
Chapter 3

Materials and Methods

3. Materials and Methods

The present chapter provides the details of nanomaterial used in the study as well as the experimental methodology adopted for the characterization of soil, synthesis, and characterization of Fe⁰ and Fe₃O₄ nanoparticle, preparation, and characterization of nanoparticle dispersion, foam, and soil remediation studies. The methodology implemented for the optimization of soil remediation process and formulation and characterization of liquid laundry detergent are also discussed in this chapter

Nanomaterial used in the study

In the current study, the potential of nanoparticles, including hydrophobic/hydrophilic SiO₂, Fe⁰, and Fe₃O₄; additives such as ethylene glycol and allyl alcohol are used to stabilize aqueous surfactant foam and application of these stabilized foams to remediate diesel-contaminated desert soil, coastal soil, and clay soil are performed.

Hydrophobic SiO₂ nanoparticle of average particle size of 55 nm and with specific BET surface area of 195-245 m²g⁻¹ and density of 2 gcm⁻³ was supplied by Evonik Canada Inc. Hydrophilic SiO₂ nanoparticles (NanoLabs) used in the study had a particle size in the range 50-80 nm surface area of 630 m²g⁻¹ and a density of 2.5 gcm⁻³. For further experimental analysis, the concentrations of both hydrophobic and hydrophilic SiO₂ nanoparticles are selected to be 1, 2, 3, 4 and 5 mg/l. In the same way the concentration of the surfactant Tween-20 (Himedia, LR Grade, purity >98%) is selected to be 0.02, 0.04, 0.06, 0.08 and 0.1 vol%. The name of the sample is decided to be represented as a combination of 'hydrophobicity' and 'concentration in dispersion'; for example, hydrophobic SiO₂ dispersion of concentration 1 mg/l is named as Hydrophobic SiO₂- 1.

Biodegradable additives, including Ethylene glycol (Molychem, India, LR Grade, purity 98%) and allyl alcohol (Qualigens, India, AR, purity 98%) are selected to be varied between 1, 2 and 3 mg/l. Similarly, here the quantity of surfactants Sodium n-dodecyl sulfate (SDS) (Fischer Scientific, AR, purity 98%) and Tween 80 (Himedia, LR, purity >98%) is selected as 0.04, 0.06, 0.08, 0.1, 0.2 wt% and vol%.

The Fe⁰ and Fe₃O₄ powder synthesized by protocols (refer to section 3.12) are selected to be 1, 2, 2.5, 3, 3.5, 4 and 5 mg/l. Similarly, the concentrations of Alkyl polyglucoside phosphate (APG-Ph, Sigma, LR Grade, purity >98%) are selected to be 0.02, 0.04, 0.06, 0.08 and 0.1 vol%. The name of the samples is decided and represented as a combination of ‘valence state’ and ‘concentration in dispersion’; for example, nano zero-valent iron dispersion of concentration 1mg/l is called Fe⁰-1 and iron oxide of concentration 1mg/l Fe₃O₄-1 in the following sections.

3.1 Remediation of diesel contaminated soil

3.1.1 Characterization of soil properties

For the current research work, we have chosen a total of three types of soils; sandy nature soil from the desert (desert soil), another sandy soil from the coastal area (coastal soil), and one clay soil. The properties of the soils such as texture, sand-, silt-, & clay- content, density, porosity, moisture content, organic matter, and specific gravity are studied and depicted in the following section.

Soil Texture Classification

The soil particles are classified into sand, clay, and silt based on their particle size distribution (Murano et al., 2015). Soil particles ranging from 4000-75 microns are classified as sand. Particles ranging from 75-2 microns are termed as silt and soil particles less than 2 microns are described as clay. Initially, the sand content of the soils is separated using a sieve shaker method, and the estimation of silt is carried out by the sedimentation method. Clay soil has negligible sand content. Thus, after identifying the silt content of clay soil the remaining soil is considered as clay. The particle size of the soils is also confirmed further by Field emission scanning electron microscope (FESEM) analysis.

Sieve Analysis

The particle size distribution of the soil samples is determined by the sieve shaker method. 500 g of the soil sample is placed in the stack of sieves British Standard Sieve (BSS) 200-5 mesh; 75-4000 micron) of 20 cm diameter and shaken for 15 mins using a mechanical shaker (HEICO Instruments, New Delhi, India). The soil collected in each sieve is weighed separately. The amount of soil that is retained until the 200 mesh sieve (>75-micron) is treated as the sand content of the soil (ASTM-D6913M-17).

Silt Test

The soil which passes through the 75-micron sieve and gets retained in the pan are analyzed for silt and clay content by sedimentation method (Pires et al., 2007). In the sedimentation method, the soil is transferred to a 500 mL measuring cylinder containing 400 mL of distilled water. The soil water mixture is mixed thoroughly to make a complete dispersion. The dispersion of soil in water is allowed to settle for 24 h undisturbed. The volume of silt deposited can be measured to identify the percentage of silt in the soil samples.

$$\text{Silt \%} = \frac{V_{\text{silt}}}{V_{\text{soil}}} \times 100 \quad (3)$$

Where,

V_{silt} - The volume of silt layer formed after 24 h

V_{soil} - The total volume of soil placed in the measuring cylinder.

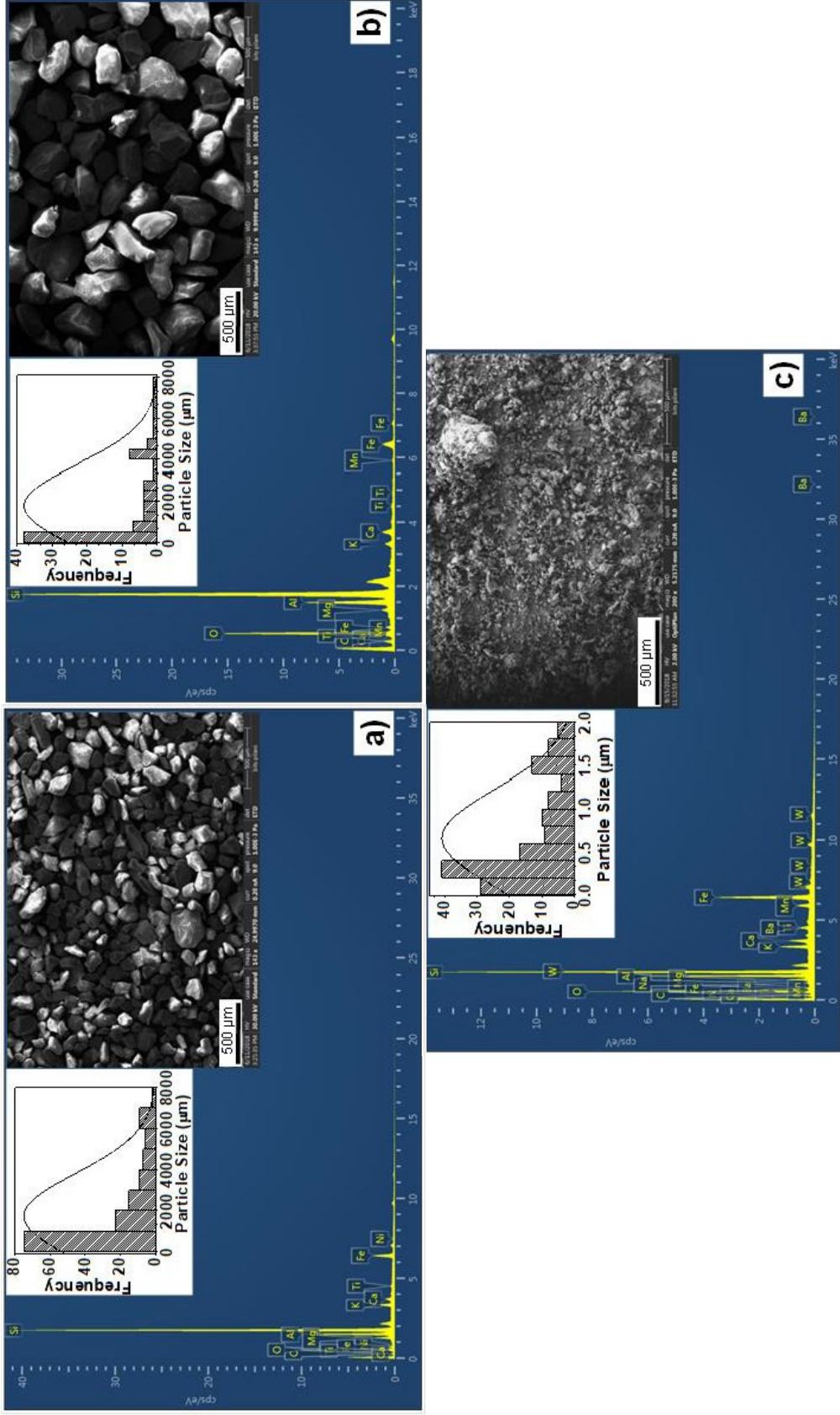


Fig. 3.1 EDX plot displaying the elemental composition of soils along with the insets displaying respective SEM micrographs and particle size distribution plot of (a) desert soil (b) coastal soil and (c) clay soil.

FESEM

Field emission scanning electron microscope (FESEM; FEI, Apreo, 15 kV) equipped with energy dispersive x-ray spectroscopy detector (EDX, Oxford) is used to characterize the morphology, microstructure elemental composition of the natural soil samples. The soil samples are dried at 110°C in a hot air oven overnight prior to SEM analysis to remove moisture content. The soil samples are coated with gold particles to make it conductive and placed on the carbon tape (Liu et al., 2015). The particle size distribution of the soils from the SEM micrographs is determined using open-source “ImageJ 1.52a” (National Institute of Health, USA) software. The particle size distribution of the desert, coastal, and clay soils calculated from SEM micrographs and shown in the Fig. 3.1.

pH test

The pH of the natural soils, contaminated soils, and soils after the treatment process are measured. 10 g of the soil sample is weighed, transferred into 100 mL glass beaker to which 20 mL of distilled water is added and stirred well with a glass rod. This is allowed to stand for half an hour with intermittent stirring. The electrode (Hanna Instruments, India) is immersed in the soil water suspension in the beaker, and the pH value is determined by pH meter. Prior to analysis, the calibration of pH meter using pH 7 buffer solution is performed. Also, the pH meter is calibrated with known pH of buffer solutions 4.0 and 9.2.

Conductivity

The conductivity of the natural soils, contaminated soils, and soils after the treatment process are quantified. Soil conductivity is measured using microprocessor water and soil analysis kit (Khera Instruments, Delhi, India). 10 g soil samples are taken in a glass beaker and mixed well with 20 mL of distilled water. The mixture is constantly stirred to ensure the retention of soil

particles in suspension. The Conductivity probe (Khera Instruments, Delhi, India) is inserted into this soil-water mixture to record the conductivity value.

Bulk density

The bulk density of soils is measured by the free-fall method using a 1000 cm³ measuring cylinder (Da C. Nhantumbo and Bennie, 2001). The pre-weighed empty measuring cylinder of 1000 cm³ is filled with soil up to the 1000 cm³ mark. The weight of the soil placed in the measuring cylinder is measured. Using this, the density of the soil can be calculated by utilizing the following equation,

$$\text{Bulk density (g/cm}^3\text{)} = \frac{\text{Dry soil weight (g)}}{\text{Soil volume (cm}^3\text{)}} \quad (4)$$

Porosity

The porosity of the soil is measured by the saturation method (Fies and Bruand, 2003; Matko, 2003; Sartori et al., 1985). Three different soils are filled separately in a 500 mL beaker to an equal volume irrespective of its weight. Then the water is added slowly until it reaches the top of the soil layer in the beaker. Porosity is determined by the percentage of the volume of water (V_w) added in the beaker to the total volume of soil (V_t) present in the beaker.

$$\text{Porosity} = \frac{V_w}{V_t} \times 100 \quad (5)$$

Moisture Content

The moisture content of the soil is measured by the oven drying method. Initially, 10 g of soil is weighed and placed in a petri dish. The soil along with the petri dish is placed in a hot air oven at 110° C for overnight (O'Kelly, 2004). The weight of the soil after drying (W_2) is measured to determine the moisture content.

$$\text{Moisture Content} = \frac{W_2 - W_3}{W_3 - W_1} \times 100 \quad (6)$$

Where

W_1 - Weight of the empty petri dish

W_2 - Weight of the petri dish along with soil prior to drying (Wet soil)

W_3 - Weight of the petri dish along with soil after drying (Dry soil)

Organic Matter

The total organic matter of various soils is measured by loss in ignition method according to standard ASTM D-2974 protocol (ASTM-D2974-14; Rowell and Coetzee, 2003). For this, 10 g of soil (M_s) is weighed in a porcelain crucible and placed in muffle furnace overnight at 440° C. The crucibles are carefully removed using tongs and weighed after drying it to room temperature.

$$\text{Organic Matter} = \frac{M_{ws}}{M_{ds}} \times 100 \quad (7)$$

Where

M_{ds} - Weight of dry soil after combustion

M_{ws} - Weight of wet soil before combustion

Specific Gravity

The specific gravity of soil is the measure of the ratio of the mass of soil to the mass of an equal volume of soil. Here the specific gravity is measured using a volumetric flask as it is suitable for all types of soil (Al-Shayea, 2001; Pu et al., 2017). The specific gravity of the soils is analyzed by taking 10 g of soil in the volumetric flask. Initially, the mass of the empty volumetric flask is noted. Mass of the volumetric flask with soil sample is measured. Also, the weight of the bottle filled with water (equal volume) was determined.

$$\text{Specific Gravity} = \frac{(W_2 - W_1)}{(W_4 - W_1) - (W_3 - W_1)} \quad (8)$$

Where

W_1 - Weight of empty volumetric flask

W_2 - Weight of the volumetric flask with dry soil

W_3 - Weight of the volumetric flask and soil and water

W_4 - Weight of volumetric flask filled with water only.

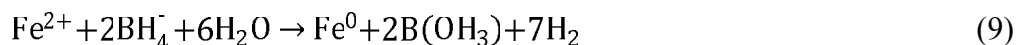
Table 3.1: Properties of the soils collected from different regions used in the remediation study shown along with statistical variation.

Soil sample ► Properties ▼	Desert Soil	Clay Soil	Coastal Soil
Texture	Sandy Soil	Clayey Soil	Sandy Soil
Sand (%)	96.5 ± 1.5	6.7 ± 1.83	96.2 ± 0.35
Silt (%)	3.5 ± 0.1	-	3.1 ± 0.17
Clay (%)	0.3 ± 1.5	93 ± 1.83	0.6 ± 0.35
Density (gcm⁻³)	1.5 ± 0.1	1.1 ± 0.014	1.5 ± 0.05
Porosity (%)	41.3 ± 1.8	69.3 ± 0.88	38.1 ± 0.78
Moisture Content (%)	3.1 ± 1.5	4.6 ± 0.89	1.5 ± 0.73
Organic Matter (%)	1.9 ± 0.3	4.1 ± 0.23	1.4 ± 0.19
Specific Gravity	2.7 ± 0.2	2.7 ± 0.014	2.1 ± 0.07

3.1.2 Preparation and characterization of nanomaterials

Synthesis of nano zero-valent iron (Fe⁰)

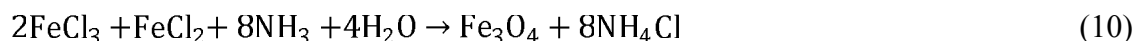
The nano Fe⁰ is synthesized by a liquid-phase reduction method (Uzum et al., 2008) using ferrous chloride (FeCl₂.4H₂O) (Molychem, LR Grade, purity >98 %) and sodium borohydride (NaBH₄) (Rankem, LR Grade, purity >98 %) as precursors according to the following equation:-



2M ferrous chloride solution is prepared with ethanol and distilled water mixture (4:1 v/v). 1M NaBH₄ solution is prepared in distilled water. The reduction of Fe²⁺ is carried by the addition of NaBH₄ solution dropwise into the FeCl₂ solution under constant stirring at room temperature. A fine black mass appears in the beaker. After completion of the reaction, a little excess reducing agent is added, and the reaction mixture is stirred for 45 min extra at room temperature to ensure the complete reduction of Fe²⁺. The black-colored product is washed several times with ethanol and deionized water to remove all acid and base residues using a centrifuge (REMI, CPR-24, Mumbai India)). Finally, the material is separated and dried in a hot air oven at 68°C overnight (Yu et al., 2015b). The powder is stored in an airtight container at room temperature, and no significant change in color is observed even after three months.

Synthesis of Iron oxide (Fe₃O₄)

Iron oxide nanoparticle is synthesized by an aqueous precipitation method (Khalil, 2015) according to the following equation (Berger et al., 1999):-



1M Ferric Chloride (FeCl₃.6H₂O) (Molychem, AR Grade, purity >98 %) and 2M FeCl₂ solutions are prepared in a mixture of ethanol and distilled water (4:1 v/v). Diluted ammonium hydroxide (NH₃: H₂O = 1:4) (Molychem, GR Grade, purity 99 %) solution is added to this

mixture dropwise with constant stirring at room temperature to ensure the formation of uniform particles and prevent particle aggregation. The resulting solid mass is washed with 25 % tetramethylammonium hydroxide (CH₃)₄N(OH) (Sigma, LR Grade, purity >97 %) solution and separated by centrifuging. The material is heat-dried at 68°C overnight and stored at room temperature.

3.1.3 Physico-chemical Characterization of nanomaterials

The phase composition, phase purity and particle size of the powders are analyzed by using an X-ray diffractometer (XRD) (Rigaku, MiniFlex II, with CuK α radiation (1.54 Å, 15 mA, 30 kV), over a 2-theta range of 10-80° and scanned at 2°/min rate. The morphology and microstructure of the gold-coated powder samples are studied with the help of a field emission scanning electron microscope (FESEM; FEI, Apreo, 15 kV) equipped with energy dispersive X-ray spectroscopy detector (EDX; Oxford) and a transmission electron microscope (TEM; FEI, TECNAI T20S TWIN). For TEM sample preparation, the powder is dispersed in ethanol using ultra-sonication and a drop of this suspension is added on a Cu grid coated with a thin carbon layer. The particle size distribution (assuming that the particles are spherical) from the micrographs is determined using open source “ImageJ 1.52a” (National Institute of Health, USA) software (Neagu et al., 2015). Information from 200-250 particles per sample is used.

3.1.4 Preparation and characterization of dispersion of nanomaterials

The iron and iron oxide samples of different concentration (1, 2, 2.5, 3, 3.5, 4 and 5 mg/l) are dispersed in deionized water by using an ultrasonic probe sonicator (Johnson Plastosonic, Mumbai, India) at 20 kHz for 45 min (Dickson et al., 2012). Alkylpolyglucoside phosphate (APG-Ph, Sigma, LR Grade, purity >98%) of different concentrations (0.02, 0.04, 0.06, 0.08 and 0.1 vol %) is dissolved in the prepared dispersion. The surfactant acts as a dispersant of heavier

iron nanoparticles and produces a stable dispersion (Kauppi et al., 2011; Mandel et al., 2015). The name of the samples is decided and represented as a combination of ‘valence state’ and ‘concentration in dispersion’; for example, nano zero-valent iron dispersion of concentration 1mg/l is called Fe⁰-1 and iron oxide of concentration 1mg/l Fe₃O₄-1 hereafter.

Measurement of Surface Tension (σ)

The surface tension of the prepared aqueous mixtures (surfactant solution, or surfactant-nanoparticle dispersion) is measured by the Pendant drop method using a Dynamic Surface Analyzer (DSA25B, Kruss GmbH, Germany). It is a two-phase method, based on the analysis of the image of pendant droplet (symmetric about a central vertical axis) suspended in the air from the tip of a syringe, used to calculate the shape and surface tension of aqueous samples (Berry et al., 2015). The surfactant solution and surfactant-nanoparticle dispersions are separately drawn into a syringe along with a needle of 1.7 mm diameter and placed vertically in a holder provided to dispense the sample. Approximately 5-10 μ L of the sample is allowed to form a pendant shaped drop at the end of the needle. The contour image of the drop is recorded by a camera connected to a computer. Surface tension (σ) of the pendant is measured from the axisymmetric image by fitting with the Young–Laplace equation (Degen et al., 2011):-

$$\Delta p = \sigma \cdot \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad (3)$$

where Δp is the Laplace pressure difference across the interface, r_1 and r_2 are the two principal radii of curvature at any point on the curved interface of the pendant, orthogonal to each other (Berry et al., 2015; Saad and Neumann, 2016). The average surface tension values with standard deviation are noted at the end of each experiment.

Measurement of Zeta Potential (ζ)

Zeta potential (ζ) of the Fe^0 and Fe_3O_4 nanoparticle in the dispersion is measured using a Malvern Zetasizer Nano-ZS instrument. Fe^0 and Fe_3O_4 (3.5 mg/l) nanoparticles are dispersed in deionized water by using an ultrasonic probe sonicator (Johnson Plastosonic, Mumbai, India) at 20 kHz for 45 min, and the APG-Ph surfactant is dissolved in the prepared dispersion. 1 ml of the prepared dispersion is transferred to a Malvern Zeta Potential cell for measurements (Murdock et al., 2008).

Measurement of Viscosity (μ)

Fe^0 and Fe_3O_4 nanopowders of different concentrations are dispersed in deionized water by using an ultrasonic probe sonicator (Johnson Plastosonic, Mumbai, India) at 20 kHz for 45 min, and the surfactant is dissolved in the prepared dispersion. The viscosity of the prepared dispersion is measured at room temperature using a digital viscometer (Labtronics LT-730, Mumbai, India) by immersing a spindle (no.1) in the 50 mL dispersion and rotated at the speed of 60 rpm.

3.1.5 Preparation and characterization of foam

The foam properties of the dispersion are analyzed using a Dynamic Foam Analyzer (DFA 100, Kruss GmbH, Germany) equipment. 50 mL of the surfactant solution with or without nanoparticle is used at an airflow rate of 0.3 L/min and injection time of 12 s. The foamability and foam stability parameters are measured for a total time of 900 s (Chattopadhyay and Karthick, 2017). The foamability is reported in terms of maximum foam volume (MFV) achieved after air injection at the given rate. The stability of foam is expressed in terms of the Ross Miles Index (RMI 30) and presented as the volume of foam formed immediately after its generation in a cylindrical glass column (Kronberg et al., 2014).

The above method is used to quantify the foam properties of various surfactants stabilized described in the present research work. For instance, foam properties of multiple systems namely 1) Tween-20 and SiO₂ nanoparticle dispersion (hydrophilic and hydrophobic) (reported in section 4.1.1); 2) SDS, Tween-80 by allyl alcohol and ethylene glycol (reported in section 4.1.2) 3) APG-Ph by Fe⁰ and Fe₃O₄ (reported in section 4.1.3) are measured by the same procedure.

3.1.6 Soil Remediation Studies

Experiments are conducted to study the activity of nanoparticle stabilized foams in terms of diesel-contaminated soil remediation by using the column flushing technique. Three different soil samples are collected from different non-contaminated regions of India, namely, sandy soil from desert region of Pilani (Rajasthan, India), sandy soil from the coastal region of Rameswaram (Tamil Nadu, India) and clay soil from agricultural farmland located at Madurai (Tamil Nadu, India). Various properties of the soils such as texture, sand-, silt-, & clay- content, density, porosity, moisture content, organic matter, and specific gravity are studied and shown in Table 1. The characteristics techniques used to determine the properties of soil are described elaborately in the supplementary data.

The collected soils are sieved through a mesh size of 30 British Standard Sieve (BSS) and washed with water to remove any debris, stones, and leaves. The washed soils are dried at 128°C in a hot air oven for 24h to get rid of microbial contaminants (Ramamurthy et al., 2009). Then the soils are contaminated artificially with diesel oil with final loading of 100 µL/gm (C_i) and stored for 7 days prior to use for remediation experiments. The schematic diagram of soil column experimental setup is shown in Fig. 3.2. The contaminated soils (100 g) are treated individually

with surfactant foam in a 30 cm long and 3 cm diameter column (Parnian and Ayatollah, 2008). A fine steel mesh is placed at the bottom of the column to hold the soil sample and collect the effluent. The foam, produced by a DFA 100, is transferred to the soil column at a flow rate of 0.3 L/min and all effluent coming out from the bottom of the column is collected. The oil content left in the foam treated soil sample is extracted by using hexane (Spectrochem, GC Grade, 99.9 % purity). For this, 15 mL of hexane is added to 1 g of treated soil sample (collected after foam treatment from the top portion of the soil column) and centrifuged at 4500 rpm for 10 mins. The Beer-Lambert law, which describes a linear relationship between the absorbance and concentration of absorbent, is applied to estimate the amount of contamination left in the soil (Swinehart, 1962).

$$A = \epsilon cl \tag{12}$$

where A is the absorbance of chemical, c is the concentration, ϵ is the molar absorptivity, and l is the path length of the light.

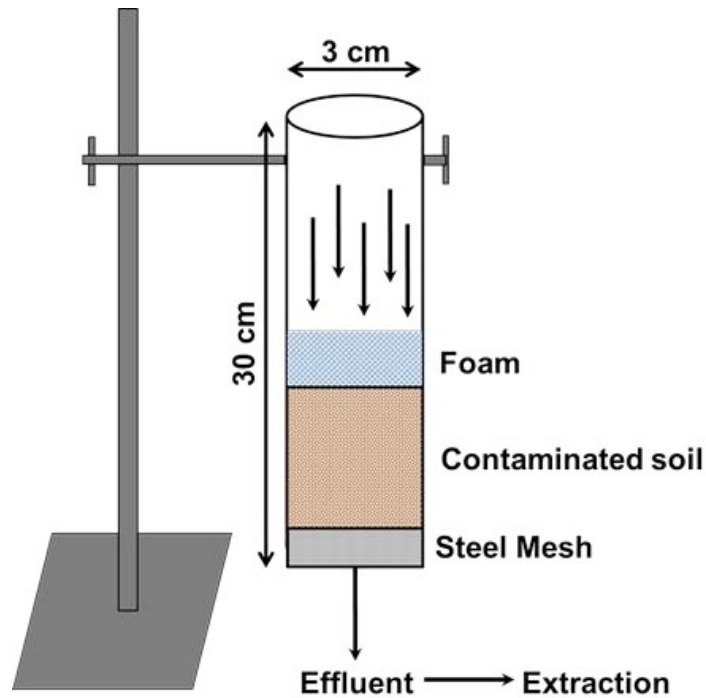


Fig. 3.2 Schematic diagram of soil column test (experimental set up)

To initiate the process of calibration, a set of known concentrations (60, 80, 100, 150 and 200 ppm) of diesel is mixed in hexane. The absorbance values of these diesel-hexane mixtures are measured by using a UV-Vis spectrophotometer (Thermo Scientific, Evolution 201) within the wavelength range of 240-800 nm. The λ_{\max} (Fig. 3.3a) is found to be 263.57 nm (Agarwal and Liu, 2017; Agarwal et al., 2016). An absorbance (at λ_{\max}) vs. concentration calibration graph is prepared from this data (Fig. 3.3b). The absorption values (at λ_{\max}) of the extracted liquid contents are obtained by UV-Vis spectrophotometer (Thermo Scientific, Evolution 201) scanning at 263.57 nm and concentration of the contaminant removed from the soil (C_t) after a certain time of treatment is acquired directly from the calibration graph. The final diesel removal efficiency ($\eta\%$) is determined by the equation:-

$$\eta\% = \frac{C_i - C_t}{C_i} \times 100 \quad (13)$$

The rate of diesel removal from different soils by surfactant foam is studied by collecting the effluent and analyzing it at regular intervals of time.

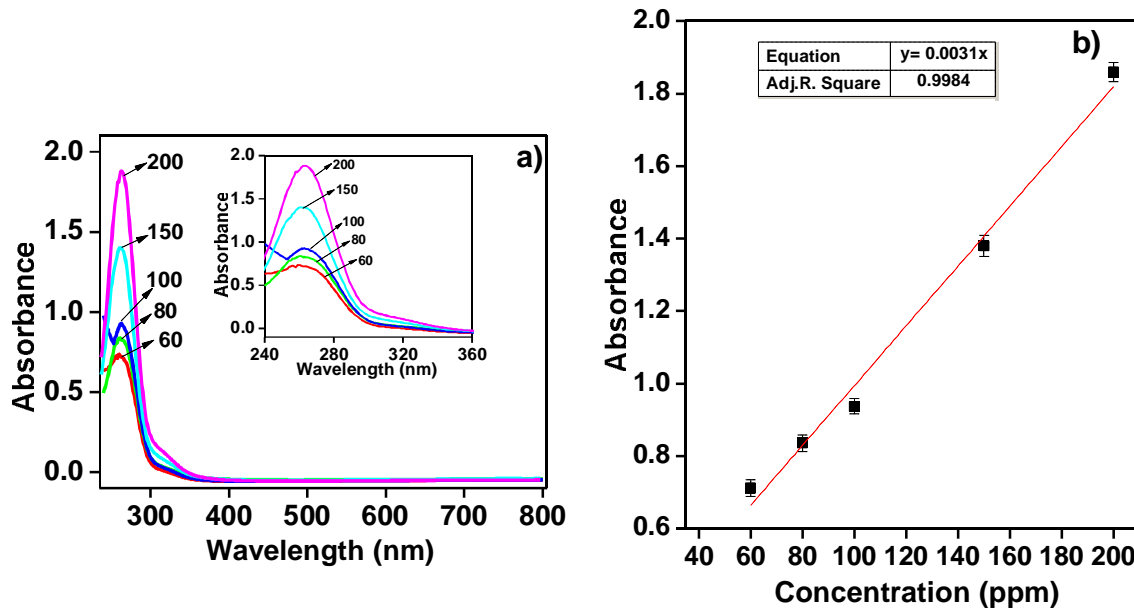


Fig. 3.3 (a) UV-vis absorption vs wavelength spectra of diesel showing maximum absorbance at 263 nm for different concentrations of diesel and (b) Absorbance (at 263 nm) vs concentration calibration graph used for measuring diesel removal efficiency.

Adsorption of surfactant on the soil

To determine the equilibrium adsorption isotherm of the surfactant, the batch experiments are conducted by using a glass cylinder of volume 250 mL. 10 g of the soil sample is taken in the glass cylinder and 20 mL of different concentrations of Tween-80 solution is added to it. The glass cylinder is shaken and tapped evenly so that added soil will uniformly distribute in the sample solution. This was left undisturbed for 24 h to attain equilibrium. After 24 h, the solution is separated from soil by filtering by the use of filter paper to measure the surfactant adsorbed onto the soil particles. The filtered solution, free of soil particles, is centrifuged for 15 min at 4000 rpm speed. The aliquot is again filtered by the use of filter paper to remove further impurities. The amount of surfactant present in the sample is estimated by UV-Vis spectrophotometer (Thermo Scientific, Evolution 201) at 208 nm, using which the amount of surfactant adsorbed was calculated based on the following equation (Ming et al., 2015):- An absorbance (at λ_{\max}) vs. concentration calibration graph for Tween-80 at 208 nm is shown in Fig. 3.4.

$$\text{Amount of surfactant adsorbed on the sandy soil (mg g}^{-1}\text{)} = \frac{(C_i - C_{\text{eq}}) \times V}{M} \quad (14)$$

Where, C_i = Initial concentration of surfactant solution (mg cm^{-3}), C_{eq} = Concentration of surfactant solution (mg cm^{-3}), V = Volume of solution in cm^3 and M = mass of soil in g.

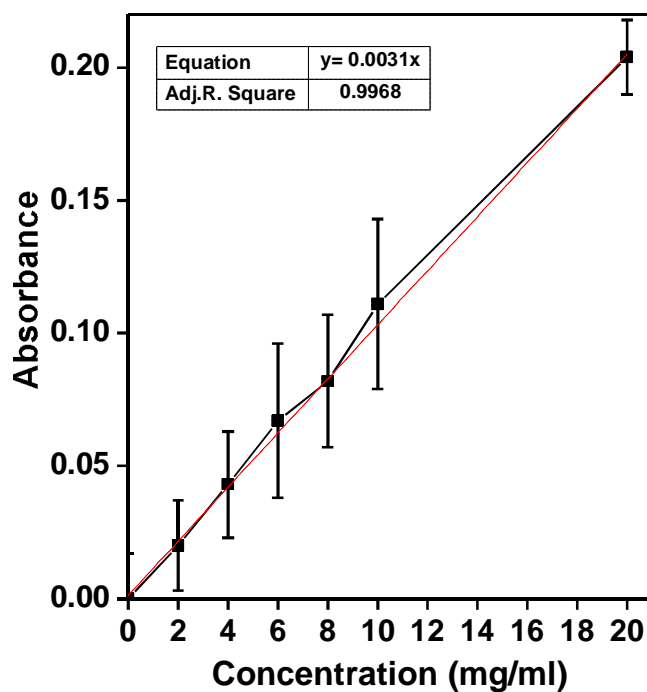


Fig. 3.4 Absorbance (at 208 nm) vs concentration calibration graph used for measuring surfactant adsorption in sandy soil.

Residual Contaminant and Residual Iron Left in the Treated Soil

TGA is a well-known technique used for studying the effective removal of different organic contaminants such as diesel, naphthalene, hexachlorobenzene, biphenyls and decane from soil (Carmody et al., 2008; Risoul et al., 1999). (Agarwal et al., 2016)) report the application of TGA for the quantification of residual diesel in the sand. (Risoul et al., 2002)) utilize TGA to estimate the amount of polychloro biphenyl removed from the soil after the thermal treatment process in a pilot-scale study. The diesel residues left in all three soils after treatment with APG-Ph (0.1 vol %) foam stabilized by zero-valent iron (Fe^0) and iron oxide (Fe_3O_4) nanoparticles (3.5 mg/l) are estimated using TGA technique. The sample is heated at a rate of $30^\circ\text{C}/\text{min}$ from 30°C to 800°C with an air flow rate of 20 ml/min. Also, the diesel-contaminated soil (samples after one day and seven days of contamination) prior to the treatment process is analyzed for comparison.

It is essential to analyze the amount of residual iron concentration left in the soil after Fe⁰ and Fe₃O₄ foam treatment. For this study, dispersions are prepared by mixing different concentrations of Fe⁰ and Fe₃O₄ powders separately with 0.1% of APG-Ph and the generated foam is passed through the column containing 50g of uncontaminated soil. Subsequently, the effluent is collected and digested with concentrated hydrochloric acid (HCl) in the ratio of 1:4. The solution, carrying iron is analyzed by using an atomic absorption spectrometer (Shimadzu, AA-7000) at 248.3 nm. The lamp is set at 12.5 mA, the air and acetylene flow rate are controlled at 9 and 1 Lmin⁻¹, respectively (Shen et al., 2011).

All experiments reported here are repeated three times, and the obtained results are expressed as mean value ± standard deviations.

3.1.7 RSM Modeling of APG-Ph foam stabilized by Fe⁰ for the treatment of petroleum contaminated soil: Experimental design

The independent variables in the present study include (surfactant concentration and nanoparticle concentration) and the diesel oil removal efficiency of the soils from the different region are selected as the response function. The interaction between the independent variables and response function is investigated using BBD. The variables are coded as low, middle, and high accordingly as -1, 0, and +1 respectively (Table 3.2). The actual values shown in Table 3.2 represent the values obtained from the experimental data. The objective function is diesel oil removal efficiency from soils, and the actual value of this independent variable x_i is coded as X_i (Dimensionless values of the independent variable) according to the following equation (Kumari et al., 2018):

$$X_i = (x_i - x_0) / \Delta x_i \quad (15)$$

Where x_0 is the value x_i at the central point and Δx_i is the step change value.

Table 3.2: Range of independent variables used in the experimental design and its level.

Independent Variables	Representation	Levels of variables		
		-1	0	+1
APG-Ph (vol%)	X ₁	0.02	0.06	0.1
Fe ⁰ (mg/l)	X ₂	2.5	3	3.5

The experimental data are analyzed using the Design Expert Version.7, (Stat-Ease, USA) software and are fitted into the empirical quadratic model to optimize the variables influencing the diesel oil removal efficiency from the soil. The quadratic model can be explained by the equation given below (Asfaram et al., 2018; Khayet et al., 2007)

$$Y = \beta_0 + \sum_{i=1}^n \beta_i X_i + \sum_{i=1}^{n-1} \sum_{\substack{j=2 \\ j>1}}^n \beta_{ij} X_i X_j + \sum_{i=1}^n \beta_{ii} X_i^2 + E \quad (16)$$

The predicted model is validated by analysis of variance (ANOVA), and the quadratic model is assessed by (R²) analysis of the result. The results are analyzed by probability values and Fischer trial.

3.2 Formulation and characterization of liquid laundry detergent

3.2.1 Selections of surfactants and additives

Anionic surfactant SLS purchased from Fisher Scientific (India) is used in the preparation of liquid detergent formulation. The non-ionic surfactants, including Tween-20, Tween-80, and Triton X-100 are supplied by Himedia (India). The other non-ionic surfactant employed in the study is APG purchased from by Sigma Aldrich (India). Sodium Carbonate obtained from SpectroChem (India) is used as a builder in the detergent formulation. Ultra-pure water prepared with the Elix Millipore system is used throughout the study. Ethanol is used as an antimicrobial agent to prevent any microbial growth. Every liquid detergent requires solubilizing agents- in the current study, urea is selected (Qualigens Fine Chemicals, Mumbai, India) as solubilizer (Uner and Yilmaz, 2015). Two other additives used to improve the detergent formulation performance are the polymer Polyvinylpyrrolidone (PVP) and Ethylenediaminetetraacetic acid (EDTA), both obtained from Sigma Aldrich (India).

3.2.2 Preparation and characterization of liquid laundry detergents

Two different sets of a liquid detergent formulation containing combinations of popular anionic and non-ionic surfactants are prepared. The first set of nine detergent formulations (S1) is prepared using the surfactants SLS, Tween-20, and Tween-80 (Table 3.3). The second set of nine more detergent formulations (S2) is prepared using SLS, Triton X-100, and APG (Table 3.4). Thus a total of 18 different detergent formulations are prepared. To prepare the liquid detergent, surfactants are dissolved in water, and other additives at respective concentrations (refer to Table 3.3 and Table 3.4) are added to the dissolved solution. The pH of the prepared formulation is adjusted to 8 using NaOH and citric acid solution (Uner and Yilmaz, 2015). The prepared formulations are stored in a stoppered glass bottle at room temperature.

Table 3.3: SET-1 (S1) comprising of nine liquid detergent formulations containing SLS, Tween-20 and Tween-80

Surfactant/Additives	Detergent Formulations								
	S1.1	S1.2	S1.3	S1.4	S1.5	S1.6	S1.7	S1.8	S1.9
SLS (wt%)	4	–	–	2	2	–	2	1	1
Tween-20 (vol%)	–	4	–	2	–	2	1	2	1
Tween-80 (vol%)	–	–	4	–	2	2	1	1	2
Sodium Carbonate (wt%)	6	–	–	6	6	–	6	6	6
Allyl Alcohol (vol%)	1	1	1	1	1	1	1	1	1
EDTA (wt%)	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Urea (wt%)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
PVP (wt%)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Ethanol (vol%)	8	8	8	8	8	8	8	8	8
Water	Make up to 100 mL of total solution								

Table 3.4: SET-2 (S2) comprising of nine liquid detergent formulations containing SLS, Triton X-100 and APG

Surfactant/Additives	Detergent Formulations								
	S2.1	S2.2	S2.3	S2.4	S2.5	S2.6	S2.7	S2.8	S2.9
SLS (wt%)	10			5	5		5	2.5	2.5
Triton X-100 (vol%)		10		5		5	2.5	5	2.5
APG (vol%)			10		5	5	2.5	2.5	5
Sodium Carbonate (wt%)	6	–	–	6	6	–	6	6	6
Allyl Alcohol (vol%)	1	1	1	1	1	1	1	1	1
EDTA (wt%)	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Urea (wt%)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
PVP (wt%)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Ethanol (vol%)	8	8	8	8	8	8	8	8	8
Water	Make up to 100 mL of total solution								

Measurement of foam properties

The influence of hardness/softness qualities of water on the foam properties of prepared detergent formulations (S1 and S2) is systematically analyzed using Dynamic Foam Analyzer DFA 100 (Kruss GmbH, Germany) by the method as described in the section 3.1.5. (Amaral et al., 2008). Water collected from RO system, hypersaline water produced artificially in the lab by addition of 35 g/L NaCl in normal water and hard water comprising 0.1 g/L of CaCO₃ in normal water are used for this purpose.

Surface tension measurement (σ)

The surface tension of all the laundry detergent formulations is measured using the drop weight method. All measurements are conducted at room temperature. The drop weight method is based on measuring the weight of a drop of liquid falling from the capillary tube (stalagmometer). This is done by considering the fact that the liquid drop from the capillary tube falls when the gravitational force equals the surface tension of the liquid-based on Tate's law (Jordi-Roger and Bernat, 2014). Considering water as the reference fluid, the surface tension is measured using eqs. (17) (Lee et al., 2009). In the drop weight method there is a high chance that some portion of the liquid drop would remain on the tip of the capillary tube thus a correction factor f , $(r/V^{1/3})$ has to be introduced to the Tate's law.

$$\frac{m_{H_2O}}{m_1} = f \frac{\sigma_{H_2O}}{\sigma_1} \quad (17)$$

where m_1 is the mass of detergent solution to be tested, m_{H_2O} is the mass of water (reference), σ_1 is the surface tension of the detergent to be tested, σ_{H_2O} is surface tension of water and f is the correction factor, r is the radius of the tip and v is the volume of drop.

Determination of detergency

The cotton and woolen fabric are chosen to measure the detergency as it is the most commonly used fabric in household washing. The fabrics are cut into pieces of dimension 8 × 10 cm to measure the detergency of the prepared formulations. The oily soil is prepared to artificially soil the fabrics. The soil is composed of 80 mL soybean oil, 10 mL dye, and 20 g calcium carbonate. 10 g of the prepared soil along with 3 g of grease is applied to the cotton and woolen fabric separately. The soiled fabrics are dried at room temperature. The artificially soiled fabric is then washed by a household washing machine at an optimum temperature of 30°C for 10 min (Lakdawala et al., 2011). The percentage of soil removed from fabric is then calculated based on the amount of soil remaining after washing the fabric, and it is represented as detergency as shown in eqs. (18):

$$\text{Detergency}(\%) = \frac{W_0 - W_1}{W_0} \times 100 \quad (18)$$

where W_0 is the weight of oily soil before washing the fabric, W_1 is the weight of the oily soil after washing the fabrics.

Characteristics of fabric surface

The surface characteristic of fabric after washing with prepared detergent formulations is studied with Scanning Electron Microscope (SEM) (Jeol/EO JSM-6390, USA). The fabric sample stained with oily soil, before washing, are also subjected to surface analysis. The fabric samples are coated with gold nanoparticles prior to analyzing the surface morphology (Shahidi et al., 2007; van Roosmalen et al., 2004).



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