

Soil remediation: Use of a sprinkling system to wash diesel-polluted soils with microemulsion precursors

Tereza N. de C. Dantas^{}, Afonso A. Dantas Neto, Ricardo H. de Lima Leite, Cátia G. F. T. Rossi, José Fabrício C. de Melo*

Federal University of Rio Grande do Norte, Natal-RN/Brazil

Federal University of Semi-Arido, Mossoró-RN/Brazil

Abstract

Pollution of soils by petroleum derivatives constitutes a serious environmental issue that has direct implications on public health. Diesel fuel is a complex combination of hydrocarbons obtained as middle distillate of crude oil and represent important hazardous components. Since diesel-polluted soils require an efficient remediation process to restore their harmless qualities, several technologies have been recommended for this purpose. Microemulsions may be used to accelerate the removal of aromatics compounds from diesel-polluted soils by increasing the solubility of apolar molecules in aqueous medium. The aim of this work is to demonstrate the feasibility of the diesel-polluted soil treatment and to investigate the effect of some operating conditions on aromatics removal. Aqueous solutions of saponified coconut oil (surfactant) and 1-butanol (co-surfactant) were used to form an in situ microemulsion with the diesel in the soil and promote the removal of the latter one. A sandy soil was contaminated with diesel (30 g/kg of soil) and used in the experiments. The effects of surfactant concentration on aromatics removal, volume of liquid washing, and two spatial coordinates were investigated using a 2⁴ full factorial experimental design. At better operating conditions more than 99.9% aromatics removal from soil was reached. The experimental results of aromatics removal

from diesel-polluted soil was adequately described as a function of the independent variables by a cubic mathematical model. On the experimental domain investigated, surfactants concentration was found to be the pivotal factor affecting aromatics removal from soil, which was less influenced by the volume of washing liquid applied.

INTRODUCTION

Combating pollution of soils is a challenge that has involved researchers from different areas in the search for technologies that allow the recovery of degraded soils. Petroleum hydrocarbons are one of the most employed energy sources in the world. The oil is also used in the production of other products and by-products, such as plastic, synthetic rubber, and fertilizers used in agriculture (Araújo Júnior, 2010). The petroleum and its derivatives, especially aromatic hydrocarbons, are among the soil pollutants that demand a special attention, due to its harmful effects to health and the high incidence of Fuel dealers such as gas stations are potential sources of contamination of soils, due to the appearance of cracks and corrosion in storage tanks is something that can happen and cause accidental spills. Numerous remediation processes for soils contaminated by oils and other products of the oil industry, have been proposed in the literature. Remediation processes include bioremediation, photo-Fenton, steam injection, and incineration in situ. However, these processes generally have high operational costs (Furtado, 2005).

The use of surfactants in the process of remediation of soils contaminated by petroleum and its derivatives has been studied by several researchers (Dwarakanath et al., 1998; Urum et al., 2005; Owsianiak et al., 2008). These studies demonstrate its potential application in the process of remediation of soils. Considering the importance of surfactants in the process of

decontamination of soils, the need for researching new technologies that use surfactants more efficiently and effectively is crucial.

This paper aims to propose an effective methodology for the treatment of soils contaminated by diesel oil washing the soil with microemulsion precursors of low cost.

METHODS

Characterization and preparation of the soil

The soil used in this study was obtained in the city of Natal-RN Brazil in an area free of contamination. Before each experiment, the soil was dried in an oven at 100°C for 12h. A granulometric study on soil using mesh sieves 12 to 65mm and, later, sieves with 100 to 400mm obtained the soil particle size distribution.

The moisture content of the soil was determined in its natural state and after kiln drying. The samples were analyzed in a thermostatic scale (Ohaus, model MB200) for 60 minutes, at the following temperatures 115°C; 130°C and 150°C.

Analyses were performed to determine the chemical composition of the soil. The analysis measured the content of elements Na, K, N, Ca⁺², Mg⁺² and Al⁺³. It was also measured the content of organic matter and pH.

For the determination of pH, soil: water ratio was 1: 2.5. The elements P, Na⁺, and K⁺ were extracted from the soil with the Mehlich-1 extractor in soil: extractor relationship of 1:10. Ca⁺², Mg⁺², and Al⁺³ elements were extracted with 1mol.L⁻¹ in a soil: extractor relationship of 1:10.

Also, analyzes of the physical composition of the soil through the determination of the granulometric particle size fractions, density, bulk density, real density, and porosity.

Surfactant preparation

The chemicals used in the experimental procedure were analytical grade except the surfactant (derived from a coconut oil of regional production saponified using NaOH in a stoichiometric reaction (1:1 ratio). The surfactant was obtained with yield of $\approx 90\%$ and was used without further purification. (Dantas et al, 2007)

Determination of the content of diesel oil in contaminated soil

For the determination of the percentile of diesel removed from soil, the experiment used a UV visible spectrophotometer. The aromatic content in the soil was estimated by extraction with hexane, followed by absorbance measurements at 256nm (aromatic B-band) of the extracts and obtained an analytical curve for standard diesel.

Study of removal of diesel

The experiment observed desorption time using different diesel wash solutions as described below.

Two solutions of different concentrations were used: 10 and 20% active matter 20% (AM) as precursors of microemulsion for removal of diesel-contaminated soil. The precursor solution was composed of water, surfactant (OCS) and cosurfactant (1-butanol), the C/S ratio was 4. Experiments were conducted in temperatures of 28°C and 50°C. This study used the same methodology described above and used the following times: 1; 30; 60; and 120 min.

Planned study of the influence of the concentration of active matter and temperature

At this study aimed to get the optimization of the experiments through statistical treatment. For this, the experiment used the strategy of central plan study using two factors: X_1 - active matter concentration, C_{AM} (%), and X_2 - temperature T ($^{\circ}C$), keeping the extraction time in 60 minutes. The variable response that will be found is the percentage of extraction.

RESULTS AND DISCUSSION

Soil characterization

The results of the sieve study show that the soil used in this study has 82.3% of its particles with meshes between 35 and 65, in that, 34.5% of the soil has a mash that is equal to 35 (this corresponds to 0.5 mm).

Through the physical analysis it was found that the studied soil can be classified as sandy, having no silt or clay its composition. The humidity content was determined gravimetrically. This parameter can be useful to understand the behavior of soil on the adsorption of contaminants. The average of humidity content was 0.2% for the dry soil and 2.2% for the damp soil.

The soil used has the chemical composition presented in table 1

Table 1- Results of the chemical analysis of the soil

Chemical element	Concentration
N (g/kg)	0.21
P (mg/dm ³)	1.2
K ⁺ (mg/dm ³)	3.8
Na ⁺ (mg/dm ³)	10.5

Ca ²⁺ (cmol/dm ³)	1.7
Mg ²⁺ (cmol/dm ³)	0.1
Al ³⁺ (cmol/dm ³)	0.0

Physical analysis of the soil

The values of real density and apparent density were, respectively, 2.56 kg/dm³ and 1.44kg/dm³. The porosity value found was equal to 43.89%. This value was important to determine the ratio solution/pore volume.

Study of the extraction time

Extraction time is a critical factor in optimizing decontamination processes. The removal of surfactant solution was studied in different concentrations and temperatures. Figure 1 shows the results of the present study.

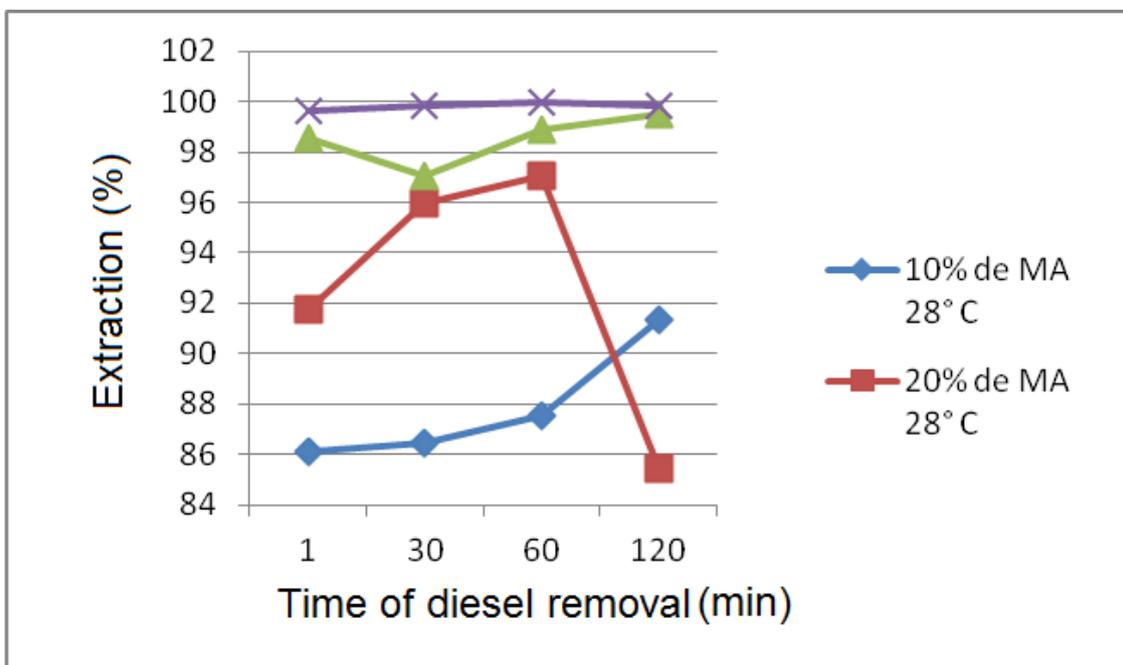


Figure 1 -Time of diesel removal with 10% and 20% of AM, at 28^oC and 50^oC

The chart in Figure 1 clearly expresses that with increasing temperature the extraction rate also increases, this is evidenced at 1min time where 10 AM removed 98.56% of contaminant, rate that is higher than the best percentage found at 28°C. At 30min, there was a decrease in the percentage of desorption to 97.08%, and followed by its optimal values, which occurred at 120min blank where 99.52% of the diesel was extracted. Similar behavior was found by Zhang, Lo and Asce (2007), who found the time of 2h as the best contact time between washing solution with surfactant SDS and the soil contaminated with diesel fuel.

Analyzing the results of a 20% extraction of AM and 50° C, there is a behavior similar to that found at 28° C and 20% AM, when the extraction reaches a peak and, then, reduces slightly. The smallest value of extraction was found at 1min, which was 99.64%, however this value was higher than that found with 10% of AM, demonstrating that the increase in active substance speeds up the extraction process. The maximum value was found at 60min; 99.94%. The difference between the times of 1min and 60min was 0.30%, being considered insignificant. Note that all values of desorption at 20 to 50°C AM extracted more than 99% of the contaminant, thus, this combined operating parameter offers good results for the extraction of diesel in soil.

In light of the results presented, comparing the concentration of 20% of AM in the two different temperatures, the fastest time removal time was 60min. Nevertheless, with 10% of AM it does not show its best time; the optimal time for this is desorption is 120min. However, at 50°C the difference in extraction percentage between 60 and 120 minutes times is 0.63%, which is less than 1%, while at a temperature of 28°C the difference is somewhat higher, 3.83%. The

differences in extraction are reported within the error margin of the experiments. This way, the time of 60min was chosen as the best extraction time for conducting the experiments, with 10% or 20% active matter (AM).

Study of removal of Diesel form contaminated soil in Agitated Bath

The study of the removal of diesel from contaminated soils using an agitated bath process was accomplished through a central composite design with two factors and a variable response. The studied variables and their values, and the results obtained are listed in table 2.

Table 2 - List of experiments and results obtained for the removal rate of diesel contaminated soil in agitated bath.

Test n°	Factors (coded values)		Variables		y (%)
	X ₁ (%MA)	X ₂ (T °C)	MA (%)	T (°C)	
1	-1	-1	0	28	85.38
2	1	-1	20	28	90.05
3	-1	1	0	50	97.38
4	1	1	20	50	99.92
5	0	0	10	39	98.66
6	0	0	10	39	98.16
7	0	0	10	39	97.60
8	-1	0	0	39	94.21
9	0	-1	10	28	86.48
10	1	0	20	39	99.72
11	0	1	10	50	99.70

The tests 1 to 4 are part of the factorial part 2², tests 5 to 7 are carried out in triplicate at the central point to the determination of experimental error, and tests 8 to 11 correspond to the axial part of the central planning. The homoscedasticity was considered for the experiment studied. The contact of the washing solutions and the soil occurred during 60 minutes, stirring until the equilibrium was reached, according to preliminary tests.

The results show that the distilled water, without addition of active matters, at room temperature (28° C), is able to remove 85.38% of diesel contamination on soil (test 1). The increase in temperature and the concentration of the active substance (OCS + butanol, C/S 4) causes, in all samples, an increase in the percentage of diesel removal. The maximum percentage of removal achieved in the samples was 99.92%, when the concentration of active matter was of 20% and under a temperature of 50°C (test 4).

Statistical analysis of individual effects for the experimental factors and their interactions on the percentage of soil diesel removal was carried out by Program Statistica 7.0. Table 3 shows the analysis of the effects, the estimation of standard errors, Student's t test for removal of diesel and the p-value for the effects. Figure 2 shows a Pareto chart of standard effects and allows for a better comparison of the significance of factors and their interactions on the variation of the response.

Table 3- Estimation of effects, standard error, Student's t test, p- value and the removal of soil contaminated by diesel as the experimental planning.

Factor	Effect	Standard Error	t value	p
Average	97.87	±0.489		
% Active matter (x_1)	4.24	±0.777	5.457	0.002809
Temperature (x_2)	11.70	±0.777	17.06	0.000023
X_1^2	-1.02	±1.196	-0.8496	0.434353 ^a
X_2^2	-8.77	±1.196	-7.331	0.000740
$X_1 \cdot X_2$	-1.065	±0.952	-1.119	0.313905 ^a

^a ($p > 0,05$)– effects considered statistically insignificant to a confidence level of 95%.

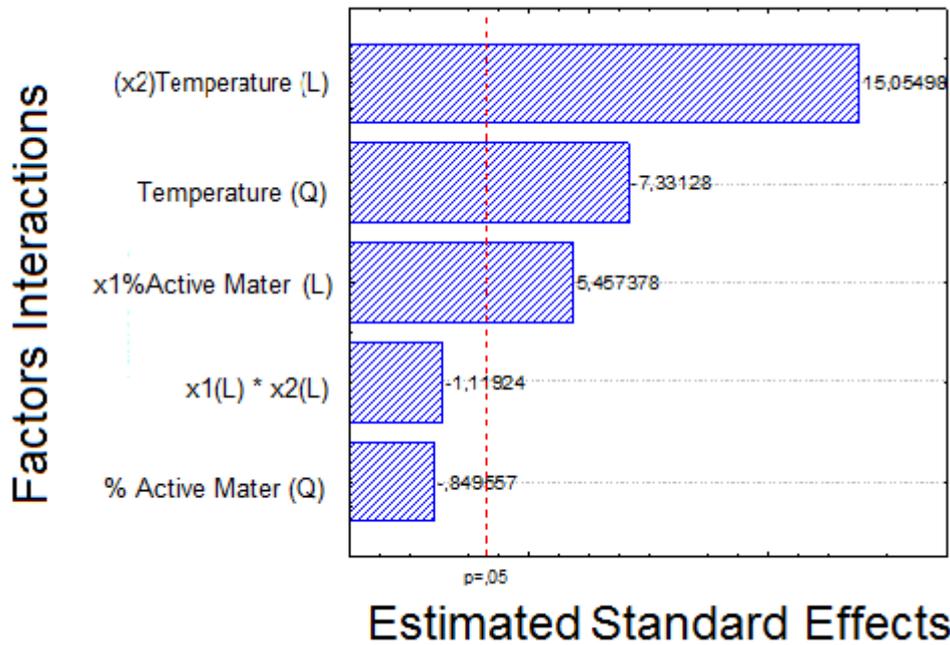


Figure 2 Pareto chart of standard effects to the factors and their interactions (L-linear; Q-squared).

Based on the data presented in table 3 and Figure 2 one can infer that the quadratic term for the variable active matter and interaction between the active substance and the temperature are not statistically significant. The term linear contribution degree was the factor that had the greatest significance on the value of the response variable. The mathematical model representative of the response variable ($y = \text{diesel removal rate}$) based on the factors, considering only the terms that significantly influence, is expressed by the equation 1.

$$y = 18,018 + 0,212 \cdot x_1 + 3,444 \cdot x_2 - 0,0373 \cdot x_2^2 \quad (1)$$

The validity of the model was established by means of the analysis of variance (Table 4), the coefficient of determination (R^2), and the comparison of the values predicted by the model and the experimentally observed (Figure 3).

Table 4- Analysis of variance for the adjustment of the model

Source of variation	Soma cuadrática	Number of degrees of freedom	Quadratic mean	F_{list} ($\alpha = 5\%$)	$F_{calculated}/$	F_{listed}
Regression	287.85	3	95.95			
Residues	6.31	7	0.90	4.35	106.6	24.5
Lack of adjustment	5.75	5	1.15			
Pure error	0.56	2	0.28			
Total	294.18	10				
$R^2 = 0.978$		% explained variation = 97.84 %				
		% maximum explainable variance = 99.80 %				

The analysis of variance shows that the proposed model in Equation 2 is of high significance, explaining about 97.84% of the variation of the removal of diesel from contaminated soils in terms of percentage of active matter and temperature within the range of variation considered. The high value for the model $F_{calculated}$, 24.5 times greater than the F_{listed} , indicates a useful regression for predictive purposes (Barros Neto, Scarminio, & Bruns, 2002). The correlation between the values predicted by the model and the experimentally observed values can be seen in Figure 3.

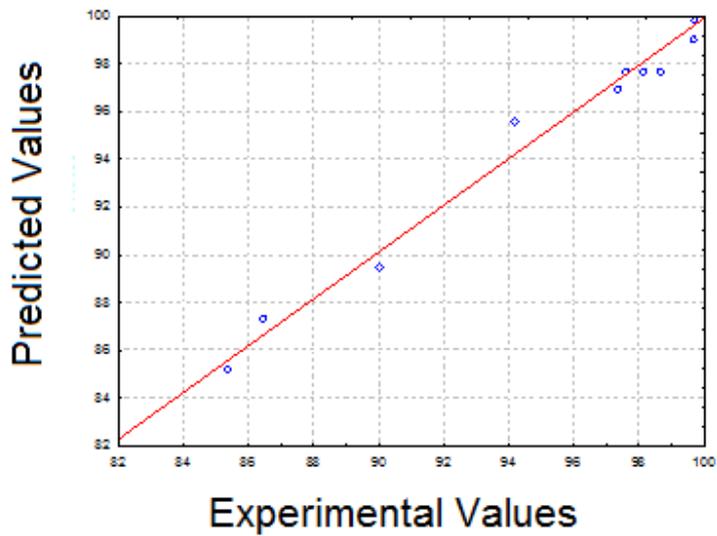


Figure 3- Comparison between observed values versus values predicted

Figure 4 shows the response surface to the removal rate of soils contaminated by diesel representing the model proposed in equation (1), obtained from experimental planning.

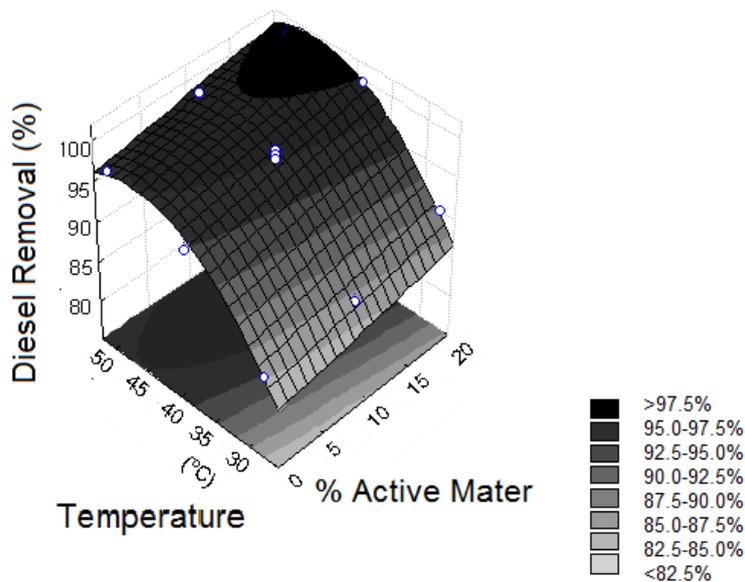


Figure 4- Surface response for the removal rate of soils contaminated by diesel described by equation 1.

The values predicted by the empirical model show that for a fixed temperature the diesel removal rate increases linearly with increasing concentration of active matter in the washing solution, as can be seen in Figure 5.

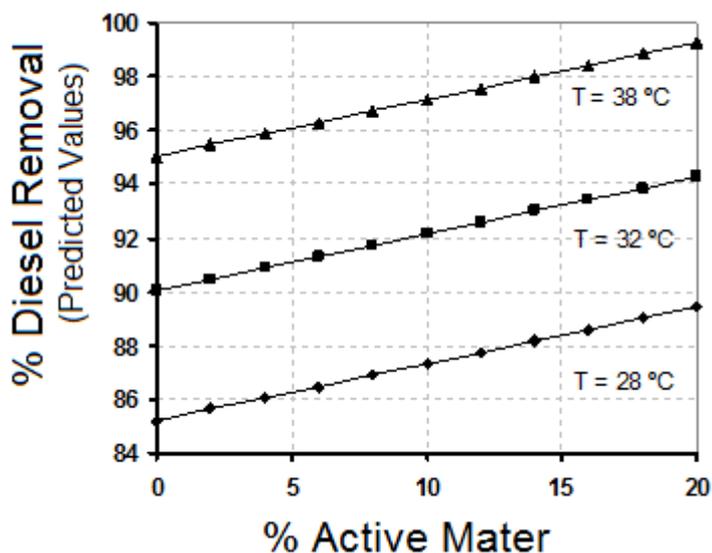


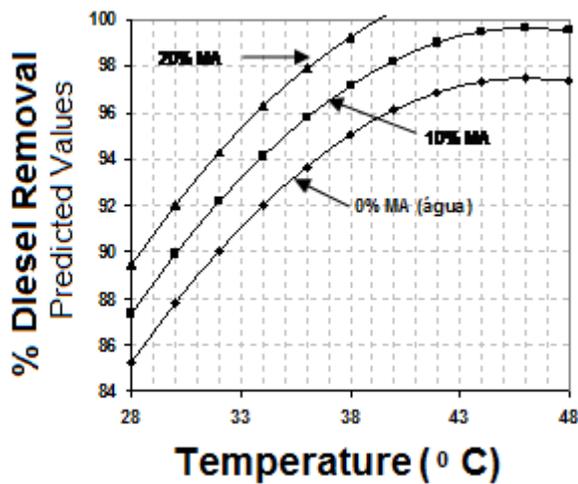
Figure 5- Variation in the percentage removal of diesel contaminated soil according to the percentage of the active matter for different temperatures.

The removal of diesel from contaminated soils in a stirred bath is directly related to the ability of solubilization of the diesel by the washing agent. This is because the increase in the concentration of surfactants (OCS + butanol) allows the formation of a greater number of micelles, enabling greater solubilization of constituents of hydrophobic diesel. A linear increase of hydrophobic contaminants removal of soil by increasing the concentration of surfactants has also been observed by Zhang and Zhu (2010) when solubilization of pyrene and phenanthrene by solutions containing mixtures of sodium dodecylbenzene

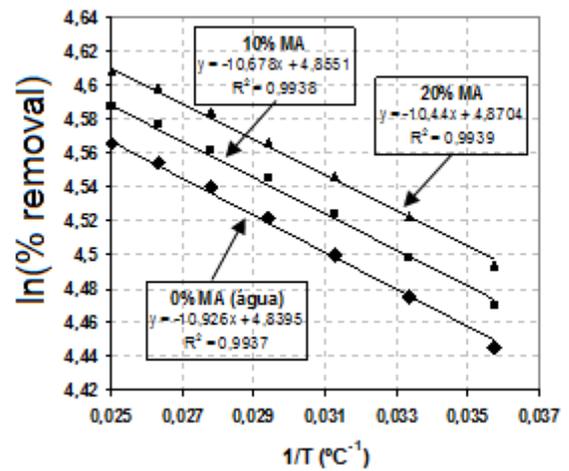
sulphonate and Tween 80. Zhang and Lo (2007) showed that the removal of marine diesel oil soil increases linearly with increasing concentration of sodium dodecyl sulfate (SDS) in the washing solution. The increase in the concentration of surfactants Triton SP-175 and Triton SP-190 caused a linear growth of apparent solubility of n-pentadecane washing solutions employed by Huang and Chang (2000).

The increased removal diesel from contaminated soil due to increase in temperature can be explained by the increased solubility of water in diesel or by the increased size of the micelles that were formed (Florence & Attwood, 2003). However, the lack of interaction between active matter concentration and temperature observed in the empirical model is an indication that the increased diesel removal caused by temperature increase is due primarily to the first mechanism.

Figure 6a shows the behavior of the removal of the diesel present in the contaminated soil as a function of temperature, pure water and various concentrations of the active matter. Considering the removal rate as being proportional to the solubility of its components in the washing solution, the values predicted by the mathematical model were adjusted to the optimal solubility equation (Equation 2). Figure 6b shows the variation of the natural logarithm of diesel removal rate in relation to the reciprocal of the temperature.



(a)



(b)

Figure 6- (a) Variation of diesel removal rate from soil as a function of temperature by washing with water and surfactant solutions of different concentrations. (b) Adjustment of the rate of diesel removal to the law of optimal solubility.

Notes on Figure 6.b show that the solubilization of diesel hydrophobic compounds by water and surfactant solutions may be represented by the law of optimal solubility (Equation 2).

$$\ln y^* = -\frac{\Delta H_{fus}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \dots \dots \dots (2)$$

Where y^* is the mole fraction of solute in saturated solution, ΔH_{fus} is the heat of fusion of pure solutes, T_0 is the melting temperature of pure solutes, R is the ideal gas constant and T the temperature in °C.

The ideal solution model describes the behavior of removing the diesel of contaminated soil as a function of temperature in the range of between 28° C and 42° C, above these values there is a deviation from ideal conditions.

The ideal behavior of washing solutions as a function of temperature corroborates with the hypothesis of the augment of diesel removal at high temperatures resulting from the increase in solubility of diesel components in the water and not the micelle growth due to the temperature variation.

CONCLUSION

In light of the results presented, the study supports the following conclusions:

The study of optimal extraction time revealed that there are differences in extraction time depending on the concentration of AM in the washing solutions. The 10% AM solution presented at the two studied temperatures the best removal result at 120min, while the solution with 20% AM had its best extraction result at 60min.

The proposed study was conducted in an agitated bath showing that temperature and amount of active matter are factors that have importance in removing the oil contaminant. The optimal removal value was of 99.2%. This maximized value was attained when the temperature was raised to 50°C and 20% active matter. The model obtained through experimental planning had a good fit with experimental data and can be applied to predict the behavior of variables and optimize the process of removal.

References

ARAÚJO JÚNIOR, A.M.. **Fontes de Energia e Sua Produção Mundial:** In: <http://www.juliobattisti.com.br/tutoriais/arlindojunior/geografia024.asp> Access

in: sept. 24th 2010.

BARROS NETO, B.; SCARMINIO, I.S.; BRUNS, R.E. **Como fazer experimentos: pesquisa e desenvolvimento na ciência e na indústria.**

Edited by UNICAMP- SP, 2002. 401p.

DANTAS, T. N. C.; MOURA, M. C. P. A.; DANTAS NETO, A. A.; PINHEIRO, F.

S. H. T.; BARROS NETO, E. L. "THE USE OF MICROEMULSION AND FLUSHING SOLUTIONS TO REMEDIATE DIESEL-POLLUTED SOIL".

Brazilian Journal of Petroleum and Gas. v. 1, n. 1, p. 26-33, 2007.

DWARAKANATH, V. KOSTARELOS, K.; POPE, G. A. Anionic surfactant remediation of soil columns contaminated by nonaqueous phase liquids.

Contaminant Hydrology, v. 38, n. 1, p. 465-488, 1998.

FLORENCE, A.T.; ATTWOOD, D. **Princípios físico-químicos em farmácia.**

São Paulo-SP: Edited by USP, 2003. 732 p.

FURTADO, M.. Remediação de Solos: Para Afastar o Perigo que se Esconde nos Subterrâneos das Grandes Cidades, Meios Legais e Econômicos Devem Fomentar Obras de Descontaminação. **Química e Derivados**, p.26-43, 2005.

HUANG, C.-W.; CHANG, C.-H. A laboratory study on foam-enhanced surfactant solution flooding in removing n-pentadecane from contaminated columns.

Colloids and Surfaces A: Physicochemical and Engineering Aspects, v. 173 n. 1, p. 171-179, 2000.

OWSIANIAK, M.; CHRZANOWSKI, Ł.; SZULC, A.; STANIEWSKI. J.;

OLSZANOWSKI, A.; OLEJNIK-SCHMIDT, A.K.; HEIPIEPER, H.J.

Biodegradation of diesel/biodiesel blends by a consortium of hydrocarbon degraders: Effect of the type of blend and the addition of biosurfactants.

Bioresource Technology, v. 100, n. 1, p. 1497-1500, 2008.

URUM, K.G.S.; PEKDEMIR, T.; MCMENAMY, S. A comparison of the efficiency of different surfactants for removal of crude oil from contaminated soils.

Chemosphere, v. 62, n. 1, p.1403-1410, 2005.

ZHANG, M.; ZHU, L. Effect of SDBS-Tween 80 mixed surfactants on the distribution of polycyclic aromatic hydrocarbons in soil-water system. **Journal of**

Soils and Sediments, v. 10, n. 1, p. 1123-1130, 2010.

ZHANG, W.; LO, I.M.C.; ASCE, M. Chemical-Enhanced Washing for Remediation of Soils Contaminated with Marine Diesel Fuel in the Presence/Absence of Pb. **Journal Of Environmental Engineering**, v. 133, n. 5, p. 548-555, 2007.