Factors Affecting Site Remediation of diesel contaminated soils using surfactants

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Abstract: - Oil spillage has a major impact on the ecosystem into which it is released pollutants into crops and aquacultures through contamination of the groundwater and soils which is one of the most concerns in term of sustainable development. In this study remediation of diesel contaminated soil in the column with 15 cm height and 4m diameter was investigated. Soil column was contaminated with diesel in amount of 10 000 and 20 000 ppm. After 72 hours washing of soil with SDS with concentration of 0.1, 0.2, 0.3 and 0.4 was started. For study the effect of the washing solution pH, all tests were repeated with 4, 7, 9 and 11 values for pH. Also for study the effect of surfactant on soil remediation, soil was washed with water without surfactant. All tests were continued up to 10 pore volume and the trend of remediation and permeability of soil during the test was investigated. Results showed that in all states the quantity of remediation for acidic states is very low and efficiency of remediation when using only water is about (1:3) of maximum amount. For soil with initial contaminant concentration of 10 000 ppm the maximum efficiency is for surfactant in the concentration of 0.3 and pH = 11 and for soil with initial contamination amount of 20 000 ppm the maximum efficiency is for surfactant in the concentration of 0.1 and pH = 11. By increasing the amount of surfactant concentration, the permeability of soil decreased and in pH = 11 the amount of permeability is maximum. With increasing initial contamination quantity rate of increasing of remediation and permeability decreased. Consequently in the low level of contamination the effect of washing solution pH value in soil remediation and permeability is more in comparing with high level of contamination.

Key-Words: - Soil Remediation; Surfactants, Solution pH; Diesel

1 Introduction

Oil& chemical industries are generating several contaminants in environment. Oil compounds' that leakage under capillary and gravity forces, will cause vertical transportation in unsaturated soils and fill in the porosity of soil. Since storage sources are distributed in several zones, soil pollution due to oil storage tanks and it's unfavorable impacts, is a significant problem in which environmentalists are involved [1]. Therefore finding a solution for soil remediation is one of high importance. Soil remediation methods are presented in three main parts; biological, physical and chemical, and all other methods are related to these three main methods. Several investigations have been performed to remediate soils contaminated with oil products, and good results have been obtained [2]. Several methods of soil remediation have been experienced in laboratory which were not applicable for full-scale usages. This study discovered the soil remediation in a column of contaminated soil with the natural penetration of surfactants by gravity which would be more reliable to use in full-scale projects. There were many studies about ex-situ soil remediation. Contaminated soil were excavated from the site and transferred to another place to be washed. Washing materials and contaminated soil were mixed by water to be remediated. These methods need less time of operation but the cost is high and in some cases soil transportation through residential zones will cause some health and environmental problems. This study will provide an overview of a laboratory research for remediation of soil in a column and under gravity force. This method is more applicable and also the cost of the operation is less than other methods mentioned above. Several contaminants transport through the soil by gravity or capillary forces [2]. This method needs less time than biological methods and weather condition has low effect on this. Researches demonstrate, this method is proper for both ex-situ and in-situ remediation methods [3]. Soil washing was used for soil contaminated with heavy metals in addition to oil [4]. Soil washing mechanism is the extracting of contaminants from water by dissolving them in solvents. In earlier studies, water was used to dissolve contaminants, however additives are used to enhance

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the washing efficiency today, which decreases the time of operation. Additives consist of washing compounds, organic and inorganic acids, Sodium Hydroxide and etc, which can remove soluble contaminants [5]. Washing methods for soils of high permeability gives more removal efficiency. Contaminants' solubility in water is a key factor in soil washing [6]. Soil washing using surfactants was innovated for soils contaminated with oil hydrocarbons. Clay content of the soil is a significant factor in washing because interfacial tension of the surfactant and clay will decrease surfactant concentration.

First, contaminated zone should be identified for in-situ washing since washing operation's efficiency is related to soil characteristics and precise information about soil is necessary; grain size distribution, physic-chemical properties and their variation through depth, moisture content, organic material content, cationic exchange capacity and permeability. Remediation of soils contaminated with oil products with less content of pollution and larger particle sizes, in same conditions, gives more removal efficiency than soils with higher pollution and smaller particle sizes [7].

Soils contaminated with oil products had the efficiency of 90% to 98% in ex-situ remediation using enhanced washing compounds [7]. Several studies had been performed to remediate soils contaminated with gasoline using surfactants [6].

There is not enough information about full scale projects of in-situ soil remediation, but the principles are that after obtaining above information, some wells are used to pass the surfactants and according to soil permeability, gravity force or pumping is used to pass the surfactant through the soil. Depends on projects' zone, materials produced during project is extracted by pumps or entered to the subsurface water then it is collected and treated.

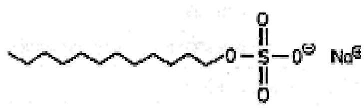
Another research held on sandy media which had the initial contamination of 1000 ppm. Medias up to pore volume of 20 were washed by anionic surfactant, JBR425, and contaminant removal was 67% for this content of surfactant [8]. PCE removal efficiency in a sandy soil, with 15cm height, 5cm diameter and with 750 ml of surfactant solvent, was 44%, 42% and 75% for anionic, nonanionic and mixture of surfactant, respectively [9].

Using surfactant for soil washing has been performed for several years, but because of problems such as soil blockage, reduction of permeability and hydraulic conductivity more investigations are needed yet. These problems are due to reactions between surfactants, organic materials and clay and congealing soil surface. Since permeability reduction causes in decreasing surfactant penetration, remediation time increases and removal efficiency decreases. Soil permeability is one of the most important parameters for soil washing which should be studied precisely due to site conditions and prior to performing any remediation. Soil blockage caused by using surfactants is one of the significant factors on efficiency of the operation [6].

2 Materials and methods

Sodium dedocyle sulfate (SDS) was used as anionic surfactant which was manufactured by Merck Company in Germany. Critical micelle concentration (CMC) of this surfactant is 0.2. Surfactant's characteristics are shown in Table 1. CMC is the most important parameter for each surfactant which describes surfactant's behavior. CMC is the concentration in which the micelles begin to form. By increasing the surfactant's amount, monomers are transformed to micelles. In this point, surfactant meets the lowest surface tension.

Table 1Characteristics of SDS surfactant.

Characteristic	Description
Surfactant type	Anionic
Chemical formula	C12H25NaO4S :5OSO2ONa
CMC (%)	0.173 – 0.23
Molecular weight	288.38 g/mol
Melting point	204 – 207 ° C
Density	20 g/ cm3 (1.1 °C)
pH	6 – 9 (10 g/l, H2O, 20 °C)
Solubility in water	150 g/L (20 °C)
Structure	

Sandy soils were selected as testing samples and have the grain size distribution of # 40 mesh to the # 200 mesh range. Soils were washed with 0.1 N sulfuric acid, afterwards distilled water was injected for washing. The samples were dried out in an oven at 62°C for 24 h. Soil characteristics are shown in Table 2.

Table 2 Soil samples' characteristics

Characteristic	Description
Soil type	Sandy
Void ratio (e)	0.68
Porosity (n)	0.4
Dry soil density, gd	1.55(gr/cm3)
Gs	2.66
pH	9
Solubility in water	150 g/L (20 °C)
Electrical conductivity	158 (ms/ cm)

Pilot plant consists of 3 plexi-glass columns with 50cm height and 4cm diameter. Surfactant mixture and water were located at the top of the pilot, in a one liter volume basin. And water is conducted to the column using a hose. Permeability measurements are performed in both constant-head and reducing-head conditions. In this study constant-head method was used. Columns were adjusted on a vibration table with 1 cm/min speed. They were filled by soil to the adequate height to achieve necessary compression and uniformity. After this step, columns were installed on a four leg steel structure, on considered positions. Fine coarse soil was used to fill on top of the columns with 1 cm height to prevent turbulences caused by water, surfactant and soil contact.

The soil columns were contaminated with adequate diesel amount to achieve the concentration of 10 000 and 20000 ppm in soil. After contamination, the columns were held for 72 hrs without any operation in order to resume reaction among diesel and soil particles, after 72hrs washing began. As the goal of this study was to optimization of the pH and surfactant amount with permeability evaluation, 10 and 20 mg/g contaminant to soil portion for initial contamination, 0.1, 0.2, 0.3, 0.4 percent of surfactants and pH values of 4, 7, 9 and 11, were examined. In order to find out the surfactant's effect, all washing operations were performed using water (buffer solution) under several pH values and contamination amount. After 72 hrs, washing began and solution basin was filled to be penetrated into the soil gradually. Washing was continued until reaching 10 pore volume and pH and TPH of outlet solution measured during 2, 4, 6 and 10 pore volumes. Times were recorded during 0.67, 1, 1.33, 2, 3.33, 4, 5.67, 6, 7.33, 8, 8.67, 9.33 and 10 pore volumes, in order to calculate permeability values and it's variations by depicting a more precise curve.

3. Results comparison and discussion

3.1. Diesel removal

For the first run, removal efficiencies were investigated for initial contamination of 10 000 ppm and then for 20 000 ppm.

3.1.1. Initial contamination of 10 000 ppm

Soil columns were contaminated with 10 000 ppm diesel, then washing was performed under different conditions. Figure 1 shows the removal efficiency under various pH values, surfactant and water amounts.

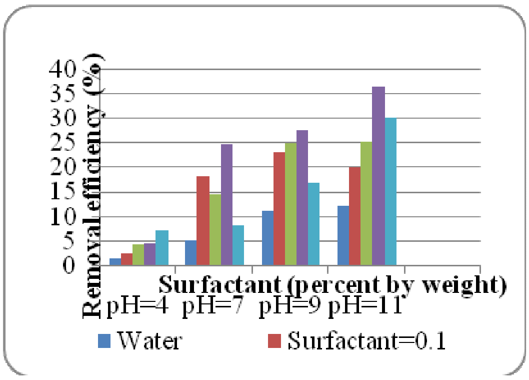


Fig. 1. Diesel removal efficiency (%) with respect to increasing surfactant amount

(Diesel concentration: 10000ppm)

According to the Figure 1, by increasing the surfactant amount, efficiency is increased and in 0.3 percent of surfactant, there was 35% removal. Efficiency increasing progress have lower rate until 0.2 percent of surfactant, after that the rate is significantly decreased. As it is understood from Figure 1, by adding the surfactant amount from 0.3 to 0.4 percent, efficiency is not only increased, but also decreased. Contaminated soil remediation is performed under progress which finally comes in to a balance in contamination, pH and surfactant amounts. The optimum point of the efficiency curve is like a parabola's extreme point that the less or more amounts of surfactant will result in a less efficiency. 0.3 percent of surfactant is the optimum point and with more amounts of surfactants, additional reactions between surfactant, contaminant and soil particles occurs that separation and removal of surfactant and diesel attached to soil is not applicable by water and results in a less efficiency. Figure 2 shows the removal efficiency variations with respect to increasing pH for different values of pH, surfactant and also water amounts.As it demonstrated in Figure 2, efficiency rises by increasing values of pH. This raise is higher for pH values from 4 to 7 and 9 to 11. As the figure shows, by increasing pH values from 7 to 9, no significant differences happened in remediation. In all cases, the efficiency is less in acidic phases in comparison with basic phases. The reason of higher efficiency in basic and neural phases would be the higher solubility of the oils.

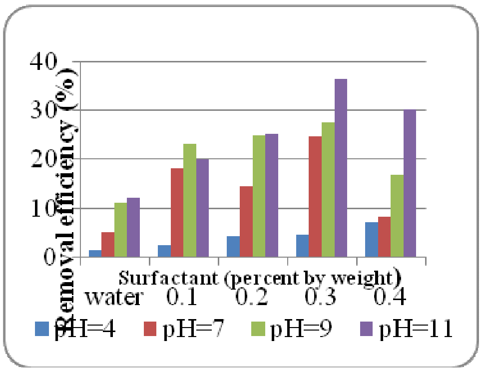


Fig. 2. Removal efficiencies (%) with respect to increasing pH values

(Diesel concentration: 10 000ppm)

3.1.2. Initial contamination of 20 000 ppm

In the second part of the experiments, soil columns were contaminated with diesel of 20 000 ppm concentration and washing was performed under different conditions. Figure 3 shows the removal efficiency under various pH values, surfactant and water amounts.

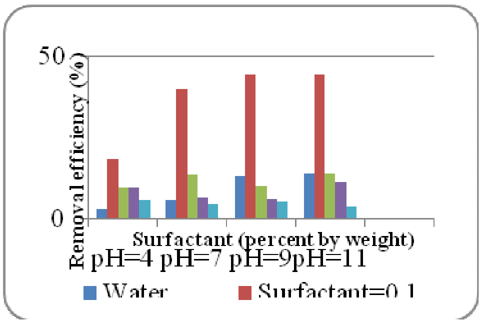


Fig. 3. Removal efficiencies (%) with respect to increasing surfactant amounts

(Diesel concentration: 20 000ppm)

According to Figure 3, by increasing the surfactant amount, removal efficiency is decreased. In all cases the initial contamination is doubled, in comparison with the last case. In contamination concentration of 10 000 ppm removal efficiency loss, begins from the 0.3 to 0.4 percent of surfactant. In second run, by increasing the initial contamination, this amount decreased to 0.1 - 0.2 percent of surfactant. The other factor which decreases the removal efficiency since surfactant amount is increasing, is the reaction between additional amount of surfactant and soil particles which makes the separation and transporting of the diesel and surfactant difficult. By increasing the surfactant amount the number of reactions increases and gel-like compounds produced at the surface of soil particles and rate of efficiency decreasing, increases. Figure 5 shows the diesel removal efficiency with respect to several pH values, surfactant and water amounts.

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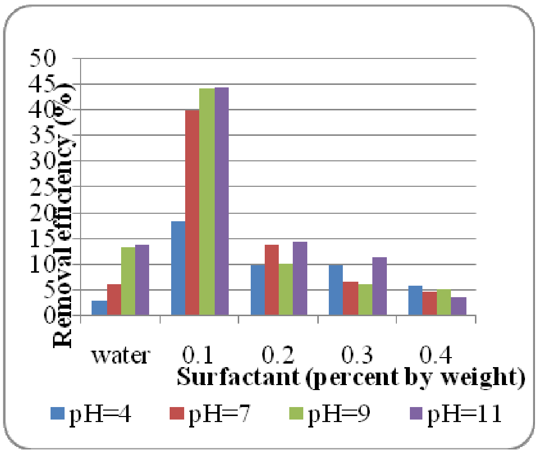

Fig. 5. Removal efficiencies (%) with respect to increasing pH values
(Diesel concentration: 20000ppm)

It is demonstrated from Figure 4, the remediation efficiency variations are not significant with respect to pH value increase. It is concluded that in higher amounts of contamination due to test's conditions, surfactant amount is a more determinant factor in comparison with pH values. In fact, pH role is making the separation of diesel and soil easy, and when the contamination is too high, prominent reaction is the reaction between surfactant and soil particles. Therefore in initial contamination of 20 000 ppm, by increasing pH values, removal efficiency wouldn't very much.

3.2. Soil permeability evaluation

Soil permeability was evaluated in initial contamination of both 10 000 and 20 000 ppm. Permeability varies during the test as a result of reactions among soil particles, surfactant and contaminant. To depict the charts of this section, permeability was measured at pore volume of 10.

3.2.1. Initial contamination of 10 000 ppm

At first, soil columns were tested for contamination of 10 000ppm. Outlet flow rates were recorded for several times during the test and permeability calculated in cm/s. Figure 5 shows the permeability values for different conditions.

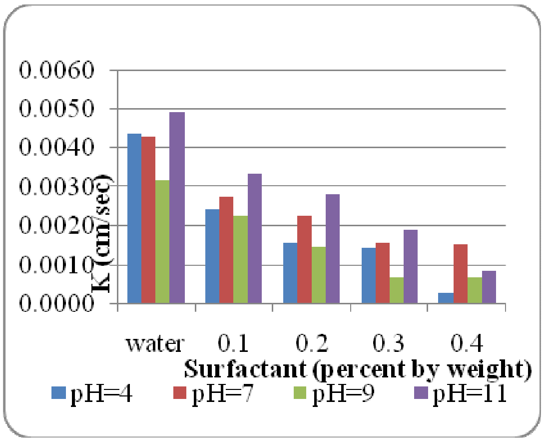

Fig. 6. Soil permeability for different conditions with respect to increasing surfactant amounts
(Diesel concentration: 10 000ppm)

As it is shown in Figure 5, by increasing the surfactant amount, permeability decreases. Permeability is the most for pH=11, except in 0.4 percent of surfactant. Differences between the permeability in pH=11 and other pH values, is the most at first (for 0.1 percent of surfantant amount). By adding the surfactant amount, this difference decreases until in 0.4 percent of surfactant which is negative. This is caused by the balance factor which has been mentioned above. Increasing pH values along with surfactant amounts cause reaction among soil particles, surfactant and diesel which results in congealing soil surface and reduction of permeability. Figure 7 shows the soil permeability for different test conditions under 10 000ppm concentration of diesel.

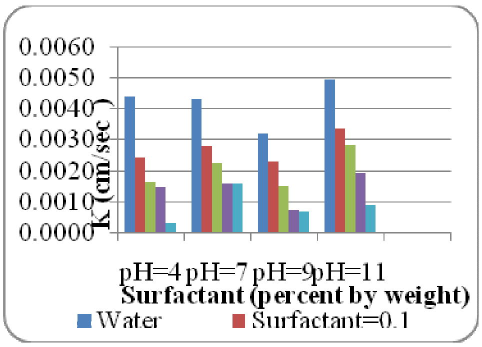

Fig. 7. Soil permeability for different conditions with respect to increasing pH values
(Diesel concentration: 10 000ppm)

According to figure 7, soil permeability for water is the most rather than other surfactants in all pH values. For pH values of 4 to 9 for all surfactants, no significant difference occurred in permeability values,

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but for pH values of 9 to 11, it was noticeable.

3.2.2. Initial contamination of 20 000 ppm

In the second part, soil columns were tested for 20 000 ppm contamination and permeability was evaluated. Figure 8 shows the permeability values for different test conditions.

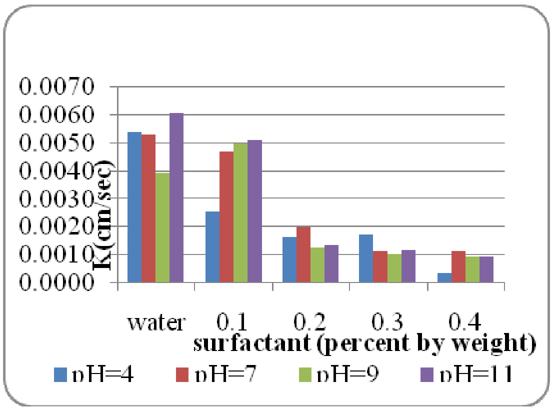

Fig. 8. Soil permeability for different conditions with respect to increasing surfactant amounts (Diesel concentration: 20 000ppm)

In this case like previous one, by increasing surfactant amount, permeability decreases. The difference between the figure 6 and figure 8 is that permeability reduces intensively for 0.2 percent and more of surfactant, in figure 8. This is caused by reactions between additional surfactant amount and contamination. In fact, extra amount of diesel in soil results in this intense loss. Figure 9 shows different amounts of soil permeability for different test conditions.

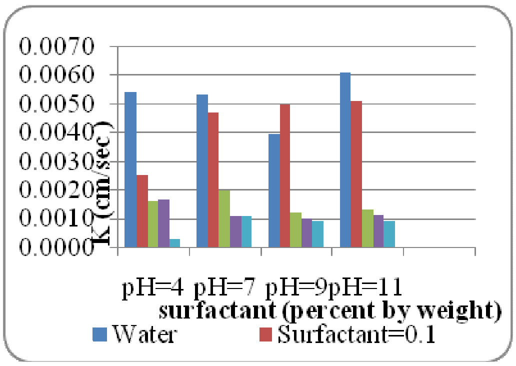

Fig. 9. Soil permeability for different conditions with respect to increasing pH values (Diesel concentration: 20 000ppm)

In this case, pH value increasing have no significant impact on soil permeability and there is a negligible soil permeability difference between pH =11 test and other tests. According to figures 7 and 9, for contamination of 10 000ppm, it is concluded that in high amount of contamination due to soil characteristics and test conditions, surfactant amount's impact on soil permeability is more significant than pH values.

4. Conclusion

Due to soil characteristics, researches should be held in each zone individually. In this study for initial contamination of 10 000 ppm and soil characteristics considered before, optimum removal efficiency obtained 35% for surfactant of 0.3 percent and pH=11. For initial contamination of 20 000 ppm and soil characteristics mentioned above, optimum removal efficiency is obtained as 45% for 0.1 percent of surfactant and pH=11, and by increasing the surfactant removal efficiency decreased. In all cases, removal efficiency for water (buffer solution) and acidic phases, are low. By increasing initial contamination, rate of removal efficiency increase, is reduced by increasing pH values, in fact in lower amounts of contamination, role of pH values in increasing efficiency is more significant. In all cases, by increasing surfactant amount, permeability reduces and in pH=11 and surfactant percent of 0.1, the highest permeability achieved. By increasing initial contamination, rate of increasing permeability is reduced by increasing pH values. In lower contamination amount, role of pH values on increasing permeability is more significant. Simultaneous assessment of remediation process and permeability for soil of 10 000ppm contamination, demonstrates that performing tests in the case of pH values of 9 and 11 and surfactant amount of 0.2 and 0.3 percent is a proper condition for soil remediation since efficiency increases in a ascending way and permeability does not reduce. . Simultaneous assessment of remediation process and permeability for soil of 20 000ppm contamination, demonstrates that performing tests in the case of pH values of 7, 9 and 11 and surfactant amount of 0.1 percent is a proper condition for soil remediation since efficiency increases in a ascending way and permeability does not reduce.

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References:

[1] Deeb, R.A, Alvarez, Cohen, (2000). Aerobic Biotransformation of Gasoline Aromatics in Multicomponent Mixture. Bioremediation Journal. 4(2), 171-179.

[2] Kueper, B.H., (1989). The Behavior of Dense, Non-aqueous Phase Liquid Contaminants in Heterogeneous Porous Media. PhD dissertation, University of Waterloo, Waterloo.

[3] US EPA, (1998). Innovative Site Remediation Technology – Soil Washing/Soil Flashing. 3, 133.

[4] Anderson (Ed.), W.C., (1993). Innovative Site Remediation Technology: Soil Washing/Soil Flushing, American Academy of Environmental Engineers.

[5] Abdul, A.S., Gibson, T.L., Rai, D.N. (1990). Selection of surfactants for the removal of petroleum products from shallow sandy aquifers. Ground Water, vol, 286-920.

[6] Ziegenfuss, P.S,(1987). The Potential Use of Surfactant and Cosolvent Soil Washing as Adjutant for In Situ Aquifer Restoration. MS thesis, Rice University, Houston, TX.

[7] Urum, Kingsley, Pekdemir, Turgay, Çopur, Mehmet. (2004). Surfactants treatment of crude oil contaminated soils. Journal of Colloid and Interface Science. 276, 456-464.

[8] Mulligan,Catherine N., Eftekhari, Farzad, (2003). Remediation with surfactant foam of PCP-contaminated soil. Engineering Geology. 70, 269-279.

[9] Lee, Dal-Heui, Chang, Ho-Wan, Cody, Robert D., (2004). Synergism effect of mixed surfactant solutions in remediation of soil contaminated with PCE. Geosciences Journal, 8(3), 319-323.