2018; Sandu et al., 2017). Also, the time required to achieve this remediation effect is higher compared to other in-situ processes (Gill et al., 2014).

Phytoremediation

Phytoremediation technique refers to the utilization of plant species to treat contaminated soil (Dudai et al., 2018). The plants tend to absorb the toxic contaminants from the soil and utilize it to develop rhizosphere microbes, which in turn, help in plant growth (Tahseen et al., 2016). Studies have reported that plant species exude organic substances into the soil environment which helps in the degradation of toxic contaminants. Plants such as maize, Jatropha curcas, decompose the petroleum contaminants (Agamuthu et al., 2010; Chaineau et al., 2000). Phytoremediation can be slow and requires specific plant species to be grown in the contaminant zone which depends on several climatic factors (Prakash et al., 2015).

Solvent extraction process

The solvent extraction process involves the use of extracting agents to separate the harmful contaminants bound to soil (Silva et al., 2005). In this technique, the solvents are mixed with the soil and stirred well by the mechanical agitation process (Wang et al., 2019). The extracted solution carrying the target contaminant is separated by methods such as filtration and centrifugation (Fraters et al., 2017). After extraction the soil devoid of contaminants can be dried to be used further (Maceiras et al., 2018). The use of solvents to extract toxic pollutants from soil has been identified to result in enhanced remediation effect. However, solvent extraction requires a tedious process of implementation of the solvents at the site of contamination and regeneration of them is difficult (Wang et al., 2015d; Wulandari, 2010). The process also requires a multi-stage operation of extraction (mixing, separation, and drying), thus incurring high operation cost (Kislik, 2012).

Oxidation process

The oxidation process, in practice since the year 1900, is described as a reliable method to oxidize soluble organic compounds using oxidants such as persulfate, hydrogen peroxide (Bowen and Williams, 1939). The chemical oxidant decreases the oxidation state by accepting an electron thereby transforms the harmful organic contaminant into less toxic products (oxd1, oxd2). Though the oxidation process brings about the notable depletion of contaminants, the complete desorption of contaminants from the soil layer is achieved by the thermal treatment of contaminated soil (McAlexander et al., 2015).

Thermal treatment

Thermal desorption, as discussed by (Lighty et al., 1988), describes a method of increasing the soil temperature above a level of the boiling point of contaminant to remove those contaminants from soil. The high thermal energy can volatilize various nutrients from the soil and alters the color. Heating the soil at a temperature of 200- 300°C changes the structure of organic matter (Vidonish et al., 2016). Processes such as incineration and pyrolysis require heating of soil at 350-1050°C which leads to the decomposition of clay minerals of soil (Paetsch et al., 2017). Alteration and decomposition of constituents of soil affect the physicochemical properties (pH, bulk density, structure, texture, porosity, particle size, etc.) and hydrological properties (infiltration capacity, hydraulic conductivity, permeability, etc.) of soil leading to the damage of soil fertility (Schnecker et al., 2014). These problems can be overcome by the biological treatment of contaminated soil. The process of biological degradation of contaminants exists since the year 1959 when Davis demonstrated the microbiology of hydrocarbon degradation in soil (Davis et al., 1959). The microbial degradation of petroleum contaminants, in particular, brings about the degradation of hydrocarbon and does not alter the property of the soil (Leahy and Colwell, 1990). However, it requires proper aeration for microbial growth (Atlas, 1991). Thus, continuously stimulated aeration is necessary to achieve efficient contaminant removal which also adds to the cost.

Surfactant foam flushing

Among various methods, surfactant foam flushing processes have proven to be promising technologies for remediation of petroleum contaminated soil and therefore have attracted huge attention in recent years (Mulligan and Eftekhari, 2003; Wang and Mulligan, 2004). Surfactants are defined as surface-active agents with a polar head, nonpolar tail and having a capability to alter the surface- and interface properties (Jackson and Fulton, 1998). Thermodynamically, a surfactant solution forms micelles at a particular concentration, which helps in the solubilization of hydrophobic contaminants from soil. On the other hand, surfactant foam is a product of surfactant solution, formed by the expansion of gas in between two thin films of the solution (Arjmandi-Tash et al., 2017). The surfactant foam flushing process involves pumping of surfactant solution or foam produced using surfactant solution along with air into the contaminated soil subsurface to achieve an effective removal of targeted contaminants. The foams occupy larger space and hence typically require a small amount of surfactant (Lee et al., 2009; Lee et al., 2014; Zhong et al., 2009; Karthick et al., 2019). Incorporating the nanoparticles along with surfactant foam enhances the foam stability and assists in enhancing the removal of contaminants from soil (Wang et al., 2015a). Also, the surfactant foam acts as an efficient vehicle to deliver nano zero-valent Iron (Fe^0) in the soil subsurface. Aqueous surfactant foam enhances the gravitational flow of remediating fluid in soil subsurface while carrying the nanoparticle along. Ding et al. (2013) achieve 100% delivery of Fe^0 nanoparticle in the soil surface with the help of producing aqueous foam using the surfactant sodium lauryl ether sulfate, as a vehicle.The major advantage of using Fe^0 nanoparticles along with stable foam is its capacity to strongly reduce hazardous petroleum contaminants in soil. Also, this particle can withstand the extreme subsurface conditions and at the same time penetrates the soil layer effectively, resulting in efficient contaminant removal (Roseta.C and Obinna.F, 2017).

1.1.3 Mechanism of contaminant removal by surfactant solution

Surfactant molecules exist with hydrophobic and hydrophilic moiety as a simple monomeric unit (Kunieda et al., 2001). As the concentration of the solution increases, these monomeric units tend to form aggregates at the solvent-surfactant interface forming a micelle structure (Yeskie and Harwell, 1988). Such a phenomenon of micelle formation is termed as micellization, and the concentration at which this occurs is termed as critical micelle concentration (CMC) (van Oss, 2008). Petroleum contaminant is either adsorbed onto the grain of soil or trapped as a droplet in the aqueous zone as shown in Fig. 1.1 (a). Depending on the nature of the contaminant, the removal of petroleum oil from the soil environment by surfactant occurs by two primary mechanisms; solubilization and mobilization (Javanbakht and Goual, 2016; Saito and Shinoda, 1967). The removal of contaminants that are trapped in the aqueous zone occurs by mobilization via the formation of microemulsion (oil contaminant surrounded by aqueous surfactant solution). Surfactant molecules, existing as micelles, detach themselves from the micellar state and attach with the contaminant layer present on the rock grains to the contaminants trapped in the soil layers. For this to occur, the nonpolar tail of the surfactant has to adsorb onto the contaminant trapped in the aqueous zone. This results in the formation of a Type-III microemulsions, which is a three-phase system, where the surfactant-rich phase is surrounded by excess oil and water on both the sides Fig. 1.1(b) (Doan et al., 2003). Generally, mobilization occurs at a faster rate than the solubilization, as the contaminants are insoluble in nature. Also, the contaminants adsorbed on the rock grain are difficult to mobilize as they are unstable and tend to detach it from the emulsion system. In this case, the surfactant molecules dissolve the contaminant by the formation of Type-I microemulsion (two-phase system, where excess oil is surrounded by surfactant phase) (Jawitz et al., 1998) and solubilize the petroleum contaminant Fig 1.1(c). Micellar solubilization is based on increasing the solubility of hydrophobic contaminants and transferring them over an aqueous phase in which they are ordinarily insoluble (Weiss et al., 1996). In contrast, the mobilization involves displacement of hydrocarbon through a reduction in the interfacial tension between the soil surface and contaminants (Vigon and Rubin, 1989). The surfactants with larger nonpolar group solubilize the contaminants to a greater extent. As solubilization occurs above CMC, the non-polar contaminants have better interaction with micelle formed, thereby enhancing the removal efficiency.

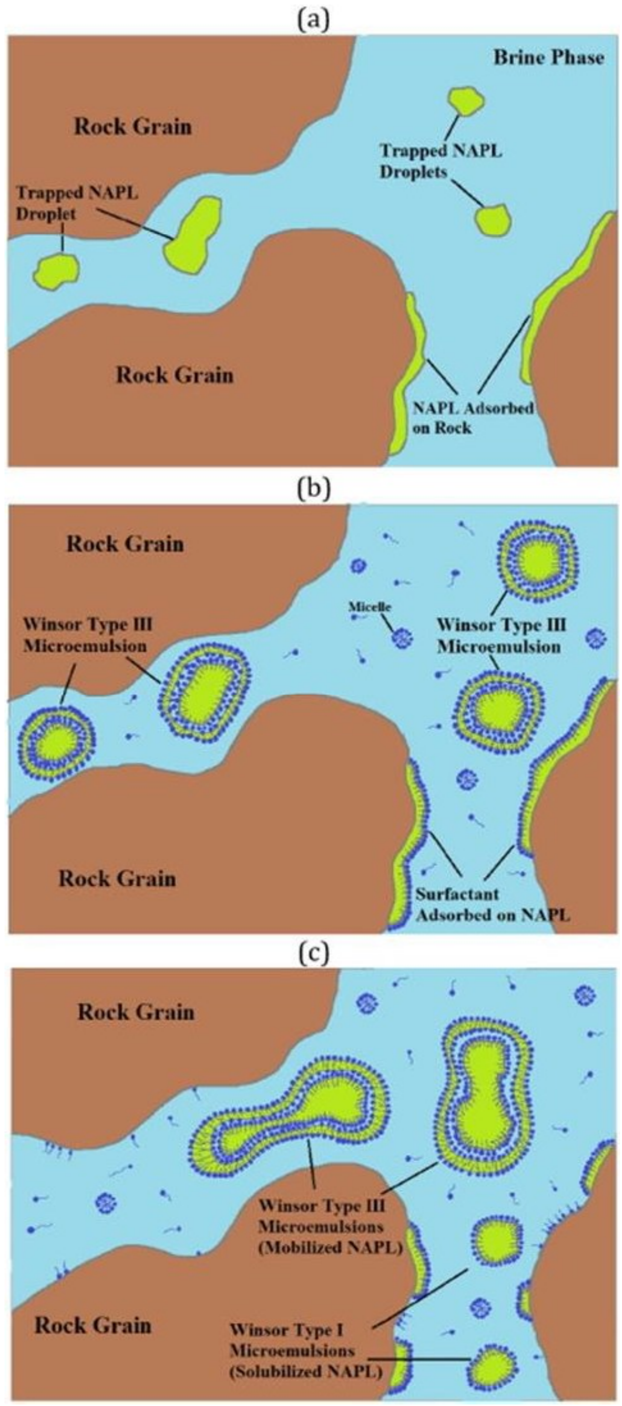

Fig. 1.1 Process of NAPL removal from contaminated aquifer: (a) trapped and adsorbed contaminant adsorbed on the soil grain and trapped as a droplet, (b) Formation of emulsion by surfactant micelle, (c) mobilization and micellar solubilization of the contaminants.
Adapted from J Javanbakht, G., Goual, L., 2016. Mobilization and micellar solubilization of NAPL contaminants in aquifer rocks. J. Contam. Hydrol. 185-186, 61-73. Elsevier (2016), with permission from Elsevier, Ref (Javanbakht and Goual, 2016)

1.1.4 Mechanism of contaminant removal by surfactant foam

The aqueous surfactant foam has been applied initially to displace oil from the subsurface. The foam is used to remove petroleum contaminants from the soil surface in the year 1980 by (Lawson and Reisberg, 1980). Aqueous foam is fundamentally characterized by two important properties prior to any desired application (Farajzadeh et al., 2009). These properties are foamability and foam stability (Martins et al., 2001). Foamability is defined as the ability of surfactant to produce foam, and it is measured by the volume of the foam generated. Foam stability is known as the propensity of foam to remain stable without decaying (King, 1944; Li et al., 2012). It plays a crucial role in crude oil displacement efficiency in porous media. To achieve better foam stability, it is essential to identify the suitable surfactant, type of gas used in foam formation, and understand the properties of soil subsurface (Shokrollahi et al., 2014). Nikolov et al. (1986) reveal that the foam stability tends to increase with an increase in hydrophobic chain length of surfactant. The stability of foam is also affected by the property of oil contaminants in the soil surface. Increasing hydrocarbon chain length of oil decreases the foam stability (Osei-Bonsu et al., 2015). Rashed Rohani et al. (2014) demonstrate the effect of oil presence on foam stability during the soil amendment processes, such as oil extraction and remediation of oil-contaminated soil. The height of foam produced with sodium dodecyl sulfate (SDS) is observed to decrease to 5 cm with the addition of crude oil. Oil enters the foam and sticks in the border of the film thus reduce the stability of foam fraction. The presence of foam in the soil is also influenced by various mechanisms and understanding of these is important to design suitable soil remediation methods.

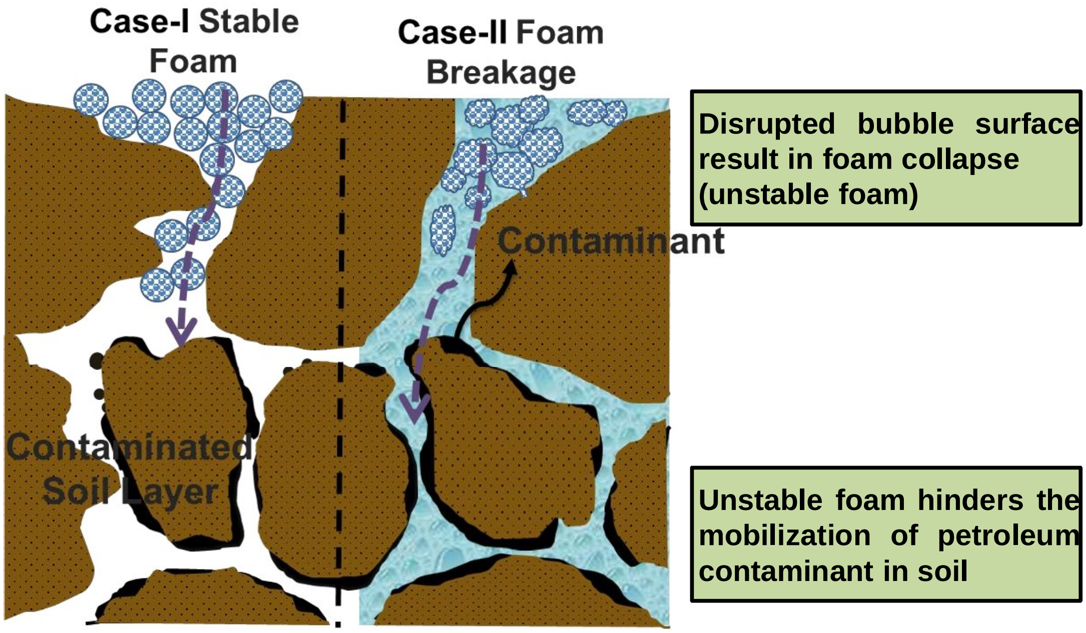

Fig. 1.2 Transport of foam in the porous contaminated soil layer. Case-I The transport of stable foam is shown. In Case-II the unstable foam due to breakage leading to transport of liquid is depicted.

During the remediation process, foam flows through soil layers, desorbs the oil from the polluted soil, and finally carries the oil away with it, leaving the pollutant-free soil behind (Yang et al., 2005). The basic mechanism for contamination removal by surfactant foam remains the same as that valid for the surfactant solution. Here the included deciding factor is the ability of the foam to propagate through the porous layers of soil (Kilbane et al., 1997). Foam flow through a porous contaminated soil media is a complex phenomenon arisen from its initial process of generation, bubble breakage, capillary pressure effects and channeling effect (Kovscek and Bertin, 2003). The rate of transport of foam in the contaminated soil layer depends strongly on the stability of the foam (Mast, 1972). The study of Mast (1972) depicts that transport of stable foam occurs through the channels of the porous layer by following a plug flow pattern (Mulligan and Eftekhari, 2003). Whereas, the unstable foam moves as liquid and gas, due to breakage of the bubble and liquid moves along the soil surface (Fig. 1.2). This leads to the lateral transport of the surfactant solution (liquid tends to spread). As a result, the flow of gas molecules decreases and the volumetric sweep of oil from the porous layer increases (Khatib et al., 1988). Highly stable foam provides more resistance to gas flow in the soil layer resulting in reduced gas mobility (Osei-Bonsu et al., 2016). This leads to a reduction of pathways available for gas permeability. Thus for the foam to achieve better remediation effect, it has to remain stable in the soil layer in the presence of oil contaminants (Osei-Bonsu et al., 2017a). Wang and Chen, (2014) experimentally investigate the resistance of foam in porous media, where they defined the foam resistance factor as the ratio of the pressure difference across soil layer by water flushing to the steady-state pressure difference achieved during foam flushing. Higher the resistance, higher is the stability of foam, and better is the remedial effect (Zang et al., 2015). A certain pressure gradient is required to initiate the flow of foam in the capillaries of the soil layer so that the foam bubbles can sustain for a longer period without being collapsed (Ma et al., 2013).

1.1.5 Mechanism of contaminant removal by nanoparticle stabilized surfactant foam

The propagation velocity of aqueous foam reduces owing to the oil present in the porous layer of soils (Simjoo et al., 2013). Schramm and Novosad, (1990) propose the dimensionless Lamella Number (L), the ratio of capillary pressure at the plateau border of the bubble (ΔP_C) and the difference in pressure at the interface of oil and water (ΔP_R), to describe the foam stability in the presence of oil. Nanoparticles could be a means to stabilize aqueous surfactant foam and increase their transport in the unsaturated zone of the soil (Espinoza et al., 2010).

The particles tend to accumulate at the oil-water interface, form a thick layer, prevent the coalescence and drainage and thereby stabilizing the foam in the soil layer (Binks, 2017). The liquid films in the foam are either stabilized by the formation of monolayer bridged by the particles or by the formation of a bi-layer of closely packed particles (Horozov et al., 2005).

Foam being thermodynamically unstable, often stabilize kinetically by adsorption of colloidal particles and surfactants, foaming agents at gas-liquid or liquid-liquid interfaces. Sun et al. (2015) demonstrate that the adsorption of nanoparticle on the surface can reduce the bubble breakage in the porous soil surface. The foam generated with the dispersion of silica nanoparticle and SDS has been stable for 1000 min, whereas the foam produces by only SDS remains stable for 100 min. At low concentration, the adsorption of SDS molecules on the surface of silica nanoparticle occurs through hydrophobic interaction, leading to reduced surface charge, which helps in adsorption of more uncharged particles on the bubble surface. Oliveira et al. (2004) demonstrate the influence of fine particles on surfactant foam. They observe that the presence of hydrophobic particles along with surfactant hinders the stability of foam by increasing the coalescence rate of the bubble.

Aqueous foam stabilized by nanoparticles reduces surface tension at the interface (Zargartalebi et al., 2015); this, in turn, leads to reduced retention of nanoparticles that it carries along (Garbin et al., 2015). Thus, foam promotes higher delivery of nanoparticles in the soil surface and has been found to increase the sweep efficiency in the reservoir (Nguyen et al., 2014). The other mechanism of enhanced soil remediation, as explained by Yu et al. (2015a), is that foam along with nanoparticles tends to flow at a higher velocity, depending on the gas that is employed in foam formation.

1.1.6 Optimization of the soil remediation process

Identifying and optimizing a significant parameter is an essential step in the development of an efficient technique. Optimizing a process by the suitable method will help in achieving the desired result and reduce the operational cost (Taki et al., 2018). Keeping in mind the multiple parameters involved, we have used the multi-objective optimization technique to attain an optimal response for the soil remediation techniques. In a conventional optimization technique, as in the case of linear regression, only a single process variable can be optimized by fixing all other variables constant at a single level (Silva et al., 2007; Zhang et al., 2009). This technique fails for the process, such as surfactant foam mediated remediation and detergent formulation, which involves multiple variables (Couto et al., 2009). Also, the conventional optimization technique doesn't take into account the interaction between the process variables which results in the consumption of higher time to optimize each parameter (Mohajeri et al., 2010). Response surface methodology (RSM) is a reliable optimization tool than the traditional one factor at a time approach, which helps to develop significant models of the desired process (Li et al., 2010). The significant advantage of the RSM approach is that it requires a minimal number of experimental runs. Also, it uses a statistical approach based on the factorial design (Rajeswari and Amirthagadeswaran, 2017). RSM is a more advantageous tool owing to the accuracy of the modeling, as well as the validation of the predicted responses (Pilkington et al., 2014). The prediction of the interactions and square terms of parameters are more significant than the conventional optimization technique such as the Taguchi technique and linear regression method (Sivaraos et al., 2014).

RSM is a mathematical-statistical modeling technique which considers the individual variables affecting a process, also the interactive influence of those variable with other process variables with the objective of optimizing the desired responses (Cavazzuti, 2013; Wu et al., 2010). A specifically targeted result is regarded as a response (y); for example, the response can be maximum removal efficiency, foam volume, stability achieved at the end of any technique/process. This response is affected by the independent variables such as concentration, operating time, flow rate, pressure, etc. These independent variables are distinguished by their defined units (ppm, s, m^3s^{-1}, Pa). However, RSM considers these as dimensionless coded variables (x_1, x_2, x_3). Considering the soil remediation process, if x_1 is the coded variable designated for the concentration of surfactant and the desired response is removal efficiency, then a negative response obtained for a positive value of surfactant concentration (x_1) would mean the removal efficiency increases with increasing surfactant concentration. The coded variable takes +1 and -1 for the maximum and lowest value of any independent variable respectively. In this way interaction between the different variables (x_1x_2, x_1x_3, and x_2x_3) can be identified for any desired process. In RSM, in case the responses are defined by the linear function of the process variables, then the first-order model is the approximating function (equ.1). Higher degree polynomial is used if there is a curvature in the desired responses (equ.2).

$$Y=\beta_0+\sum_{i=1}^{n}\beta_i X_i+E \qquad (1)$$

$$Y=\beta_0+\sum_{i=1}^{n}\beta_i X_i+\sum_{\substack{i=1\\j>1}}^{n=1}\sum_{j=2}^{n}\beta_{ij}X_iX_j+\sum_{i=1}^{n}\beta_{ij}X_i^2+E \qquad (2)$$

The desired response (y) obtained using the model equation can be verified with the experimental values to assure the validity and adequacy of the developed model. Residual defines the difference existing between the response obtained using experimentally measured and model equation. RSM employs three levels factorial design-3^k factorial design (k denotes the number of factors), Box-Behnken design (BBD), Central composite design (CCD), and D-optimal design (Rakić et al., 2014; Vera Candioti et al., 2014). The BBD is considered to be most efficient in generating higher-order responses using minimal experimental values, and it also consumes less time in achieving effective optimized parameters than that of the CCD and D-optimal designs (Ferreira et al., 2007; Vaez et al., 2012). BBD is based on the full and fractional factorial design points where these points are located in the middle of the edges as well as at the center of the cube (Rao and Kumar, 2012). The BBD requires three levels for each process parameter (factors) (Ait-Amir et al., 2015). The major advantage of BBD over CCD is, it produces final optimum conditions within the range of selected parameter whereas CCD may produce optimum conditions beyond the selected parameters (Zolgharnein et al., 2013). RSM approach has been applied in various soil remediation technique including supercritical fluid extraction, Fenton oxidation, phytoremediation, surfactant solution enhanced remediation and bioremediation (Joshi and Lee, 1996; Meskar et al., 2018; Ravanipour et al., 2015; Titah et al., 2018; Zhang et al., 2009).

1.2 Role of surfactant foam in the formulation of liquid laundry detergent

Laundry of everyday clothes is done manually by hands prior to the advent of machines till the late 19th century (Bushman and Bushman, 1988). The washing of fabrics is still done manually in many parts of the world (Oberoi et al., 1983). During manual washing the dirt adhered on the fabrics are removed by scrubbing, twisting, or whipping. The machines use electrical power to produce a rotational motion inducing a liquid flow to generate the twisting and deformation of the fabrics (Pakula and Stamminger, 2010). Be it either manual or machine washing, the removal of dirt, the prime goal of washing is achieved only when a chemical detergent is used. Thus, detergent determines the efficiency of the washing process; this has led to a huge market penetration of detergent brands in industrially developed countries. Laundry and washing of daily used clothes, home textiles and fabrics is still one of the major prevalent household works in the world. Chemical laundry detergent has a large domestic market owing to which enormous changes have occurred in the surfactant technology over the last century (Scheibel, 2004). The global domestic cleaning product market is estimated to be USD 75,580 million in the year 2017 which is expected to double in the next decade (https://www.futuremarketinsights.com/reports/laundry-care-market). This high global demand has a strong influence on the surfactant industry. Laundry detergent is a complex mixture of surfactants, fillers, builders, and solubilizers (Timar-Balazsy, 2000). Surfactant, being the primary component, resembles the major influencing factor in formulating an effective detergent product (Ou and Zhao, 2017).

Detergents can be classified into industrial detergent and household detergents, depending on the intended application. The industrial detergents are used for cleaning the hard surface, whereas the household detergents are used in cleaning the household fabrics and soiled utensils.

The ability of any detergent to remove the soil (dirt) from the desired surfaces either hard surface or fabric is measured in terms of detergency. It is difficult to quantify the detergency of any detergent as the evaluation includes multiple variables. In addition, the test of detergency must consider laboratory conditions in correlation to the practical applicability and reaction of consumer desirability (Jurado et al., 2003).

For any liquid to produce foam, there has to be the presence of surfactant molecules that reduces the surface tension (Langevin, 2017). Foam can be defined as bubbly liquid formed in a liquid containing surfactants as a dispersion of gas by external action such as agitation or stirring (Bui et al., 2016; Kovscek and Bertin, 2003). The surface-active molecules adhere to the interface of gas and liquid which in turn affects the tendency of the liquid to foam and stability of the dispersion (Shrestha et al., 2007). This brings up the two important parameters of foam, namely foamability and foam stability (Karakashev et al., 2011). Foamability defines the ability of surfactant to foam (how easily foam is produced) (Salonen et al., 2010), and foam stability refers to the time required to lose 50% of foam volume (how easily foam can collapse) (Schellmann et al., 2015). In other terms, foam stability can be referred as the resistance intrinsic resistance of bubble lamella to decrease the interfacial area, and this does not necessarily imply thermodynamic stability (Murray, 2007). The properties of foam depending on the method of foam generation and also on the properties of the surfactant used to produce the foam (Skauge et al., 2019). Moreover, these properties are not related to each other directly; instead, these properties are controlled by various external factors. The foamability is affected by surface tension and critical micelle concentration (CMC) of the surfactant (Arciniega Saavedra and Gracia-Fadrique, 2016) whereas, the foam stability is affected by the independent surface factors such as molecular packing at the film and surface viscosity (Jong and Nguyen, 2018). The foam stability tends to reduce when the foam starts to collapse (Spina et al., 2016). The foam collapse occurs due to the drainage of liquid from the foam and bubble disproportion (Ettelaie et al., 2003). In order to prevent foam collapse, it is necessary to select suitable surfactant that opposes the drainage by increasing the surface tension gradient (Saint-Jalmes, 2006). This phenomenon plays an important role in various industrial applications of surfactant namely plastics, paints, coating technology, agrochemical and textile processing (Schramm and Novosad, 1990).

The surfactant is the major component affecting the detergency of any household laundry product, the choice of selecting a surfactant in preparing a detergent formulation is important (Shivaji Biranje et al., 2015). The selection of raw material is also an essential factor in the formulation of a well-balanced detergent. The major additives used in the detergent formulation include builders, solubilizers, and polymers. Each of these components aids in the improvement of detergent performance (Siwayanan et al., 2014). For instance, the presence of water-soluble polymer in the detergent formulation helps in preventing the re-deposition of oily soil on the fabric after being removed by the detergent action (Ayele et al., 2016; Do et al., 2015). Builders used in the detergent mixture eliminate the water hardness thereby increasing the performance of the detergent (Sheng et al., 2012). Enzymes have been incorporated in modern detergents so as to remove any organic compounds such as fat, oil secretions, and protein, which are insoluble in water (Zhang et al., 2014). The use of environmentally friendly surfactants and other additives prepared from biodegradable products have been pursued, producing detergent formulations in the last decade (Yea et al., 2018). Detergents prepared with a mixture of surfactants have a greater impact on the removal of soil from fabrics (Jadidi et al., 2013). Non-ionic surfactants such as alkyl polyglucoside (APG) show a synergistic effect when combined with anionic surfactants (Szumała and Mówińska, 2016). This behavior is important in achieving better detergency (Joshi et al., 2005; P. Gunjikar et al., 2006). Properties such as surface tension, soil removal efficiency and interaction of surfactants in the mixed system are the key areas considered essential for detergent formulation. Detergent foam is a dispersion of gas bubbles in a liquid or solid matrices (Drenckhan and Hutzler, 2015). Aqueous foams have been proven to clean the soiled fabric surface since the year 1940 (Reuter and Mettin, 2016). The cleaning of the soil from the solid surface of textile fabric occurs by the oscillation and collapse of the bubbles on the surface. Water hardness affects the detergency drastically by forming unstable and inert precipitates. The recent work by Gotoh et al. (2016) shows the importance of analyzing various properties of detergents in different hardness levels of water. The hardness of water affects the foaming behavior of the surfactant. Higher the hardness of water, typically higher is the amount of detergent required and water. Thus a detergent has to be formulated considering the fact that the foam performance is good in various water hardness levels (Blagojević et al., 2016; Tanthakit et al., 2010).

1.3 Motivation for carrying out current research work

Remediation of soil contaminated with petroleum oil is a challenging task (Hemond and Fechner, 2015; Miller et al., 2000). Petroleum contaminant is released into soil mostly by spillage during production, storage, and transport (Zheng et al., 2018) and from industrial activities. Owing to its high density, petroleum oil penetrates deep into soil subsurface as well as its higher solubility leads to contamination of the groundwater table (Leharne, 2019). Humans are exposed to such contaminants by direct contact of soil through dermal exposure, inhalation and ingestion of contaminated groundwater (Hentati et al., 2013; Park and Park, 2010). Enormous industrial growth has transformed human life and its society in the past ten decades. Though industrial activity has brought a better lifestyle and various growths, it has also lead to the most intractable pollutants in the environment. It is necessary to identify and evaluate sustainable technology to counter this threat to the environment.

Surfactant foam mediated technique has been effectively applied to treat petroleum-contaminated soil. Aqueous surfactant foam is a dispersion of gas in the liquid produced by the expansion of gas in the solution. The foaming process involves the formation, growth and stabilization of the gas bubbles in the aqueous medium. Owing to their biphasic nature, surfactant molecules adsorb at the gas-liquid interface and decrease the surface tension thereby resulting in the effective mobilization of diesel from contaminated soil. Foams can be stabilized by various additives ranging from salts, polymers, micro and nanoparticles. In this work we have utilized biodegradable additives- Ethylene glycol and Allyl alcohol to stabilize foam for the effective removal of oil from the diesel-contaminated soil.

Nanotechnology has been used to treat various environmental problems; the potential of nanomaterial to treat contaminated soil is the primary motivation behind carrying out the current research. Nanoparticle stabilized foam can effectively enhance the remediation also foam acts as a suitable vehicle to efficiently deliver nanoparticles in soil subsurface (Shen et al., 2011). Iron, being a fourth abundant element on earth occurs in various forms ranging from oxides, oxyhydroxides minerals in nature. Iron nanoparticles are proven to be a strong reducing agent which donates an electron to the contaminant species and result in degradation of petroleum contaminant in soil (Kovscek and Radke, 1994; Langevin, 2017; Roseta.C and Obinna.F, 2017). In addition, the mechanical and thermal stability of nanoparticles silica nanoparticles makes it robust in the soil subsurface due to its higher resistance towards soil conditions. In addition, the nanoparticles adsorb strongly at the gas-liquid interface producing highly stable foam suitable for contaminant removal. Thus utilizing iron nanoparticle stabilized surfactant foam may be a suitable technique to treat petroleum-contaminated soil. Thus utilizing iron nanoparticle stabilized surfactant foam may be a suitable technique to treat petroleum-contaminated soil. Apart from its usage in environmental clean-up, surfactant foam is of great importance in other applications, especially the household detergent industry. Analysis of the foaming tendency of the laundry detergent becomes essential owing to its importance in producing a better washing performance. Through this study, we highlight the importance of foaming behavior and the cleaning performance of new liquid household laundry detergents.

1.4 Objectives of the research work

Surfactant foam finds its application in various fields ranging from environmental to treat contaminated soil, domestic household laundry industry, the energy sector to recover oil from subsurface and pharmaceutical industries to deliver drugs. Thus, with the aim to develop a technique and to analyze the surfactant foam behavior in multiple applications the following objectives are reached:

- To study the foam stabilization effect of additives including allyl alcohol, ethylene glycol on nonionic surfactant (Tween-80), anionic surfactant (SDS) and nanoparticles such as SiO_2 on nonionic surfactant (Tween-20), Fe_3O_4 and Fe^0 on nonionic surfactant (APG-Ph).
- To study the remedial effect of these systems for the removal of diesel oil from soils contaminated with petroleum oil (diesel) spills.
- To determine the optimum surfactant foam parameter for the surfactant foam mediated soil remediation process.
- To generate surfactant foam that will be suitable for better detergent performance and to characterize them.

A brief background of the environmental problem associated with petroleum contaminants, methods available to treat petroleum-contaminated soil, contaminant removal mechanism by surfactant systems, optimization technique to treat contaminated soil, as well as the role of surfactant foam for laundry detergent formulation and application are discussed in this chapter. Also, the research objectives of the current work are presented in this chapter.