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Remediation of crude oil polluted soil using washing process with surfactant in batch reactor

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ABSTRACT/RESUME

Abstract: *The objective of this work is to study the power of surfactant solutions on the remediation of soils contaminated by crude oil during a batch washing process. We used as surfactants Sodium dodecyl sulfate (SDS), Sodium dodecyl benzenesulfonate (SDBS). In this study, we examined the effect of various parameters: level of contamination, type of surfactant and contamination Age on the surfactant elimination of oil from soil.*
The results obtained in this study showed the potential of surfactants in the cleanup of soils contaminated by hydrocarbons, and the structure of surfactants has a crucial effect on the kinetic elimination. The calculated correlation coefficients (R2) suggest a good closeness-of-fit range for the first and second order kinetic model. It varies between 0.87 and 0.94 for first order kinetic model and between 0.75 and 0.89 for second order kinetic model.

I. Introduction

The immense use of crude oil in various fields of industry and domestic application, remain the first energy source considered hazardous organic matter for human health and the environment due to their genotoxic, mutagenic and carcinogenic potential. The high hydrophobicity of crude oil show a strong tendency to be sorbed with organic matter in the soil and in incorporation into soil micropores [1-3].
In general the contamination of soils by petroleum derivatives maybe is the result of accidents, spills during transportation, leakage from waste disposal or storage sites, or from industrial facilities, this contamination caused an important environmental problem and has become an issue of increasing concern, and presents a challenge for environmental scientists and engineers [4-7]. In the literature the environmental scientists explore different approach chemical, physical, biological and the combination of this processes for the remediation of contaminated soil [4, 8-10]. Their removal from contaminated soils is difficult because they have strong fat solubility, high interfacial tensions due to their hydrophobicity [1,11].
The increasing attentions have received for the problems associated of crude oil contaminated site in environmental media [3, 11-12]. Cleaning up is an innovative technology to resolve this problem of contamination using surfactant to increase the solubilization of oil. Solubilization of oil by the surfactants is a key factor in the remediation of soils contaminated by hydrocarbons [13-16] .
The term surfactant is used to characterize organic compounds soluble in water and having the particularity of aggregating at the interfaces between water and other substances that are poorly soluble in water. These compounds have two different parts: a hydrophilic part (generally ionic head) and another lipophilic (tail consisting of an apolar carbon chain). Depending on the load carried by the hydrophilic part, there are anionic surfactants (negatively charged), cationic surfactants (positively charged) and amphoteric (both positively and negatively charged). Regardless of their historical use as soaps or detergents, the many properties of surfactants have a great practical importance in the industry area. For example, surfactants are used in the production and processing of foods, agrochemicals, pharmaceuticals, personal care and laundry products, petroleum, mineral ores, inks, fuel additives and lubricants, paints, coatings and adhesives, and in photographic films. Surfactants are also used in a wide range of biological systems and medical

applications, soil remediation techniques, and other environmental, health and safety applications [14-18].
The objective of the present work is to study the effects of anionic surfactant solutions and even the structure of surfactants and the nature of sand on the kinetics desorption of crude oil contaminated soils during a batch washing process.

II. Materials and methods

II.1. Materials

We used in our study an Algerian crude oil come from collect center located in Haoudh Elhamra (HassiMessaoud, South of Algeria). Anionic surfactants were obtained either directly from the manufacturer or through a distributor and were used without further purification (table.1).

Table 1. *Characteristics of the selected surfactants*

Surfactant	Molecular formula	MW	CMC(mM) [17]
SDS	C12H25SO4Na	288.38	8.3
SDBS	C12H25C6H4SO3Na	348.5	3-2.8

In this study we used two kind of sand comes from two large oil operating area in lgeria(table.2):

- Sand from Adrar town is about 1500 km south of Algiers.
- Sand from Operating station hydrocarbons Rhourde-nouss, located in Ouargla 820 km south of Algiers.

Table 2. *Characteristics of the selected sand*

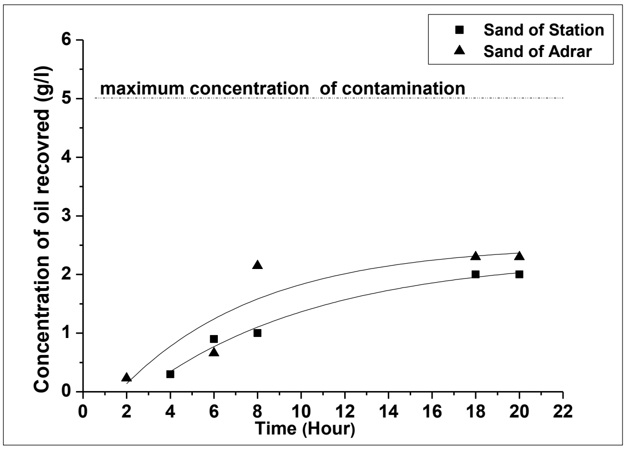
Sand	pH	Humidity	Density	dp(mm)
Station	7.13	0.109	2.667	0.333
Adrar	7.12	0.280	2.64	0.231

II.2. Methods

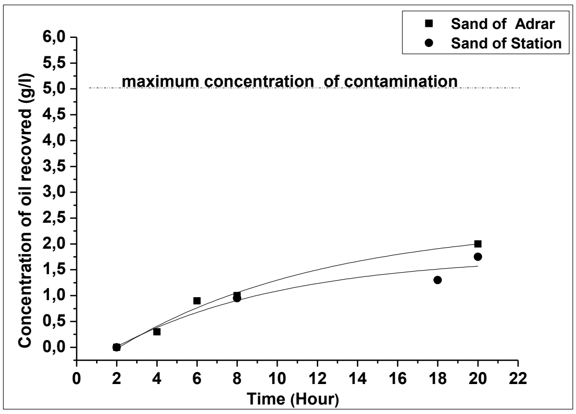
For all experiment we chose 25g and 50g of oil contaminated in a 1kg sand for Periods of one month and ten (10) months, has late to see the effect of age contamination on the washing process by surfactants solutions. For washing, we tend to take samples as a function of time. We put into an individual 250 ml glass vial sample consisted of 100 ml surfactant solution containing 10 gr of contaminated sand. The sample vials were sealed with a screw cap to prevent any loss from the solution. These samples were then shaken at 200 rpm for a period of 2, 4, 6, 8, 18 20 hours using a magnetic stirrer at room temperature to ensure maximum solubility, After stirring, the mixture is filtered using filter paper and diluted by (1/50)for the COD analyses.
The concentration of solubilized oil was determined by COD method. The surfactant concentration was kept constant in both the reference and measurement cells to eliminate the effect of surfactant. The COD value was determined by standard methode and the concentration of solubilized oil was deduced from the standard curve of crude oil established in water solution.

III. Results and discussion

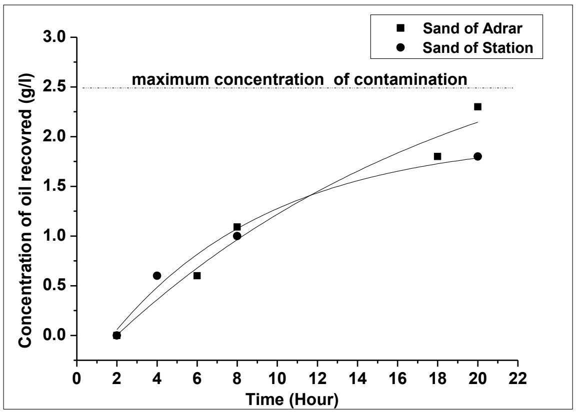
Figures 1, 2 and 3 show the profiles of crude oil desorption versus time in aqueous solutions containing anionic surfactants in the washing processes carried out with two kind of sand and surfactants. We observe for three figures 1-3 an increase in the recovered oil content followed by stabilization. We note that for the two grains sand the curves are similar. The concentration of oil in the liquid phase increases during washing until reaches a maximum.
The results indicate that for same concentrations of the highest concentration of surfactants in the oil solution were found with the surfactant SDBS. However, the lowest was achieved with SDS, for different oil content and for the two grains sand.



Figures 1. *Oil desorption Evolution in the presence of SDBS for 10 months ofcontamination (50g/1Kg)*



Figures 2. *Oil desorption Evolution in the presence of SDS for 10 months of contamination (50g/1Kg)*



Figures 3. *Oil desorption Evolution in the presence of SDS for 1 months of contamination (25g/1Kg)*

Figures 1-3 shows that the structure and the CMC of the surfactants (Table 1) at a remarkable effect on the decontamination process. The results obtained show the concentration of oil recovered by the surfactants clearly show the effectiveness of the anionic surfactant in decontamination processes, according to Pennell et al. (1993) anionic surfactants are still qualified by their solubilizing power, which allows even at low concentrations of moderately solubilize apolar substances.

The figures 1-3 indicate that the nature of sand and surfactant has a very significant effect on the evolution of the concentration of oil in the liquid phase. Moreover, we find that the maximum of concentration is reached after 20 hours of washing. According to the figures 2-3 the age of of contamination has a remarkable effect in the desorption process.
In the order to study the kinetics desorption of crude oil from contaminated soil, two kenitics models are proposed, it is a first order kinetic model and the second model kinetics that describes the crude oil concentration in the liquid phase for all surfactants, expressed by the following equations:

- First order kinetic model:

$$\frac{dS_C}{dt} = k\left(S_C^{\ *} - S_C\right) \qquad (1)$$

Where SC* represent the concentration of oil saturation (g/l), SC is the concentration of oil in the aqueous phase at time t (g/l) and k is the mass transfer coefficient (Hour-1).
By integrating (Eq.1), we obtain the following equation:

$$S_C = S_C^{\ *}\left(1 - e^{-kt}\right) \qquad (2)$$

The parameter k for each surfactant was obtained by fitting Eq. (2) to the experimental data. The evolution of the crude oil desorption in the function of time represented on figure 1, 2 and 3 show that the desorption kinetics follow a first-order kinetic model (Eq.1). The fitting results are given in Table 3, where a perfect fit to a first-order kinetic model was obtained for the two surfactants and a kind of sand. Comparing the models with the experimental data of each surfactant, the calculated correlation coefficients (R2) suggest a good closeness-of-fit range. It varies between 0.87 and 0.945.

- Second model kinetics:

$$\frac{dS_c}{dt} = k(S_c^* - S_c)^2 \qquad (3)$$

Where SC* represent the contration of oil saturation (g/l), SC is the concentration of oil in the aqueous phase at time t (g/l) and k is the mass transfer coefficient (L2 g-1Hour-1).

By integrating (Eq.3), we obtain the following equation:

$$\frac{1}{S_c} = \frac{1}{S_c^*} - \frac{1}{kS_c^{*2}}\frac{1}{t} \qquad (4)$$

The parameter k of each surfactant was obtained by plotting 1 / Sc as a function of 1 / t, are in the following results:

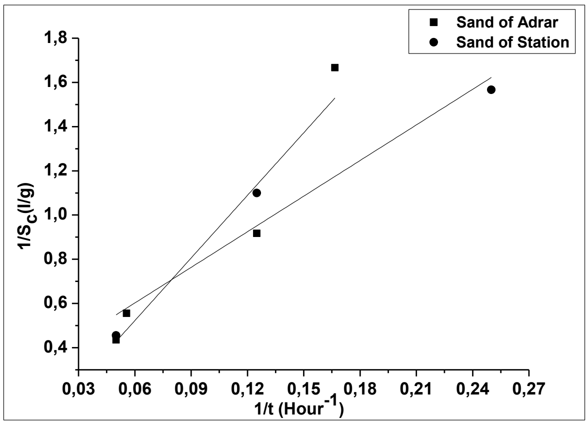


Figure 4. *Evolution of the second order kinetics for a month of contamination 25g / 1kg in the presence of SDS*

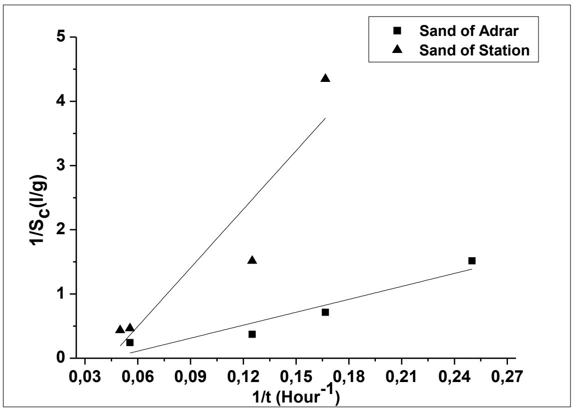


Figure 5. *evolution of the second order kinetics for 10 month of contamination 50 g / 1kg in the presence of SDBS*

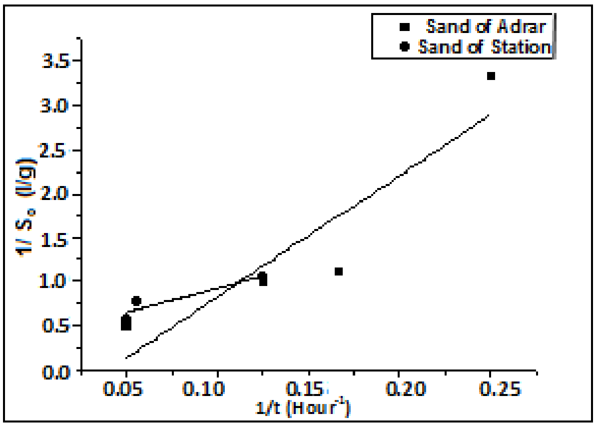


Figure 6. *Evolution of the second order kinetics for 10 month of contamination 50 g / 1kg in the presence of SDS*

From the previous curve, it is clear that the experimental data meet with theoretical data. The correlation factor (R2) is varied between 0.75 and 0.89.

In examining the reliability of the proposed models, we calculated the factors correlation of the two equations and the kinetic constants of each model. These are added together in the following table:

Table 1. *Mass transfer coefficients, correlationCoefficients of crude oil*

First model kinetics	**10 Months of contamination 50g/1Kg**				**1 Months of contamination 25g/1kg**	
Sand	SDBS		SDS		SDS	
	R^2	K (h^{-1})	R^2	k(h^{-1})	R^2	k (h^{-1})
Station	0.87	0.0003	0.88	0.038	0.926	0.048
Adrar	0.88	0.018	0.92	0.0247	0.945	0.002
Second model kinetics	**10 Months of contamination 50g/1Kg**				**1 Months of contamination 25g/1kg**	
Sand	SDBS		SDS		SDS	
	R^2	K ($L^2/g^{-1}h^{-1}$)	R^2	K ($L^2/g^{-1}h^{-1}$)	R^2	K ($L^2/g^{-1}h^{-1}$)
Station	0.800	0.585	0.758	0.266	0.891	0.152
Adrar	0.867	0.147	0.761	0.230	0.882	0.002

In comparison of first model kinetics with the second model kinetics,The correlation factor (R2) for the first model kineticsis varied between 0.87 and 0.94 and for Second model kineticsis varied between 0.75 and 0.89, we conclude that oil desorption kinetics is much closer to the first order model as the second order. Indeed, these results indicate that the kinetic constant values depend on the nature of surfactants and sand. Hence, the kinetic of the crude oil desorption appears to be influenced by the structure of surfactants [14,16].

IV. Conclusion

The objective of this work was to study the effectiveness of the washing process by anionic surfactant solutions in the remediation of soil contaminated with hydrocarbons using batch reactor. The results obtained in this study, show that the anionic surfactants are very effective in cleaning soil contaminated by hydrocarbons. Indeed, the effectiveness of these surfaces agents in a batch washing process is always meaningful. The results obtained in this study show that SDBS present the best results compared to SDS in terms of performance, and the kinetics desorption depends on the nature of surfactants and sand.

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