

## Research Article

# Effect of Soil Texture on Remediation of Hydrocarbons-Contaminated Soil at El-Minia District, Upper Egypt

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Soils polluted by waste lubricant oils may affect the hydrosphere compromising the quality of drinking water resources and threatening the aquatic ecosystems. The objective of this study focused to remove waste-lubricant oils from different polluted sites in El-Minia governorate. In this respect some samples were collected from four different industrial sites and identified as sand, loamy sand, clay loam and loam. Then the field conditions were simulated using two experimental models packed with contaminated soil. The remediation processes carried out in both models using surfactant enhanced by air injection then by water washing. The parameters such as soil type, soil heterogeneity, time and washing process was investigated. The results indicated that the high efficiency of oil removal is obtained from sand where the clay loam gives the worst results. The results also reveal that, the high flushing and washing duration time can be attributed to the high percentage of mud in some sites over other sites. This means that the performance of surfactant flushing/water washing can be adversely affected by geologic heterogeneity. Finally, it's suitable to use pressurized liquid technologies in heterogeneous media, but cleanup times will be longer and more difficult than for the other similar homogeneous media.

## 1. Introduction

Throughout the world, subsurface contamination has become a widespread and pervasive problem. A major problem in the soil or groundwater remediation is the removal of hydrophobic organic compounds. Nonaqueous phase liquids (NAPLs) usually enter the unsaturated zone as discrete liquid phases, which move due to gravitational and capillary forces [1]. They frequently enter groundwater systems after they have been spilled on the surface and pass through the unsaturated zone (Figure 1). The major organic chemical waste categories include organic aqueous waste (e.g., pesticides), organic liquids (e.g., chlorinated solvents), oils (e.g., different fuels and fuel additives), and sludges or solids containing organic compounds. The most common local source of soil and water contamination by petroleum hydrocarbons are

industrial plants, land disposal sites of danger residues, petrol stations, car service stations, and vehicle accidents. The total petroleum hydrocarbons include saturated alkanes, aromatic hydrocarbons, fuel oxygenated additives (e.g., methyl t-butyl ether (MTBE), ethanol, butanol), and other compounds containing sulfur or nitrogen. These compounds are harmful or even toxic to the growth and development of plants and animals, being a source of long-term water and air pollution. They are also dangerous to the human health [2]. Accidental surface release and improper disposal of petroleum products (e.g., jet fuel, refinery wastes, diesel, lubricating used oil, etc.) and volatile organic solvents are recognised as two of the most widespread causes of groundwater contamination by chemical compounds. Flooding and/or accidents, oil from the waste pit may spread to the surrounding fields causing pollution [3].

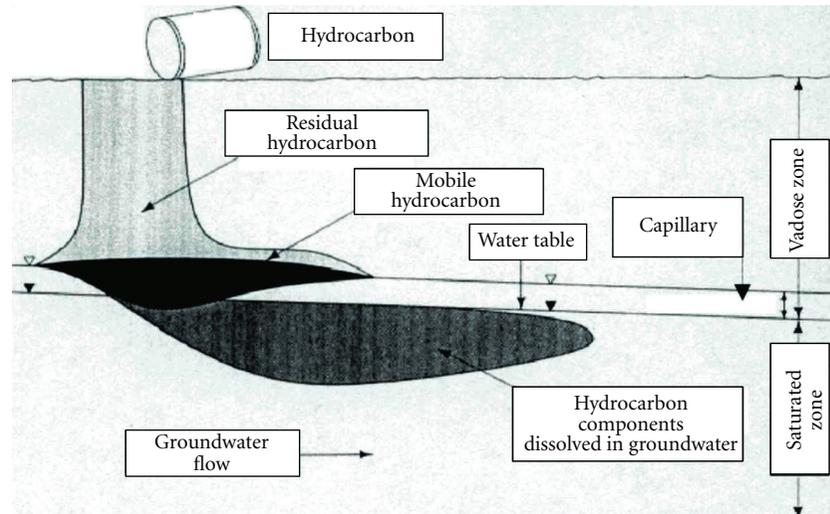


FIGURE 1: Illustration of the subsurface distribution of an NAPL spill [4].

Nonaqueous phase liquids (NAPLs) that are less dense than water, including many petroleum products or fuels, such as gasoline, heating oil, lubricating oil, kerosene, jet fuel, and aviation gas, are termed light nonaqueous phase liquids (LNAPLs) and these commonly collect and pool at, or above, the water table. The other type of NAPL is denser than water and named dens nonaqueous phase liquids (DNAPLs) include chlorinated hydrocarbons or chlorohydrocarbon such as carbon tetrachloride, 1,1,1-trichloroethane, chlorophenols, chlorobenzenes, tetrachloroethylene, and polychlorobiphenyls (PCBs). The latter are thus particularly difficult to remediate [5]. Matters become even more complicated since these contaminants are often mixed with metals. A considerable amount of hydrocarbon oils can be held in voids in the soil in the form of residual saturation and can lead to long-term contamination of groundwater through the action of rain water, if not removed in time [6]. During the transportation of NAPLs through the subsurface, a portion of the organic phase also retained within the pores of the soil matrix as an immobile ganglia or globules due to interfacial forces.

*Physical Properties of Soil.* The procedure selected to contain spills on land will vary with the amount and type of oil spilled, the type of soil, and the terrain. Less viscous oil and more porous soil will allow greater and more rapid penetration and lateral migration in the soil. Groundwater is very susceptible to contamination, unless protected by a low permeability layer such as clay. The organic contaminants like petroleum hydrocarbons, halogenated organic compounds, or other organic compounds are bind strongly inside the soil matrix and present for long time at the contaminated sites. Knowledge of physical properties of soil is most important for designing the parameters of remediation process. The mechanisms of interaction between the soil and contaminants are also important to know. Soil can be defined as loose material composed of weathered rock, other minerals, and also partly decayed organic matter, that covers large parts of the land surface [7]. The soil is

composed of three phases: solid, liquid, and gas phases. The soil components include about 50% by volume mineral particles, 25% water, 20% air, and 5% organic matter. With the exception of a few organic soils, the bulk of soil material is mineral in character and has been derived from solid geological deposits [8]. The mineral constituents of the soil are represented by the particles of widely varying size, shape, and chemical composition. Three groupings of soil particles are in common use, namely, sand, silt, and clay. The groups are subdivided according to requirements.

*Long-Term Contamination.* The NAPL that remains in the unsaturated zone is an important source of contamination because it is dissolved by (1) the passing recharge water and (2) the passing groundwater as the water table rises. Such sources of contamination can last for many years and contaminate large volumes of groundwater. However, in addition to these pathways, contaminants also can be transported through the unsaturated zone. This transport pathway may spread the contaminants over a much broader area of the aquifer. In recent years, there has been an increasing interest in the remediation of NAPLs source zones [9]. Because of the low solubility of hydrophobic organic compounds in water, the residual organic phase usually represents a long-term contamination source for soil and groundwater. Owing to the tendency of contaminants to tightly bind or adsorb onto the soil particles. Subsurface contamination by the organic compounds is a complex process and difficult to treat due to many reasons like the tendency of adsorption of contaminants onto the soil matrix, low water solubility, and limited rate of mass transfer for biodegradation, and so on [10]. As many organic compounds have low solubility in water, so they may leach from the soil for a longer period of time and thus ultimately become a continuous source of the soil and groundwater contamination. The use of surfactants can improve the mobility of hydrocarbon contaminants in soil-water systems by solubilising adsorbed hydrocarbons through incorporation in surfactant micelles [11].

This work aims to remove NAPL (waste-lubricant oils) polluted soils and collected from different industrial sites in El-Minia governorate. The air flushing as distributive system enhanced by surfactant and different water flooding cycles were used in this study. Two models were designed to simulate the injection wells and treatment tanks. Nonionic surfactant solutions Nonyl phenol ethoxylate (NPEO<sub>9</sub>) were used at constant concentrations (3%) beyond its critical micelle concentration. The results discussed based on soil heterogeneity to select the suitable remedial techniques (*in situ* or *ex situ*).

**1.1. Samples Locations.** The design of optimal remediation schemes often requires some “prediction” of the distribution of contaminants within the subsurface over time. These predictions can be used to evaluate different remediation scenarios. Two-dimensional random sampling designs commonly exist for contamination sampling over space [12]. According to Jessen [13] which proposed high accuracy can be improved by better sampling and procedures, so samples collected with low bias and high precision from the centre of contamination zone.

**1.2. Soil Sampling and Site Assessment.** Determining the extent and spatial distribution of NAPL ensures that the chemical flood targets the proper subsurface volume. There are many techniques that investigators have used to map NAPL distribution. Perhaps the most precise and appropriate parameter to measure characterizing an NAPL source zone is saturation.

Saturation is defined as the fraction of the soil pore volume that is filled with NAPL. Depending on the degree of saturation, NAPL will exist as either free-phase NAPL or as residual NAPL. Free-phase or mobile NAPL exists when the saturation is high enough to form pore-to-pore connections over a large area, producing a continuous fluid capable of flowing under an imposed gradient or its own gravitational potential. Residual or entrapped NAPL exists when the soil pores have been drained of mobile NAPL, leaving behind some amount of liquid trapped by capillary forces or the surface tension that holds a liquid to a solid surface. NAPL at residual saturation is discontinuous and immobile, unable to flow under normally imposed hydraulic gradients.

A sampling technique was developed for allowing the decision makers to determine the minimum number of field realizations necessary to achieve a reliable remediation design [14]. This section provides collecting and analyzing soil samples from the NAPL zone. Soil samples can be used to provide an estimate of how NAPL is distributed in the source zone by providing contaminant concentration data that can be converted to saturation estimates. Soil samples also provide an indication of the vertical heterogeneity in the zone of interest. Laboratory analyses will yield a measurement of the total concentration in the soil samples. Soil samples are also collected to measure grain-size distribution, and the fraction of organic contaminant of the geologic media. Grain-size analyses are used to define heterogeneity and point permeabilities in the subsurface and should be collected at a

TABLE 1: Physical properties of the used lubricating oil.

Specific gravity at 20°C	0.875
Flash point, close cup Pensky Martin (°C)	140
Water and sediment (vol%)	1.28
Water content, the Dean and Stark method (vol%)	0.79
Viscosity at 37.8°C, cst	209.235
Ash content (wt%)	0.714
Asphaltene content (wt%)	4.995

frequency sufficient to define the major hydrostratigraphic units in the NAPL zone [15].

Representative soil samples were collected from different locations: (A) Helwan cement Co. El-Minia factory site, (B) PEPSI Cola El-Minia factory site, (C) Egyptian Co. for productive Electricity site, and (D) Middle Egypt Mills Co. site, as shown in the map Figure 2, and the lithological succession shown in Figure 3. In the selected sites, the contaminant (waste lubricant oils) distribution on the surface was observed to be inconsistent. Visual observation and random estimates of the oil content indicated variety of infiltration rates up to a depth of 40 cm. Accordingly, three samples, weighing 1 kg each, were collected from different depths going upto a maximum of 40 cm from the top layer beneath the ground surface [16]. Samples were stored in plastic buckets and homogenised in a mixer and it was air-dried for 3 days before selecting a sample for analysis and cleaned for sieving [17]. Size classification was achieved by sieving into gravel, medium, coarse, fine, and very fine sand also silt + clay fractions.

## 2. Materials and Methods

### 2.1. Materials

- (1) Commercial nonionic surfactant nonyl phenol ethoxylate (NPEO<sub>9,3</sub>) was used without treatment.
- (2) The *n*-hexane used for extraction step was obtained as analytical grade solvent of used oil from the soil.
- (3) Polluted soils from different sites in El-Minia governorate were collected to study the actuality of contamination problem and efficacy of treatment trains. Physical properties of the used lubricating oil are given in Table 1.

**2.2. Experimental Setup.** The actual contamination field conditions is simulate and designed in two experimental set-up models and as shown in Figures 4 and 5. The downflow mode was applied in this experiment.

### 2.3. System Operation

**2.3.1. First Laboratory Model.** The first lab model simulate injection well was consisted of a cylindrical column having dimensions (105 cm × 5 cm × 4.5 cm) capped with a stainless steel valve top. The outlet end of the column was fitted with a fine wire mesh screens (50 μm diameter) to prevent soil

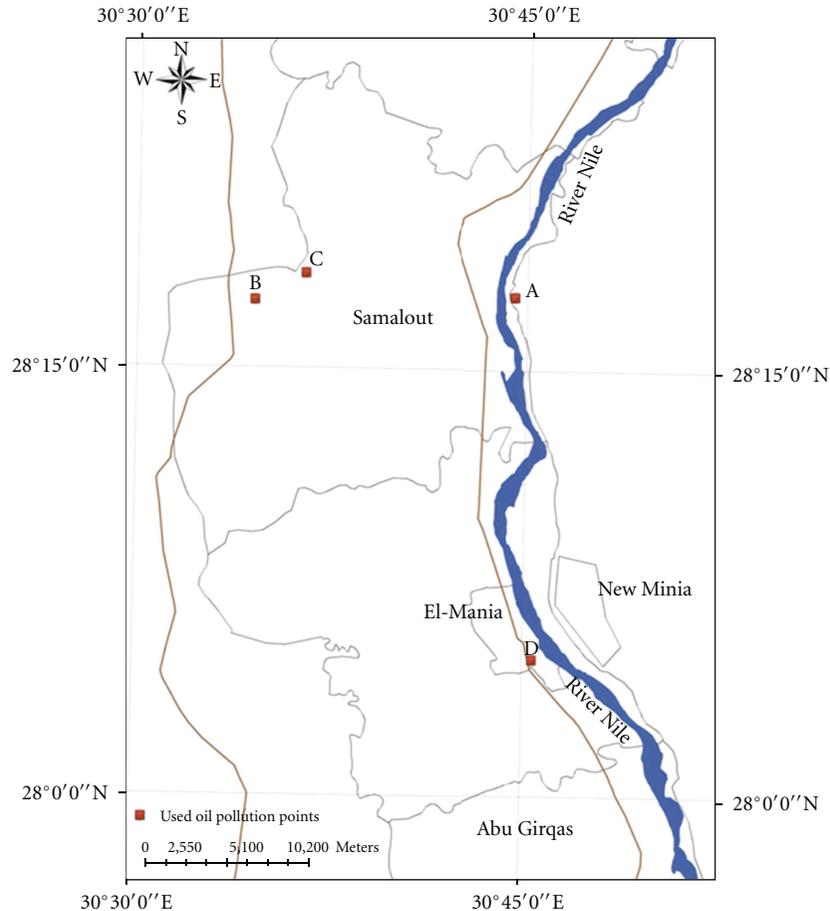


FIGURE 2: Location map of some oil polluted sits in Minia governorate.

from washed out, then 31 cm of contaminated soil (1 kg) was packed in the column filled with surfactant solution to avoid entrapped air. After that the air was injected using air compressor to provide air and to pump surfactant solution and water across contaminated soil. The air was inlet from the side of the column to create turbulent air current, to provide better distribution of the injected air with similar and strong focusing at all points of soil surface. Air-flushing systems operated by pulsed mode (i.e., turning the system on and off at specified intervals), the pulsed air (cyclical) injection intermittently is thought to achieve more extensive, better distribution, and mixing of the air in the contaminated saturated zone, thereby allowing greater contact with the dissolved phase contaminants [19]. A fixed 300 mL of nonyl phenol ethoxyl (NPEO<sub>9,3</sub>) surfactant solution of 3, 5 and 7% concentrations were injected individually at constant (2 bars) air pressure into different polluted field samples having concentrations of 2.55%, 12.7%, 5.8%, and 4.37% for loamy sand (site A), sand (site B), loam (site C), and clay loam (site D), respectively.

**2.3.2. Second Lab Model.** The second lab model simulates treatment tank were designed to remediate field samples of sites C and D because they contain high percent of silt and clay respectively. The treatment tank consisted of

bottle having dimension (37 cm × 15.5 cm × 15 cm). The pores membrane was located below the half of bottle and covered with a fine nylon mesh screens (60 μm diameter) to prevent emulsion formation due to presence of silt and clay having very small grain size range and to facilitate of their washing out during the experimental work. Then 31 cm of contaminated soil (1 kg) was packed in the bottle. After that the air was injected using air compressor with a pressure not reach to 2 bar. Each samples were stirred with water after surfactant was washing out and then subjected to air pressure at 1.5 bar for two minutes, this step was repeated twice using 4 liters of water to wash out silt or clay that restrict air injection, emulsion extraction, and treatment process.

**2.4. Treatment of Contaminated Soils.** For all experiments the treatment of contaminated soils was carried out in two steps: flushing with surfactant solution then washing by many polishing cycles of water. The effluent samples were collected in a beaker and kept at room temperature for analysis, also soil was taken after each run to evaluate the percentage of waste oil remaining in the soil after each run.

**2.5. Determining Oil Removal.** *n*-hexane (C<sub>6</sub>H<sub>14</sub>) was used to extract the waste oil as herein after by Khalladi et al. [20] and Marek et al. [21].

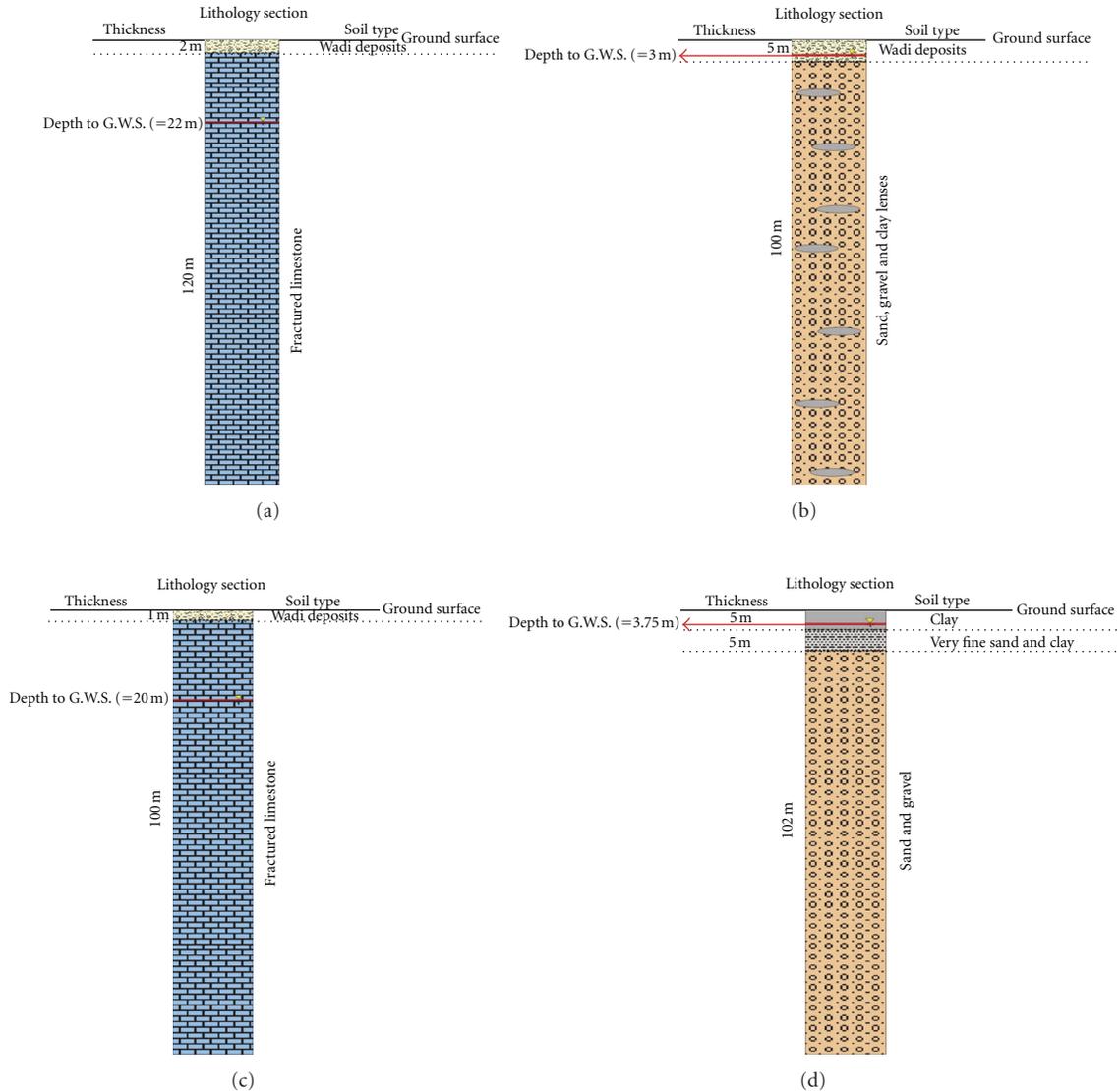


FIGURE 3: Lithology section of the investigated area [18].

**2.6. Extraction and Analysis.** Samples under distinct extractions: *oil in soil* phases and *oil in water* phases.

**Oil in Soil.** 2 g of rinsed soil were mixed with 10 mL of *n*-hexane in a glass test tube and shaken laterally for 5 min then left at rest for separation, then the *n*-hexane/oil extract was removed and the mixture was poured in a beaker. Each rinsed soil was washing four times to ensure completely clean from residual oil, this process was repeated till the extract gave the same absorbance reading as a pure *n*-hexane (zero absorbance) by using ultra violet spectroscopy.

**Oil in Water (Emulsion).** The remaining pollutant concentration was determined after stopping the water washing cycles. 5 mL of liquid effluent (oil-in-water emulsion) were collected and mixed with 25 mL of *n*-hexane in a separating funnel; stirred for 2 min then left at rest for separation; the upper organic layer was separated by using separating funnel.

### 3. Results and Discussion

We need to define the vertical and lateral extent of contamination in soil to determine if active remediation is necessary (i.e., if *in situ* action will take place, and if so, to what degree). From there, the vertical and lateral extent of contamination must be delineated to a level that is at or below the subsurface soil risk-based screening level.

**3.1. Measuring Pollutant Concentrations.** For many industrial sites, pollutant concentrations are highly variable, especially if the pollutants are immobile and there are multiple phases of polluting activity. It is known that the procedure selected to inhibit spills on land will greatly vary with the amount and type of oil spilled also with the type of soil and the terrain. Less viscous oil and more porous soil will allow greater and more rapid penetration and lateral migration in the soil.

To verify that the polluted soil is not contaminated above acceptable limits, confirmatory samples (discreet) will be

TABLE 2: Waste lubricant oil concentrations in soil samples from A, B, C, and D sites.

Samples locations	Samples Classification	Waste oil concentrations from 0–10 cm (g/kg)	Waste oil concentrations from 10–20 cm (g/kg)	Waste oil concentrations from 20–40 cm (g/kg)	Average waste oil concentrations (g/kg)
Site A	Loamy sand	35.70	22.67	18.14	25.50
Site B	Sand	130	125.58	125.58	127.05
Site C	Loam	60.32	58.64	55.29	58.08
Site D	Clay loam	52.96	43.51	31.73	42.73

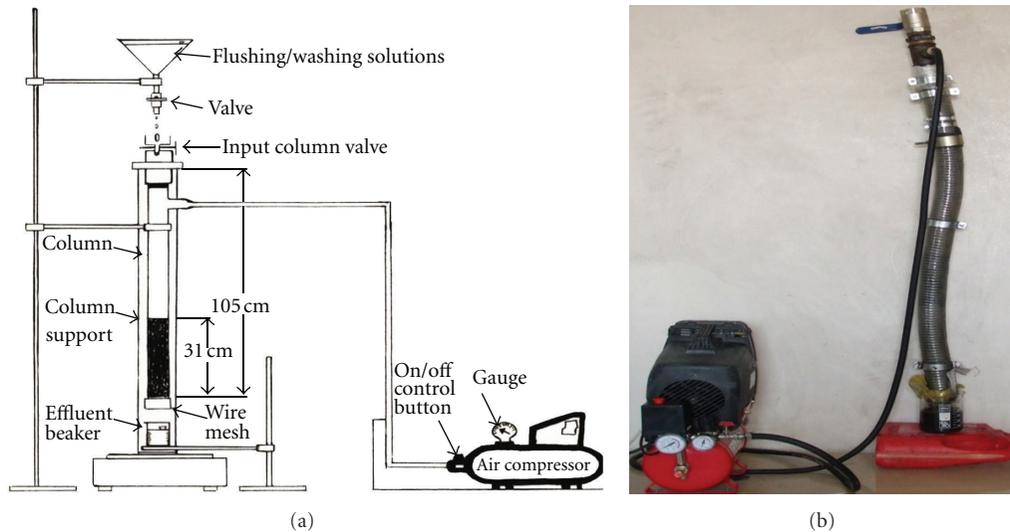


FIGURE 4: The laboratory experimental model simulates injection well.

taking from different sites A, B, C, and D. The soil samples are selected according to [22] who state that it is up to you to determine how many soil samples are needed to be representative of the conditions remaining in the site.

The contaminated soils were selected by choosing four different location sites. Each site samples were taken separately from different depths (0 up to 40 cm). The proportion percentage of oil in each depth was then determined and added together and their average were taken and consider as representative sample for each site and defined by average waste oil concentration, and the samples analyzed based on our knowledge of waste lubricant oil and initial sample results are given in Table 2.

The results in Table 2 indicate that the average residual oil concentrations in contaminated site A, C, and D caused by movement of oil mobile phase (free phase) and thus their concentrations in the soil are not homogeneous, and recorded the following values 2.5%, 5.8%, and 4.2%, respectively. Also the pollutant concentrations at sampling points, or indeed from within layers of similar appearance, show heterogeneous nature of contaminant distribution. The oil percentage in site B is 12.7% this means that such site existing in continuous region due to high pollutant concentration. From all results we can conclude that the processes of adsorption-desorption play important roles in controlling the migration rate as well as concentration distributions. These processes tend to retard the rate of

contaminant migration and act as mechanisms to reduce concentrations.

### 3.2. Effect of Soil Heterogeneity versus Pollutant Extraction.

First lab model (Figure 4) that simulates injection well was used for treatment of all representative polluted samples sites (A, B, C, and D). Results of treatment site A and site B are given in Tables 3 and 4, respectively. The data indicated that only those sites are completely fulfilled and take action towered treatment by injection well simulated lab model. This can be attributed to that the sample from site A is loamy sand, while sample from site B are sand, thereby these types of soil are suitable to treated *in situ* (*in situ*) during injection and subsequently extraction wells. Our conclusion is identical with Okx and Stein [23] who stated that it's possible to treatment the polluted soil from gravel to fine sand by *in situ* methods. On the other hand they confirmed the impossibility of *in situ* treatment for soil samples from sites C and D because their analysis indicated that they classified to Loam and clay loam types. To solve this problem the author suggest to go behind Boelsma et al. [24] who used Figure 6 to discussed how far the pressurized liquid extraction can be applied with different soil texture and they mentioned that its suitable to use pressurized liquid extraction technology for sandy clay, sandy clay loam, sandy loam, loamy sand, and sand, and they represented by shaded areas at which pressurized liquid extraction is typically

TABLE 3: Results of soil treatment from site A.

Flushing cycles	Pulsing time from zero-2-zero bar (minute)	$(m_{oR})$ original weight (g/kg)	$(m_o)$ amount of oil removed (g/kg)	% of oil extracted
3% NPEO <sub>9</sub> + first air pulse	91	25.5	9.1	35.69
Water + second air pulse	80	25.5	8.39	32.90
Water + third air pulse	60	25.5	2.01	7.89
Water + fourth air pulse	51	25.5	1.55	6.08
Water + fifth air pulse	51	25.5	0.95	3.73
Water + sixth air pulse	51	25.5	0.91	3.57
Water + seventh air pulse	51	25.5	0.87	3.41
Total results of site A	435	25.5	23.78	93.26

TABLE 4: Results of soil treatment from site B.

Flushing cycles	Pulsing time from zero-2-zero bar (minute)	$(m_{oR})$ original weight (g/kg)	$(m_o)$ amount of oil removed (g/kg)	% of oil extracted
First group set				
3% NPEO <sub>9</sub> + first air pulse	25	127.05	10.72	8.44
Water + second air pulse	17	127.05	5.15	4.05
Water + third air pulse	14	127.05	4.33	3.41
Water + fourth air pulse	10	127.05	4.02	3.16
Water + fifth air pulse	9	127.05	3.28	2.58
Water + sixth air pulse	8	127.05	3.05	2.40
Water + seventh air pulse	8	127.05	2.98	2.35
Sum of first group set	91	127.05	33.53	26.39
Second group set				
3% NPEO <sub>9</sub> + second air pulse	21	127.05	12.66	9.96
Water + eighth air pulse	12	127.05	6.08	4.79
Water + ninth air pulse	12	127.05	5.54	4.36
Water + tenth air pulse	10	127.05	5.22	4.11
Water + eleventh air pulse	10	127.05	5.19	4.09
Water + twelfth air pulse	10	127.05	5.03	3.96
Sum of second group set	75	127.05	34.69	27.30
Third group set				
3% NPEO <sub>9</sub> + third air pulse	35	127.05	25.53	20.09
Water + thirteenth air pulse	3	127.05	3.12	2.46
Water + fourteenth air pulse	2	127.05	3.04	2.39
Water + fifteenth air pulse	2	127.05	2.88	2.27
Water + sixteenth air pulse	1.45	127.05	2.61	2.05
Water + seventeenth air pulse	1.45	127.05	2.99	2.35
Water + eighteenth air pulse	1.45	127.05	2.5	1.97
Water + nineteenth air pulse	1.45	127.05	1.44	1.13
Water + twentieth air pulse	1.45	127.05	1.39	1.09
Water + twenty-one air pulse	1.45	127.05	1.3	1.023
Water + twenty-two air pulse	1.45	127.05	1.26	0.99
Water + twenty-three air pulse	1.45	127.05	1.13	0.89
Water + twenty-four air pulse	1.45	127.05	0.98	0.77
Water + twenty-five air pulse	1.45	127.05	0.59	0.46
Sum of third group set	56.5	127.05	50.76	39.95
Total results of site (B)	222.5	127.05	118.98	93.65

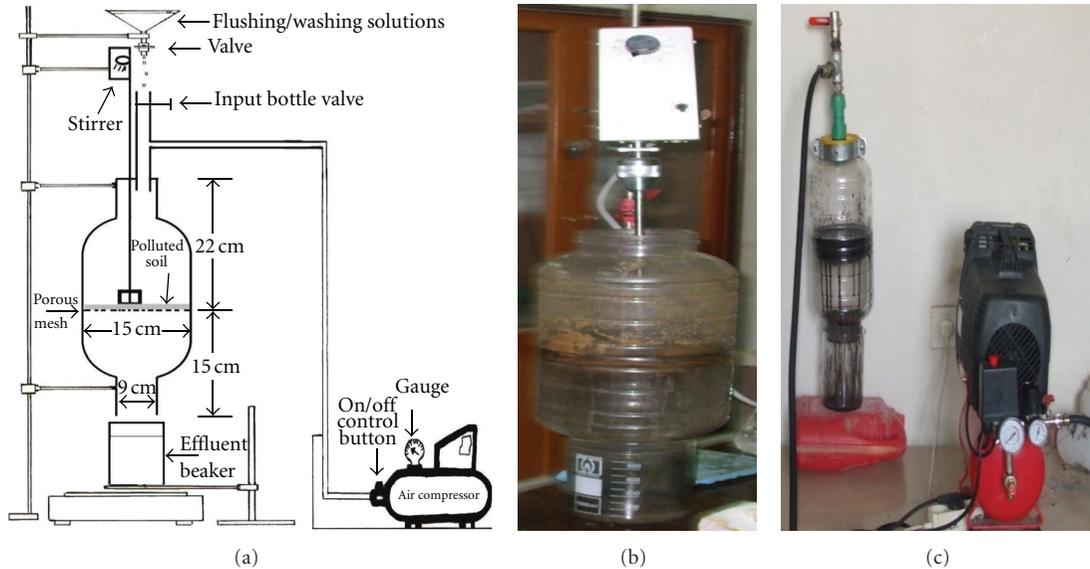


FIGURE 5: The laboratory experimental model simulates treatment tank.

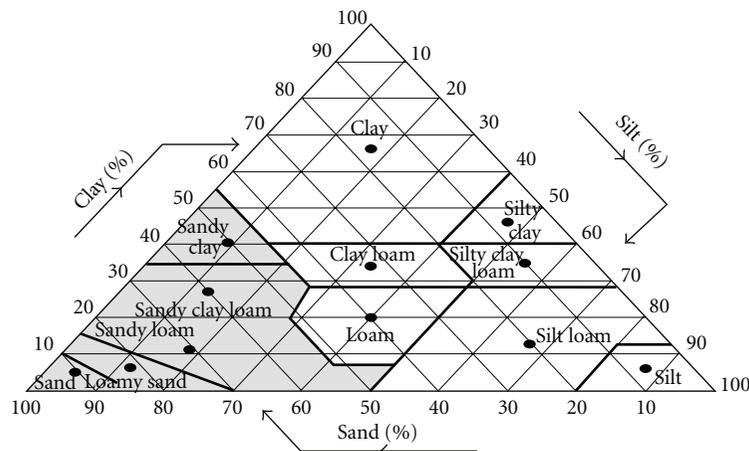


FIGURE 6: Triangular diagram illustrate the soil texture classification [37].

effective. Therefore, the pressurized liquids technique that was used in current study is considered. Grain size analyses of the samples in current study have been determined using the standard sieving ( $>2- <0.004$  mm), the results of grain size distribution of the current samples (A–D) are represented in histograms Figure 7. The grain size values reveal that contaminated soil samples that treatment by pressurized liquid extraction (i.e., use of injection solutions) are represent different soil type. These soils are loamy sand, sand, loam and clay loam, for the site A, B, C, and D, respectively. Soil heterogeneity plays a major role in controlling the concentration of contaminants extracted from the contaminated soil. It was also found that the efficiency of remediation depended on the type of the soil and it was much higher for the sand than for the clay soil. This difference can be explained by much looser structure of the soil particulates in the sandy soil and much higher stickiness and plasticity of clay [25]. Clay soil is plastic, consisting mainly of hydrous silicate of aluminum. At the microscopic level, clay is composed of fine particles

(diameter  $<2 \mu\text{m}$ ), adhering easily to one another [2]. The effect of pressurized liquid extraction on the removal of waste oil are calculated according to Couto et al. [26] and expressed as in (1),

$$\eta(\%) = \frac{m_o}{m_{oR}} \times 100, \quad (1)$$

where ( $\eta$ ) is a remediation efficiency at any time,  $m_o$  is the total amount of oil removed by the remediation fluids in a given period of time, and  $m_{oR}$  is the original mass of oil in the soil.

**3.3. In Situ Methods for Treatment of Contaminated Soils.** The representative sample from site A was found to be loamy sand soil texture and containing 2.55% (25.50 gram/kg) waste lubricant oil. The results in Table 3 reveal that, the percentage of removed oil is significantly increased with decreasing air pulsing time. That is, the first air pulse removed out 35.86% of waste lubricant oil recorded after 91 minutes and that

TABLE 5: Comparison between treatment conditions related to site A and site B samples.

Sample	No. of NPEO <sub>9</sub> flushing cycles	No. of water washing cycles	Total flushing duration (minute)	Total washing duration (minute)	Mud (silt + clay) (%)
Site A	1	6	91	344	19
Site B	3	24	81	141.5	0

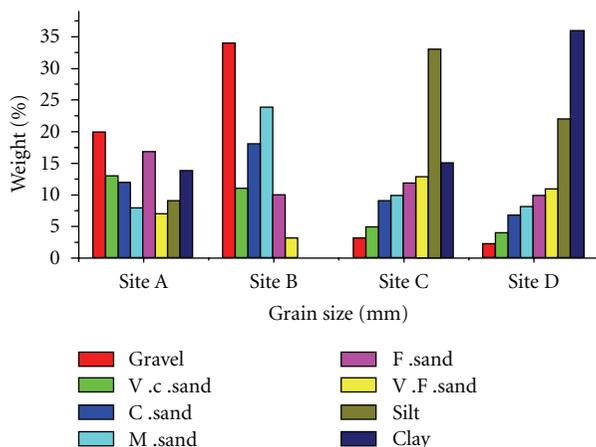


FIGURE 7: Histogram illustrates the grain size distribution of the studied polluted samples.

time is decreased to 51 minutes beginning from the fourth washing cycle and fixed at that value till the seventh run is finished.

Also, it is found from the first surfactant solution run to the sixth water washing run the time of pulsed emerge nearly decrease to half. Such drastic increase in pressure time drop is attributed to decrease in aqueous phase, which results from cleaning or opening of air channels [27, 28].

The waste lubricant oil concentrations in site B is 12.70% (127.05 gram/kg) and is classified as soil sand texture as given in Table 2. The oil removing from site B is carried out using injection well-simulated lab model and is divided to main three air-flushing cycles with 3% surfactant solution followed by different water washing cycles runs, so the total washing water cycles runs reached to twenty-five. The results in Table 4 reveal that at the first group 8.43% of oil was removed after surfactant flushing and that values was decreased to 3.08% after the sixth water run was finished, that is, till the emulsion created during surfactant flushing have been completely push out. On the other hand the total waste oil removal from the first flushing group set is 29.82% recorded after surfactant flushing followed by six water washing cycle and at total time equal 91 minute.

This result is not satisfied due to the degree of saturation and age of waste oil in this sample not solubilized yet. This deduction matched with Zhou and Rhue [29] they confirmed that, the solubility of hydrocarbons depends on the type and quantity of surfactant, and the age of contamination. Beck et al. [30] emphasized the biphasic nature of contaminant release from the solid phase; where compounds are not degraded or lost fairly quickly from soil, their chemical and biological availability decreases rapidly over periods of minutes to hours, then slowly over periods

of weeks to months through sorption and diffusion processes referred to as “ageing” [31].

In the second flushing set group is carried out on the remaining soil using 300 mL of 3% surfactant solution followed by five water washing cycles and the results are given in Table 4. The results reveal that, the percentage of removed oil was 9.96% from residual oil after first surfactant flushing run and decreased to 4.79% for next run (water washing cycle). The later water washing cycles remove oil out from 4.36% to 3.96%. On the other hand 27.30% of residual waste oil after the first treatment run was extracted with total time equal 75 minute. It is clear that the percentage of oil recovery proceed in reverse order with adsorption process (adhesion of oil on the surface of the soil). Sorption has a rapid phase within 48 h and a slower desorption phase that can take weeks even years [32]. In response, the effort is to quickly recover or cleanup spilled waste lubricant oil both from the ground surface and from subsoil. Reducing of waste lubricant oil concentrations in the soil below those corresponding retention capacities (saturation values) by fast recovery will stop spreading of waste lubricant oil in soil dramatically.

For the third flushing cycle, as revealed in Table 4 the results indicated that 20.09% was pushed out during this flushing run with air pulse time recorded 35 minutes for emerge. This means that solubility originated coherently with the third flushing solution. Also the time dropped from 35 minute where stable at 1.45 minute from eighteenth to twenty-seven air pulse. Such drastic increase in pressure time drop is attributed to decrease in aqueous phase, which results from cleaning or opening of air channels as mentioned by Clayton [27] and Chao et al. [28]. Finally, the total waste lubricant oil recovery of site B is 93.65%.

**3.4. Effect of Treatment Time and Soil Heterogeneity-Related Issues.** The results in Table 5 reveal that the total flushing durations are 91 and 81 min, total washing durations are 344 and 141.5 mins for sites A and B, respectively. The high flushing and washing duration time can be attributed to the high percentage of mud in site A over site B, that is, 19% and zero, respectively. This means that the performance of surfactant flushing/water washing can be adversely affected by geologic heterogeneity, because soil heterogeneities can cause poor-pressurized liquids sweep of the area targeted for remediation, although heterogeneity may reduce effectiveness. With increasing silt and clay content in polluted soil, the corresponding treatment duration time has been directly increased as showing in Figures 8 and 9. Thus, pressurized liquid technologies work in heterogeneous media, but cleanup times will be longer and more difficult to estimate than for similar systems in more homogeneous media.

TABLE 6: Results of soil treatment form site (C).

Flushing cycles	Pulsing time from zero-2-zero bar (minute)	( $m_{oR}$ ) original weight (g/kg)	( $m_o$ ) amount of oil removed (g/kg)	% of oil extracted
3% NPEO <sub>9</sub> + first air pulse	2	58.08	49.36	84.99
Water + second air pulse	2	58.08	7.82	13.46
Total results of site (C)	4	58.08	57.18	98.45

In general, sites having high clay or silt content in soils are not typical *in situ* candidates for this technology [33]. In an environment with low permeability layers or units interspersed with higher permeability zones, fluids preferentially flow through higher permeability zones, thereby reducing the performance of the chemical injected in the lower permeability zones. In general, high permeability soil is favored for pressurized liquids since numerous pore volumes can be passed through the contaminated area. Layered systems are difficult to remediate due to limited contact in less permeable areas. Also, fractured rock is extremely challenging due to the flow complexity in the fractured media. However, these challenges are relevant for all remediation technologies. Comparisons under the same conditions in these difficult media should be performed determine if surfactant flushing is able to remove contaminants faster than other technologies [34].

**3.5. Ex Situ Methods for Treatment of Fine-Grained Contaminated Soils.** As mentioned before and illustrated in Figure 6, both of sites C and D characterized by loam and clay loam could not able to applying the injection well simulation lab model (*in situ* treatment), therefore another lab model has been used and known by simulates treatment tank (*ex situ* treatment) and its outline is given before in Figure 5. The (*ex situ* treatment), that is, sediment relocation has been used internationally as an operational response to treat oil spills throughout the world [35]. *Ex situ* involves the excavation of contaminated soil for treatment in aboveground. The soil may be transported to special facilities where remediation may be carried out in special reactors or vessels, which are specially designed for this purpose (*ex situ* or in tank method) [36]. An example of this process is the washing of heavily polluted soils in special tanks. The polluted soil may also be transported and spread on a surface prepared to prevent the spread of contamination in lateral and vertical directions. Beds arranged in this way form the so-called prepared beds, upon which the remediation process will take place. This method is especially suitable for soils contaminated with oil products.

*Ex situ* treatment have been applied for treatment polluted soil tacking from site C that containing original weight 58.08 g/kg waste lubricant oil and characterized by loam soil texture. The results in Table 6 reveal that the percentage of removed oil is 84.99% after first flushing cycle using 3% nonionic surfactant solution. This high percentage of oil removal has been realized under low pressure equal 1.5 bar and at very short time duration about 2 minutes. By the same manner at the same time and pressure the second air injection (water washing cycle) was applied to push out

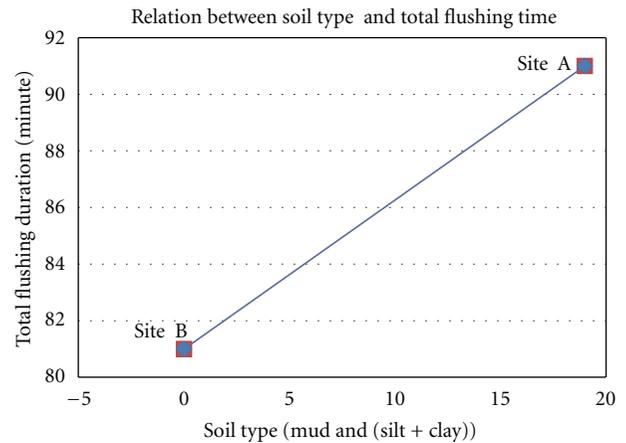


FIGURE 8: The relationship between mud % and surfactant flushing time (minute).

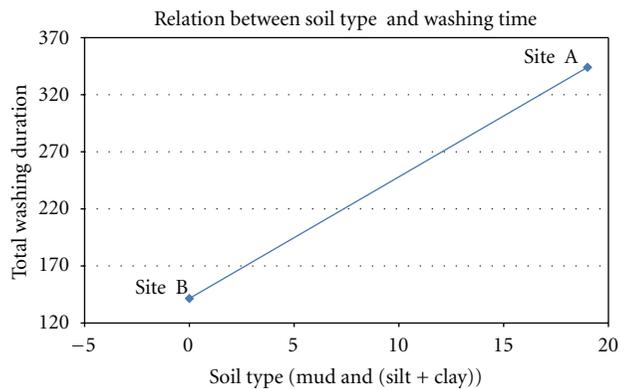


FIGURE 9: The relationship between mud % and water washing times (minute).

13.46% from residual oil. So the total percentage of extracted waste lubricant oil rises to 98.45%. Both flushing and washing cycles follow on stir periods to wash out very fine grains which subjected to measure the grain size diameter via petrographic microscope and the photomicrograph are given in Figure 10. Such figure represent photomicrograph of higher clay content and polluted oil patches in loam soil of site C sample are ranged from 0.063 mm to less than 5  $\mu$ m. The same treatment manner has been applied to treatment of site D sample that containing 42.73 g/kg original weight wastes lubricant oil and characterized as clay loam soil texture. The results in Table 7 reveal that the percentage of removed oil is 44.35% after first flushing cycle using 3% nonionic surfactant solution under pressure of 1.5 bar and duration time 2 minutes. The percentage of oil removal in the second air injection (water washing

TABLE 7: Results of soil treatment from site D.

Flushing cycles	Pulsing time from zero-2-zero bar (minute)	( $m_{oR}$ ) original weight (g/kg)	( $m_o$ ) amount of oil removed (g/kg)	% of oil extracted
3% NPEO <sub>9</sub> + first air pulse	2	42.73	18.95	44.35
Water + second air pulse	2	42.73	11.78	27.57
Total results of site (D)	4	42.73	30.73	71.92

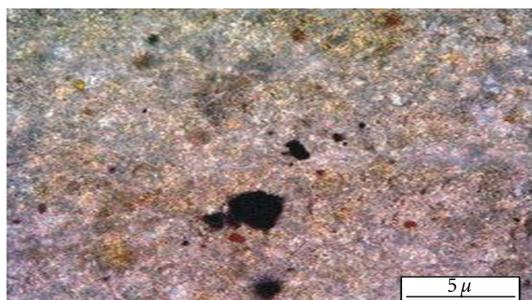


FIGURE 10: Photomicrograph show the higher clay content and oil pollution patches in loam soil of site C sample.

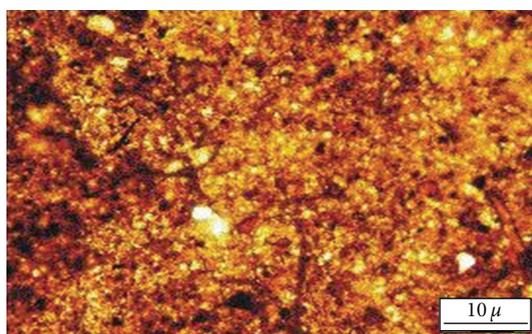


FIGURE 11: Photomicrograph shows the higher clay content and a lot of oil patches in clay loam soil of site D sample.

cycle) is 27.57% from residual oil. So the total percentage of extracted waste lubricant oil rises to 71.92%. Both flushing and washing cycles follow on stir periods to wash out very fine grains and after that the sample was subjected to measure the grain size diameter via petrographic microscope and the photomicrograph are given in Figure 11. Such figure represent the that the photomicrograph of higher clay content and oil pollution patches in clay loam soil of site (D) sample are ranged from 0.063 mm to less than 10  $\mu$ m.

The efficiency of detoxification (i.e., waste lubricant oil removal) rate and extent for a waste is a function of soil type arises in Tables 6 and 7. The data reveals that the loam soil give satisfied results, where clay loam gives worse results, this because of its higher stickiness and plasticity. Also clay loam soil (site D) contains swelling clay that reduces permeability and emulsion formation, as mentioned by Kujawski et al. [2]. The swelling clay results from absorption of aqueous solution (water) which causes loss of surfactant due to soil sorption, sorbed surfactant molecules of the solids also increase contaminant sorption. This phenomenon was observed for 2-methynaphthalene [38], PCP [39], and other

compounds. Our results are in agreement with Kibbey and Hayes [40] they mentioned that loss of aqueous surfactant due to soil sorption may significantly increase the surfactant doses required to enhance site remediation.

Generally, in the *ex situ* process the removal efficiency can be better controlled and the cleanup period is relatively short. This accomplished during soil treatment process of site C and site D samples, which carry out through separates fine soil (clay and silt) from coarse soil (sand and gravel). Since hydrocarbon contaminants tend to bind and sorb to smaller soil particles (primarily clay and silt), separating the smaller soil particles from the larger ones reduces the volume of contaminated soil. Soil washing depend on clay and silt separation process also recommended by Riser-Roberts [41]. Also soil treatment in aboveground reactors allows a greater process control that is generally impossible with *in situ* techniques. Mass transfer of organic compounds (desorption from solids) is greatly increased in *ex situ* remediation process because its more applicable to fine-grained, low permeability soils which are not amenable to *in situ* techniques. In general, *ex situ* remediation is favored over *in situ* techniques for heavily contaminated soil and relatively localized and shallow contamination [42]. *Ex situ* soil washing is commonly used for treating contaminated soils by separating the most contaminated fraction of the soil for disposal. Surfactant enhanced *ex situ* soil washing can offer the convenience, efficiency and economy desirable for innovative and alternative soil washing technologies. However, surfactant selection guide-lines are needed to be evaluated in *ex situ* soil washing is important for the soil remediation industry [43].

On the other hand, RAAG [44], Chu and Chan [45] reported that the smaller volume of soil, that contains the majority of clay and silt particles, can be further treated by other methods (such as bioremediation) or disposed in accordance with environmental regulations, whereas to clean the larger volume of soil is considered to be nontoxic and can be used as backfill.

#### 4. Conclusions

Soil remediation by surfactant solutions flushing is a common practice successfully done in a pilot-scale and field-scale studies, where the apparent contaminant solubility in surfactant solutions can be hundreds to thousands times higher than its water solubility if a traditional pump and treat method is applied. This example of the use of a treatment train for creosote-contaminated soil, and if applied either *in suit* or *ex situ* were involves: (1) free product removal as it possible using a pumping system, (2) flushing with

surfactants and washing by water using air-sparging technology as distribution system and to insure kinetic energy for emulsion formation and moving, and (3) biodegradation of the residual contamination, by air sparging or air stripping.

### Studied Soil Reach

The research work carried out throughout this study at Water laboratory Geology Department, El-Minia University, Faculty of Science, El-Minia, Egypt, and divided into two main parts: *the first part* is a laboratory study started since April 2009 ending July 2009, in this respect a simulated lab model is designed and packed with artificial polluted soils submerged with nonionic surfactant in presence of air sparging as mentioned in experimental part, where *the second part* is started in August 2009 ending in January 2010 by applying the results of the first part on some rails-polluted areas located in El-Minia, the results are not mentioned in this article, as well as they are not published or sent for publication till now.

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