Journal of Babylon University/Engineering Sciences/ No.(4)/ Vol.(24): 2016

Experimental Investigation of Phenanthrene Pollutant Removal Efficiency for Contaminated Sandy Soil by Enhanced Soil Washing

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Abstract:

Polycyclic aromatic hydrocarbons (PAHs) are environmental concerns that must be removed to acceptable level. This research assesses two agents (Na_2EDTA and SDS) to remediate contaminated sandy soil, spiked with 500mg/kg phenanthrene. Five sets of experiments (batch) are applied to investigate the optimal of five influencing factors on soil remediation: Na_2EDTA-SDS concentration, liquid/Solid ratio, stirring speed, pH value of flushing solution and mixing time. The results of batch experiments showed that SDS has high phenanthrene removal efficiency (90%), while Na_2EDTA shows no phenanthrene removal. pH has no effect on phenanthrene removal. To study the influence of flow rates on the removal efficiency of contaminants, two column tests with hydraulic gradient of 0.2 and 1.2 conducted by SDS solution. The results illustrate that high phenanthrene removal from soil obtained by 1.2 hydraulic gradient condition. The SDS flushing solution removed approximately 69% and 81% of phenanthrene from soil under low and high hydraulic gradients, respectively. It was concluded that phenanthrene removal depend on surfactant micelles formation. Overall, the study showed that soil flushing removal efficiency for contaminants depends on the flushing agents selectivity and affinity to the contaminants and the condition of hydraulic gradient.

Key words: contaminated sandy soil, phenanthrene pollutant, Enhances soil washing**.**

المستخلص

الملوثات الهيدروكربونية العطرية المتعددة الحلقات من أهم الاعتبارات البيئية التي يجب إزالتها إلى مستويات مقبولة. في هذا البحث استخدم نوعين من المحسنات (Na_2EDTA و SDS) لمعالجة التربة الرملية الملوثة، وقد تم تلويث التربة ب(500 ملغم/ كغم) من الفينانثرين. تم إجراء خمس مجاميع من التجارب المختبرية للتوصل للظروف المثلى للعوامل المؤثرة على معالجة التربة الرملية وهي: تركيز Na_2EDTA–SDS، نسبة سائل المعالجة /التربة، سرعة التحريك، قيمة الرقم الهيدروجيني لمحلول التنظيف وزمن المعالجة. أظهرت نتائج التجارب المختبرية إن كفاءة الSDS في ازالة الفينانثرين عالية بحدود (90٪) أما الNa_2EDTA فلم يظهر أي إزالة للفينانثرين. وأيضا تم التوصل الى أن الرقم الهيدروجيني (pH) ليس له أي تأثير على إزالة الفينانثرين. ولغرض دراسة تأثير الانحدار الهيدروليكي (معدل الجريان) على ازالة الملوثات فقد تم إجراء تجربتين باستخدام نظام العمود (عمود الغسل) وبقيمتي انحدار هيدروليكي (0.2 و 1.2) على التوالي باستخدام محلول SDS. أظهرت النتائج أن إزالة الفينانثرين القصوى من التربة الرملية تم الحصول عليها بقيمة الانحدار الهيدروليكي العالية (1.2). ان محلول المعالجة الSDS قام بازالة ما يقارب 69٪ و81٪ من الفينانثرين من التربة الرملية باستخدام قيمتي الانحدار الهيدروليكية (0.2 و 1.2) على التوالي. من النتائج المستحصلة في هذا البحث يظهر أن إزالة الفينانثرين تعتمد على تكوين المذيلات (micelles formation). وبشكل عام، بينت الدراسة أن إزالة الملوثات من التربة الرملية تعتمد على انتقائية محلول المعالجة وتقاربه مع خصائص الملوث المطلوب إزالته وقيمته الانحدار الهيدروليكية المستخدمة للمعالجة.

الكلمات المفتاحية: الترب الرملية الملوثة، التلوث بالفينانثرين، تعزيز التربة بالغسل.

1.1Introduction

Soils contaminated with polycyclic aromatic hydrocarbons (PAHs)poses potential threats to ecological and human health. PAHs are chemical compounds, more than two bonded aromatic rings arranged in clustered or linear formation to form PAHs. PAHs usually contain atoms of carbon and hydrogen, sometimes atoms of sulphur, nitrogen and oxygen may substitute in the aromatic ring forming heterocyclic aromatic compounds (Gan *et. al*.,2009).The sources PAHs soil contamination are natural and anthropogenic. PAHs release to the environment from forest fires, volcanic,emissions of vehicular, wood burning and industrial combustion of fossil fuel. Also organic matter incomplete combustion and pyrolysis released PAHs (Lua *et. al.*, 2010).

PAHs contaminated soil has potential risks on human health and environmental (Gan *et. al.*,2009).The PAH contaminants in soils is an important concern because their mutagenic, teratogenic and carcinogenic characteristics. They tightly have a tendency to adsorb to the soil organic matter making them less vulnerable to chemical and biological degradation. PAHs long presence in soil stimulates the PAH restoration molecules into the micropores of soil and increasing PAHs resistance for remediation (Lua *et. al.*,2010).

Several ex-situ/in-situ methods for soil remediation have been developed, to eliminate contaminants from soils including solidification/stabilization, electrical process, phytoremediation, vitrification, and bio-slurry reactors, soil washing/acid extraction, phytoremediation, soil flushing (Jiang *et. al.*,2011).A specific condition of contaminated site may require a combination of procedures to allow the optimum remediation for the dominant conditions. Physical, Biological and chemical remediation may use in conjunction with another one to reduce the contamination to acceptable level.In spite of many technologies available for the contaminated site treatment, the selection governed by site and contaminant properties, costs, time limitations and regulatory requirements, (Khan *et. al.*, 2004).

Soil flushing is an in situ technique for contaminated soil remediation. The application flushing technique consists of solution injection through the infiltrating systems beneath or above the water table in contaminated soils (Yeung, 2009). The solution leach through the polluted zone; the extracted solution are collected and treated elsewhere. The main part of this technique is flushing solution treatment that poses great complications (Hamberg,2009).It can apply to specific soil environments, in which non-permeable materials should underlain the contaminated zone (Lesˇtan *et. al.*, 2008).

An aqueous extracting solution can be applied by horizontal or vertical injection wells, surface flooding, leach fields, sprinklers, basin or trench infiltration systems.The same extracting agents are used for both soil flushing and washing, including water, bases /acids, chelating agents,reducing/oxidizing agents and cosolvents/surfactants (Evanko and Dzombak,1997).The performance of flushing technique depends upon contaminant properties, such as solubility, so it is beneficial to define applicable solubility range and be specific about the targeted contaminants (Saichek and Reddy, 2005).

Surfactant is amphiphilic (hydrophilic and hydrophobic) compound. Lower than the critical micelle concentration (CMC),surfactants found as monomers while at CMC, the monomers of surfactant are aggregate to form micelles (Mulligan *et. al.*, 2001). Micelles in the solution have a hydrophobic inner and hydrophillic outer, which the first is the active phase which can interact with contaminants of low polarity. This interaction produce an increase in the PAHs contaminants apparent solubility of, thus, increasing desorption and dissolution of contaminants. Additionally, surfactants produce emulsions and decrease interfacial tension which mobilize strongly bound contaminants (Mulligan *et. al.*,2001; Reddy and Saichek, 2003).

The objective of this research is to assess the effectiveness of chelating agent and surfactant extractive (Na_2EDTA and Anionic surfactant SDS) for PAHs treatment from contaminated soil. Sets of experiment batches applied to investigate the flushing agents performance and column experiments to assess the influence of hydraulic gradient conditions.

1.2 Materials and Methods:

1.2.1 Soil Characterization

Natural soil specimen freshly collected from a non-contaminated farmland in Kufa, a city located in the Najaf Governorate in Iraq. Fifty kilograms of soil were taken from a depth ranged between 30 cm to 60cm below ground surface. A homogenized soil sample analyzed for different chemical constituents and physical characteristics. All these characteristics are shown in Table 1.

Table (1): Physicochemical properties of the soil specimen.

Soil parameters	Description
Soil type	Sandy silt
Soil texture: Sand Silt	 84% 16%
Porosity	37.2 %
Bulk density	1.47gm/cm^3
Moisture content	13%
Soil pH	7.54
Electrical conductivity	2.98 mS/cm
Organic content	9.89 %
Cation Exchange Capacity	4.6 meq/100gm
Cd $_{\text{initial}}$ Phenanthrene $_{\text{initial}}$	NA NA

1.2.2 Contaminants

Phenanthrene (phen) ($C_{14}H_{10}$), a hydrophobic organic compound which consists of three rings, is selected in the study as representative PAH contaminant. Phenanthrene aqueous solubility is 1.1 mg/ l at 25 C^o. To prepare phenanthrene contaminated soil, the soil is air-dried to be ready to contaminate with (500 mg /kg soil) of Phenanthrene, then, 500 mg of phenanthrene is dissolved in 50 ml cyclohexane, and manually shaken for 20 min to complete dissolution of the solute. In a stainless steel container, 100 g of clean air dried-soil is placed and a few drops of the Phenanthrene-cyclohexane solution are added, the mixture is manually homogenized using a stainless steel spoon. The process of mixing is repeated for the1 kg soil sample until the solvent-PAH well reasserted with dry soil sample. The resulted Phenanthrene-contaminated soil is dried at room temperature overnight, and then stored in stainless steel jar in a ventilated hood in the dark. The Phenanthrene-spiked soil is used after one week to mimic the field contamination (or to achieve the contaminant adsorption to soil particles).A sample of each prepared mixture is analyzed by the direct method to determine the concentration of Phen in the soil.

1.2.3 Flushing Solutions

Sodium dodecyl sulfate SDS is selected according to its significant capability to enhance the solubilization of hydrophobic organic compounds including phenanthrene (Mulligan *et. al*., 2001).

1.2.4 Chemical Analysis

A shimadsu high performance liquid chromatography (HPLC) unit type: LC2010AHT is used for the separation and quantification of phenanthrene existing in the surfactant aqueous solutions. The HPLC is coupled with a stationary phase C-18 5µ reverse phase column of 250mm length and inner diameter of 3.6mm. Two LC-20AD pumps, Shimadzu variable UV/V (195-1100 nm), detector SPD-20A, injection-type autosampler, and one degasser are provided for the HPLC system. The mobile phase consisted of 100% by volume pure acetonitrile (99.5%) and 0.8 ml/min flow rate. The UV detector monitored the absorbency of phenanthrene 280nm wave length. Samples are run by HPLC in duplicate; some time in triplicate for more accuracy.

1.3 Batch Experiments

Five sets of experiments are conducted to study the effect of the five affecting factors on phenanthrene removal with SDS and Na_2EDTA. The five factors are:(1) SDS and Na_2EDTA concentration,(2) Liquid/Solid ratio,(3) Stirring speed,(4) pH value (5) Washing time. When one of the factors tested at changed values to achieve the optimal value, the other four factors held constant. The value producing the higher removal was adapted in the following tests. Air-dried soil and flushing solution added into flask and all experiment conducted at room temperature. After the experiment were finished, the solution filtered through filter paper (Whatman No.1) and then, analyzed for phenanthrene high performance liquid chromatography (HPLC).

1.3.1 Results of Batch Experiments

Na_2EDTA and SDS is investigated to examine phenanthrene removal efficiency as mentioned above, Na_2EDTA appeared to be inefficient to remove phenanthrene in all five batch steps as illustrated in figures (1to 6).Also, chelating agent flushing solution is found to be inefficient in removing phenanthrene from contaminated soil. This may be belonged to the difference between the characteristics of Na_2EDTA, phenanthrene is a nonionic compound while the Na_2EDTA are ionic compound; therefore, it have not the ability to solubilize the phenanthrene. As there is no significant effect for Na_2EDTA as shown in (Fig.1), the results for SDS batch only are concerned and discussed.

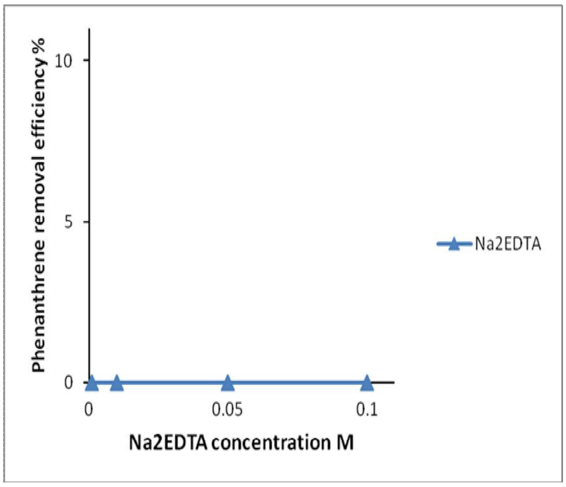

Fig (1): The effect of Na_2EDTA concentration on phenanthrene removal efficiency.

1.3.1.1 SDS Concentration

The results showed that the increasing of SDS concentrations increased phenanthrene removal efficiency and reached an optimum removal of (100%), after which the removal efficiency tends to decrease as illustrated in figure (2). Increasing SDS concentration led to micelle formation which is essential to solubilize the phenanthrene contaminant, Micelle formation will form the hydrophobic sink to the phenanthrene contaminant. Further increase in SDS concentration, the micelle formation will degeneration (admicelles formation will cause the losing of the hydrophobic property of SDS), the surfactant will loss her hydrophobic characteristic which is responsible about phenanthrene removal. It is one of the advantages of surfactant that it can remediate with very low concentration.

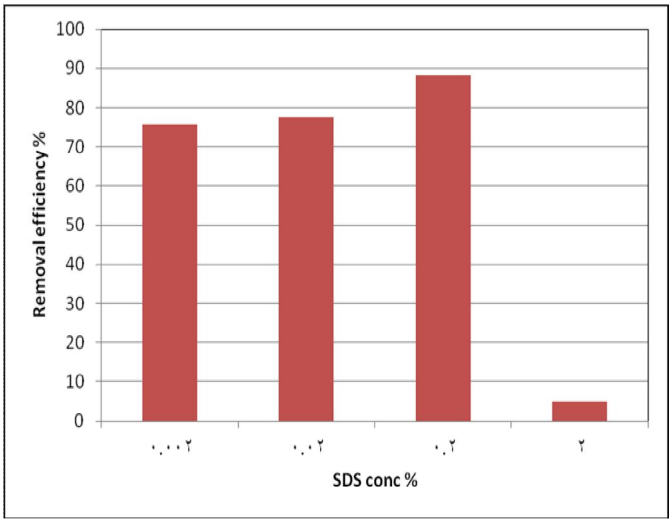

Fig (2): The SDS concentration effect on phenanthrene removal efficiency.

1.3.1.2 L/S Ratio

Experimental results showed that the phenanthrene removal efficiency increased with increasing L/S ratio as shown in figure (3). Increasing L/S lead to an increase in removal efficiency, more micelles will be generated which is responsible about phenanthrene solubilization, therefore more capacity of phenanthrene solubilization. Further increase of L/S ratio after value 15 will be worthless because no increase in removal efficiency is to be gained.

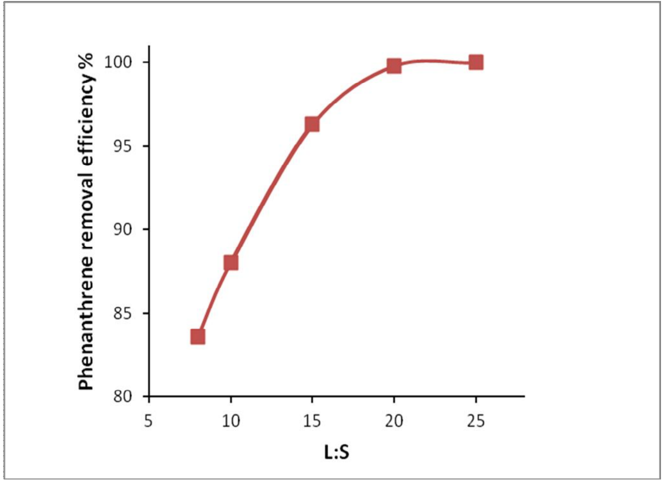

Fig (3): The effect of L/S ratio on phenanthrene removal efficiency.

1.3.1.3 Stirring Speed

Experimental results reveals that the Phenanthrene removal efficiency is increased with the increasing of stirring speed for values up to 210rpm, after that efficiency tends to decrease as shown in figure (4). This decrease may be related to the moving of slurry in bulk formation with less relative movement under high stirring speed which reducing the collision and accordingly lowering phenanthrene removal.

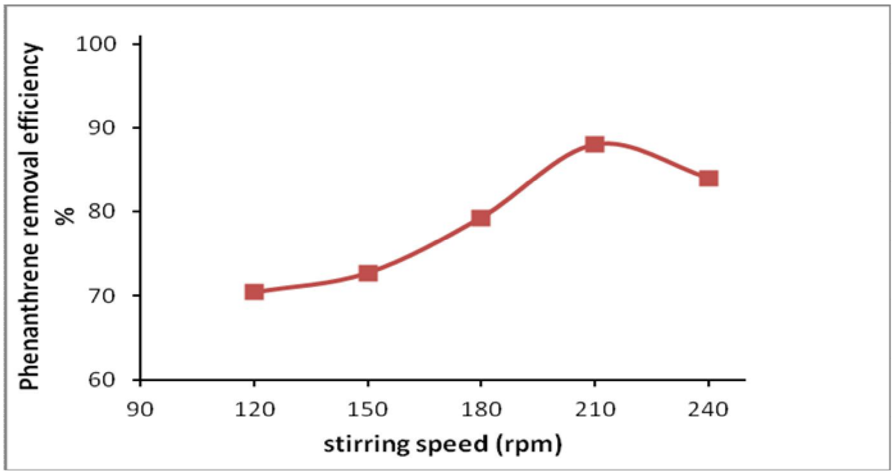

Fig (4): The stirring speed effect on phenanthrene removal efficiency.

1.3.1.4 pH value

Varying pH values do not cause any variation in phenanthrene removal efficiency.It illustrated in figure(5).This behavior approves that the micelles formation for (SDS) and phenanthrene solubility do not affected by pH variations (Yeung, 2009).

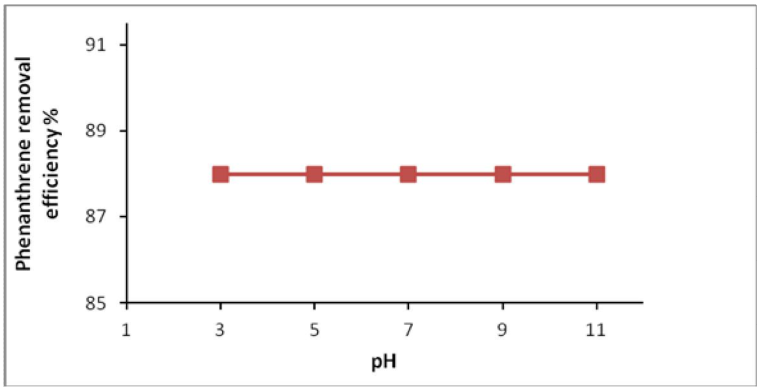

Fig (5): The effect of pH variation on phenanthrene removal efficiency.

1.3.1.5 Mixing Time

Results show that the optimum mixing time is (1.5hr.) as illustrated in figure (6) which phen removal efficiency after this value has no longer changed, this may be belonged to rate – limited dissolution and/or desorption of phenanthrene.

1.3.1.6 Effect of Na_2EDTA addition to SDS solution

No significant effect have been appeared to the addition of Na2EDTA addition to SDS solution on phenanthrene removal efficiency, A slight decrease in efficiency is occurred according to such addition as shown in figure (7).

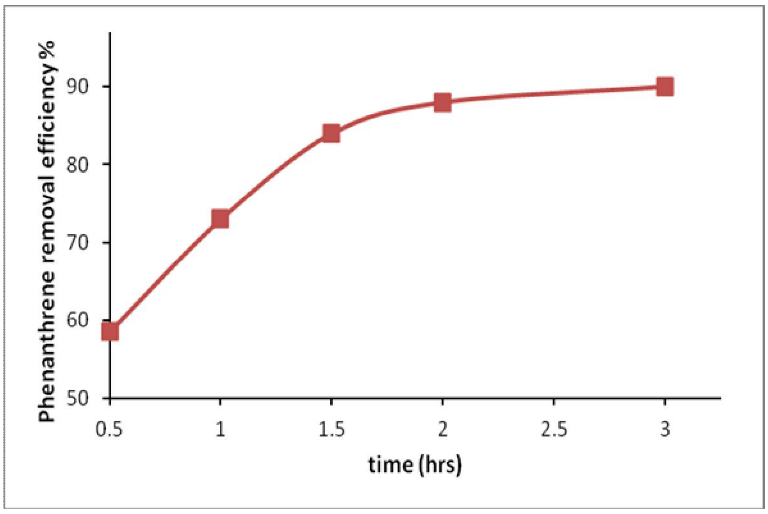

Fig (6): The effect of mixing time on phenanthrene removal efficiency.

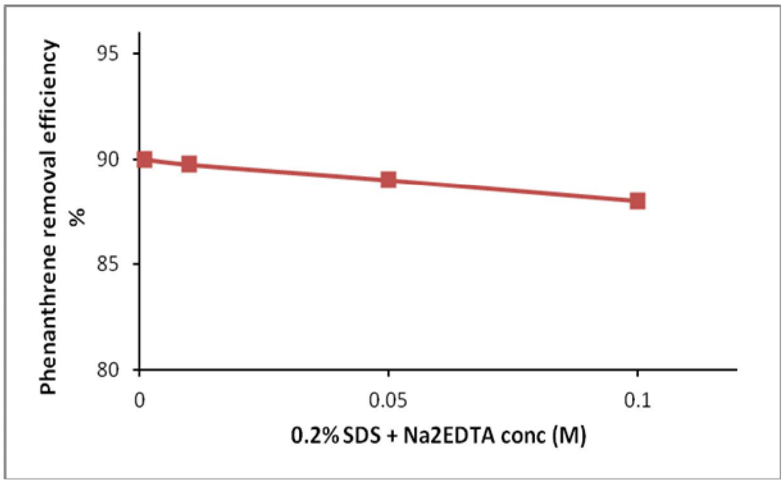

Fig (7): The effect of Na_2EDTA addition to SDS solution on phenanthrene removal efficiency.

1.4 Continuous (Column) Experiments

Two column experiments are conducted to investigate the removal efficiency of the target pollutants (phenanthrene) and the influence of hydraulic gradients on the removal efficiency, the results are illustrated in table (2) and figure (8).The optimal conditions of batch experiments are applied to the column experiments, SDS concentration and L/S.

Hydraulic conductivity of soil depends upon many features, include the organic content, structure, void ratio and saturation of soil and viscosity of the fluid flowing in soil (Saichek and Reddy,2005).The low percent of silt, clay, organic matter and CEC indicate higher soil permeability for contaminants and may be amenable to remediate by soil flushing/washing (Wuana *et. al*., 2010).

Table (2): The experimental results of flushing column test.

Soil contamination	Treating solution	Test No.	Hydraulic gradient	Hydraulic conductivity
Phenanthrene	0.2% SDS	Ex 1	0.2	$3.965*10^{-4}$ cm/sec
		Ex 2	1.2	

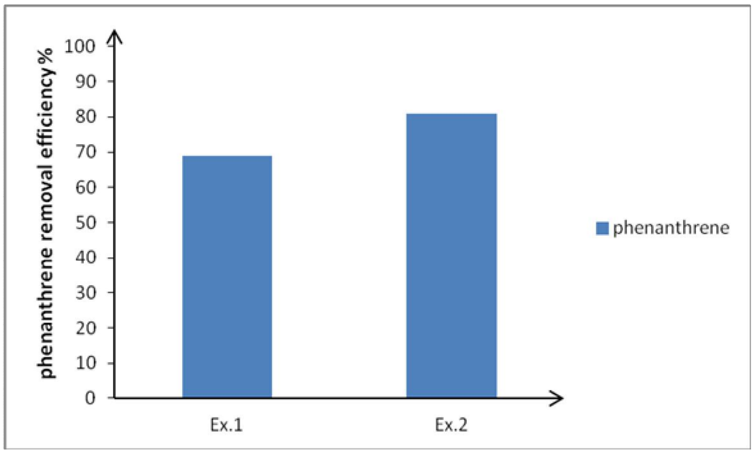

Fig (8): The effect of hydraulic gradient on contaminant removal efficiency in column experiments.

The column experiments were applied for phenanthrene contaminated soil. The influencing factor on phenanthrene retention in soil and on the soil flushing remediation will be discussed. Phenanthrene (and all PAHs) interacts with soil by physical interaction. The factor affected the presence of phenanthrene in soil is the soil type. The soil with finer size distribution that containing (clay, silt) affect the soil flushing remediation. Finer grain size causes high binding affinity to phenanthrene contaminants. Also, the presence of organic material and its molecular structure, can bind with hydrophobic organic compounds (such as phenanthrene) through variety mechanisms.Therefore, this will prevent desorption of phenanthrene from soil to the flushing solution. These contaminant-organic matter interactions affect the flow flushing in soil.

1.4.1 Column Experiments Results

In this study, Surfactants monomers aggregate located in the column to compose micelles which have unique characteristics (the inner hydrophobic and the hydrophilic exterior of the micelle). The exterior (hydrophilic) is the cause of making micelles soluble in water, while the interior (hydrophobic) is responsible for providing sink for phenanthrene, which increases the solubility of phenanthrene. CMC is the surfactant concentration above which micelles form. As a result, the phenanthrene removal during SDS flushing is dependent on the micelles number formed and its stabilities (Reddy and Saichek, 2003).

As illustrated in table (2), two values of hydraulic gradients (flow rates) of flushing agent for phenanthrene contaminated soil are investigated. Overall, the experiments of higher hydraulic gradient are resulted maximum total contaminant mass removal for phenanthrene as illustrated in figure (8).It is attributed to that the phenanthrene may strongly held in soil particles pores which indicates that the desorption and the solubilization seems to be a rate limited process. Therefore, high hydraulic gradient increases the rate of the contaminants desorption.

1.4.2 Phenanthrene Removal

The results showed that phenanthrene removal during the SDS flushing in Ex2 was higher than that of Ex1. The 1.2 % hydraulic gradient resulted in higher removal efficiency. This points to that in the SDS experiment; more number of micelles formed with a higher hydraulic gradient situation, causing effective phenanthrene removal. The 0.2% hydraulic gradient in Ex1 assists the desorption of phenanthrene into SDS flushing solution and its removal less than 1.2%.

In condition of higher hydraulic gradient (1.2%), SDS removal efficiency was (81%) for phenanthrene, while SDS flushing removal efficiency in condition of 0.2% hydraulic gradient was (69%) for phenanthrene. In 0.2% hydraulic gradient conditions, the SDS removal efficiency decreased. Therefore, maximum removal efficiency can be obtained in condition of high hydraulic gradient.

1.5 Conclusions

- In the batch experiments, the contaminants removal efficiency from the soil depends upon the treating solution.Na_2EDTA solution was inefficient to remediate phenanthrene (no removal efficiency was shown), while SDS solution had (90%) phenanthrene removal efficiency.
- In the column experiments using SDS solution, the removal efficiencies of phenanthrene at 0.2% and 1.2% hydraulic gradients were 64% and 81% from phenanthrene contaminated soil, respectively. The removal of phenanthrene with surfactant (SDS) is dependent on the number of the formed micelles and its stability, which enhance phenanthrene solubilization through micelles formation that provided the hydrophobic sinks for phenanthrene.
- High hydraulic gradient increases the contaminants mobilization and removal, where low hydraulic gradient decreases the desorption/solubilization of contaminants. The time in low hydraulic gradient is greater compared with that for high hydraulic gradient due to hydraulic conductivity.
- The study revealed that the contaminants removal efficiency in soil flushing remediation technique governed by the selection of treating solution and its affinity toward the target contaminant.

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