

HYDROCARBON SOIL TREATMENT TEST WITH SODIUM DODECYL SULFATE (SDS)

Allaramadji Ngarmadji Constant^{1*}, Madjitouloum Betoloum Salomon^{2*}, Ngaram Nambatingar¹ and Mahmout Yaya³.

¹Department of Chemistry, Faculty of Exact and Applied Sciences, University of N'Djamena (UNDJ), Chad.

²Department of Chemistry, Faculty of Sciences and Techniques, University Adam Barka of Abeche (UNABA), Chad.

³Laboratory of Research on the Natural Substances, University of N'Djamena (UNDJ), Chad.

ABSTRACT: *The depollution test was carried out through the surfactant washing process. The effects of variation in SDS concentration (0.5-1 g/L), contact time (10-60 min) and soil particle size (<50 µm - <250 µm) were studied on the efficiency of depollution through a complete factorial plan. Quantitative analyzes performed on the different fractions of a soil sample showed that the fine fraction (<50µm) is the most polluted. In fact, the contents of n-alkanes in soil particles of sizes <50 µm range from 4.79 to 65.90 µg/g of sample MS and in sizes of <250 µm, from 0.91 to 30 µm, 70 µg/g of MS. PAH contents in fractions <50µm range from 3.46 to 103.5 µg/g of sample MS and in fractions <250 µm, from 2.90 µg/g to 21.85 µg/g of MS. These hydrocarbon levels obtained are much higher than the guide values defined by the French Environment and Energy Management Agency. The application of this washing process has made it possible to achieve overall hydrocarbon abatement rates of up to 97.3%. As a result, the optimum for the minimum content of residual hydrocarbons (≈10 µg/g DM) is obtained at a concentration of 0.75 g/L, a contact time of 60 min and a particle size of soil < 50 µm. This process, which makes it possible to obtain an interesting yield of extraction of pollutants, could thus be used for the remediation of soils and sediments polluted by hydrocarbons in general and PAHs in particular.*

KEYWORDS: Test, treatment, soil, hydrocarbons, SDS

INTRODUCTION

Pollutants from petroleum products include the hydrocarbons group, which is subdivided into three sub-categories: petroleum paraffins, monocyclic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs). Polycyclic aromatic hydrocarbons are compounds known to pollute the environment and are known by their carcinogenic and/or mutagenic characteristics (Mzoughi et al., 2002). As result, they occupy a special place within the environmental concern. This interest is also due to their persistence in the environment and their toxicity (Ouahiba et al., 2009).

In addition to their carcinogenic and/or mutagenic properties, polycyclic aromatic hydrocarbons (PAHs) have a very marked hydrophobic character (Viglianti, 2009) and are more easily adsorbed on particulate matter (Lan, 2009). The environmental impact of these persistent, hydrophobic molecules with toxic effects (mutagenic and carcinogenic) makes it necessary to characterize, determine the degree of pollution or decontaminate the sites concerned.

Washing extraction is a method of soil remediation that consists in extracting the pollutant (s) by dissolution using an appropriate reagent for the purpose of "washing" the soil by mobilizing the contaminant without destroying it or in certain case by transforming it by chemical reaction.

While a considerable body of literature exists on the use of surfactants for the treatment of groundwater, the effect of surfactants on the washing of contaminated ex-situ soils is a less rich theme (Abdul et al., 1990; Edwards et al., 1991).

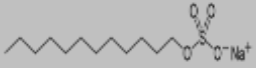
The key to effective soil washing is the arrangement and configuration of process units, and the characterization and understanding of pollutant-soil interactions (Mann, 1998).

MATERIAL AND METHODS

Surfactant used

The reference surfactant used is sodium dodecyl sulphate (in English, sodium dodecyl sulphate or SDS or / NaDS). It is a strong ionic surfactant, commonly used in biochemistry and molecular biology.

Table 1: Characteristics of the SDS

Sodium dodecyl sulphate (SDS) or sodium lauryl sulphate		
Molecular structure		
		
Brute formula		C ₁₂ H ₂₅ NaO ₄ S
Molecular weight	g/mol	288,38
Density	g/cm ³	1,01
Fusion point	°C	206
Solubility in water	g/l	100
Purity	(%)	98
CMC	mM	7-10
Biodegradation	(%)	> 99

Concentrations of n-alkanes and PAHs of the sample as a function of particle size

The concentrations of n-alkanes and PAHs were determined by chromatographic analysis (GC/FID) on soil particles of sizes <250 µm and <50 µm. The results from this analysis are reported in Tables 2 and 3 respectively for the n-alkane series and the polycyclic aromatic hydrocarbons (PAHs).

Table 2: Content of n-alkanes in fractions <50 µm and <250 µm (µg/g DM)

Names	Raw formulas of the compound	Fraction <50 µm	Fraction <250 µm
Decane (C10)	C ₁₀ H ₂₂	4,79±0,18	9,55±0,49
Undecane (C11)	C ₁₁ H ₂₄	28,70±0,99	30,70±0,57
Dodecane (C12)	C ₁₂ H ₂₆	16,55±0,92	14,10±0,57
Tridecane (C13)	C ₁₃ H ₂₈	16,00±0,28	6,63±0,28
Tetradecane (C14)	C ₁₄ H ₃₀	11,30±0,28	8,73±0,33
Pentadecane (C15)	C ₁₅ H ₃₂	12,85±0,21	9,90±0,01
Hexadecane (C16)	C ₁₆ H ₃₄	16,75±0,64	10,50±1,98
Heptadecane (C17)	C ₁₇ H ₃₆	16,30±0,28	9,55±0,49
Octadecane (C18)	C ₁₈ H ₃₈	11,65±0,35	3,57±0,04
Eicosane (C20)	C ₂₀ H ₄₂	34,00±0,26	14,35±1,06
Tetracosane (C24)	C ₂₄ H ₅₀	26,90±0,55	0,91±0,02
Heptacosane (C27)	C ₂₇ H ₅₆	23,00±0,28	18,25±0,49
Octocosane (C28)	C ₂₈ H ₅₈	65,90±0,85	18,55±1,34

Table 3: PAH concentration in fractions <50 μm and <250 μm ($\mu\text{g} / \text{g DM}$)

Names	Raw formulas	Fraction <50 μm	Fraction <250 μm
Naphthalene	C_{10}H_8	3,46 $\pm$ 0,03	3,65 $\pm$ 0,18
Acenaphthylene	C_{12}H_8	nd	nd
Acenaphthene	$\text{C}_{12}\text{H}_{10}$	8,74 $\pm$ 0,04	2,90 $\pm$ 0,11
Fluorene	$\text{C}_{13}\text{H}_{10}$	7,22 $\pm$ 0,14	5,41 $\pm$ 0,12
Phenanthrene	$\text{C}_{14}\text{H}_{10}$	13,00 $\pm$ 0,14	11,45 $\pm$ 0,07
Anthracene	$\text{C}_{14}\text{H}_{10}$	5,21 $\pm$ 0,35	nd
Fluoranthene	$\text{C}_{16}\text{H}_{10}$	39,75 $\pm$ 0,21	13,15 $\pm$ 0,49
Pyrene	$\text{C}_{16}\text{H}_{10}$	10,35 $\pm$ 0,21	21,85 $\pm$ 0,35
Benzo [a] Anthracene	$\text{C}_{18}\text{H}_{12}$	nd	nd
chrysene	$\text{C}_{18}\text{H}_{12}$	20,30 $\pm$ 0,14	9,90 $\pm$ 0,01
Benzo [b] fluoranthene	$\text{C}_{20}\text{H}_{12}$	48,10 $\pm$ 0,14	19,65 $\pm$ 0,07
Benzo [k] Fluoranthene	$\text{C}_{20}\text{H}_{12}$	43,55 $\pm$ 0,35	14,45 $\pm$ 0,49
Benzo [a] pyrene	$\text{C}_{20}\text{H}_{12}$	103,5 $\pm$ 2,12	nd
Indeno [1,2,3-c, d] pyrene	$\text{C}_{22}\text{H}_{12}$	7,40 $\pm$ 0,14	5,96 $\pm$ 0,26
Dibenzo [a, h] Anthracene	$\text{C}_{22}\text{H}_{14}$	41,35 $\pm$ 0,21	8,09 $\pm$ 0,26
Benzo [g, h, i] perylene	$\text{C}_{22}\text{H}_{12}$	19,90 $\pm$ 0,57	3,99 $\pm$ 0,08

nd: compounds not detected by the method

Experience plans used for the depollution test

In order to carry out the contaminated solid matrix depollution test as a function of the concentration of the SDS solution, the contact time and the particle size in the experimental domain, presented in Table 4, a complete factorial plan to two levels and three factors was used. The two-level factorial plan seems sufficiently adapted to the resolution of this type of problem and it has the advantage of appealing only to very basic mathematical knowledge (Ortigosa, 1993).

The experimental domain of the concentration of the SDS solution (X_1) was defined from the critical micelle concentration (Yeom et al., 1995) whereas the one of the contact time (X_2) was defined from the work of Nouhan (2005). Finally, the experimental domain of soil particle size (X_3) was defined based on preliminary tests. These 3 factors have the advantage of being easily controllable.

The residual hydrocarbon content Y (response) depends on the factors presented above; which is mathematically translated by the relation: $Y = f(X_1, X_2, X_3)$. The experiment will also consist in highlighting the effects of certain factors on the response.

The formula of the number (N) of experiments for a complete factorial plane is $N = 2^k + n_0$, with k , the number of variables of the factorial plane, n_0 the number of experiments at the center $n_0 = 1$. For $k = 3$, $N = 2^3 + 1 = 9$ experiments.

So that the influence of the variable does not depend on the unit used, the real variables have been transformed into reduced variables. We then define the levels of variables: the high level (+1), the low level (-1) and the center (0). Table 4 presents the factors and levels of variation used.

Table 4: Factors and Levels of Variation of the Full Factorial Design

Factors (unit)	coded variable	Low level (-1)	Center (0)	High level (1)
Concentration of the surfactant solution (g / L)	X_1	0,5	0,75	1
Contact time (min)	X_2	10	35	60
Fraction of the solid matrix (μm)	X_3	50	150	250

For a first-degree model with interaction, the representative points of a three-variable experiment plane are located in a 3-dimensional space. The answer is a polynomial function of the first degree with respect to each of the factors taken independently. It is noted:

$$Y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_{1,2}X_1X_2 + a_{1,3}X_1X_3 + a_{2,3}X_2X_3 + a_{1,2,3}X_1X_2X_3$$

Since the mathematical model associated with the factorial plane is established with the reduced centered variables, the coefficients of the polynomial then have a very simple meaning: mean, α_0 ; main effects, α_i ; interaction, α_{ij} and α_{ijk} (Goupy, 2001). The estimation of the coefficients is given by the following equation:

$$a_i = (X'X)^{-1} * X'Y$$

Where:

X is the matrix of the model (Table X);

X' the transposed matrix of the matrix of the model;

$(X'X)^{-1}$ the inverse matrix of the matrix of the model, and Y the response (the content of residual hydrocarbons).

Table 5: Experience Plan Associated with the Three Factors

Experiences	Reduced variables			Actual variables			Response
	X_1	X_2	X_3	X_1	X_2	X_3	Y
1	-1	-1	-1	0,5	10	50	
2	+1	-1	-1	1	10	50	
3	-1	+1	-1	0,5	60	50	
4	+1	+1	-1	1	60	50	
5	-1	-1	+1	0,5	10	250	
6	+1	-1	+1	1	10	250	
7	-1	+1	+1	0,5	60	250	
8	+1	+1	+1	1	60	250	
9	0	0	0	0,75	35	150	
10	0	0	0	0,75	35	150	
11	0	0	0	0,75	35	150	
12	0	0	0	0,75	35	150	

Hence the matrix of the following model (Table 6)

Table 6: Model Matrix

X_0	X_1	X_2	X_3	$X_1 X_2$	$X_1 X_3$	$X_2 X_3$	$X_1 X_2 X_3$
+1	-1	-1	-1	+1	+1	+1	-1
+1	+1	-1	-1	-1	-1	+1	+1
+1	-1	+1	-1	-1	+1	-1	+1
+1	+1	+1	-1	+1	-1	-1	-1
+1	-1	-1	+1	+1	-1	-1	+1
+1	+1	-1	+1	-1	+1	-1	-1
+1	-1	+1	+1	-1	-1	+1	-1
+1	+1	+1	+1	+1	+1	+1	+1
+1	0	0	0	0	0	0	0
+1	0	0	0	0	0	0	0
+1	0	0	0	0	0	0	0
+1	0	0	0	0	0	0	0

In this matrix, we have the following meanings:

- X_0 corresponds to the constant factor a_0 ;
- X_1 , X_2 and X_3 the values of the variables studied;
- X_1X_2 , X_1X_3 and X_2X_3 the interactions considered in pairs;
- $X_1X_2X_3$ the interactions between the three variables.

Thus, obtaining the equation of the model will make it possible to express the effect of the different factors and their interactions on the response.

Erlenmeyer floor washing

Under various operating conditions defined according to our experimental design, 1 g of soil is placed in a 75 ml Erlenmeyer flask and 25 ml of the washing solution is then added. An agitation of 125 rpm is imposed during the time of contacting. Subsequently, the contaminated wash solution is separated from the "clean" soil by filtration (Whatman 934-AH, 1.5 μm porosity), chromatographic analyzes to identify and determine the nature and contents of the family. hydrocarbons are then carried out on the "decontaminated" soil.

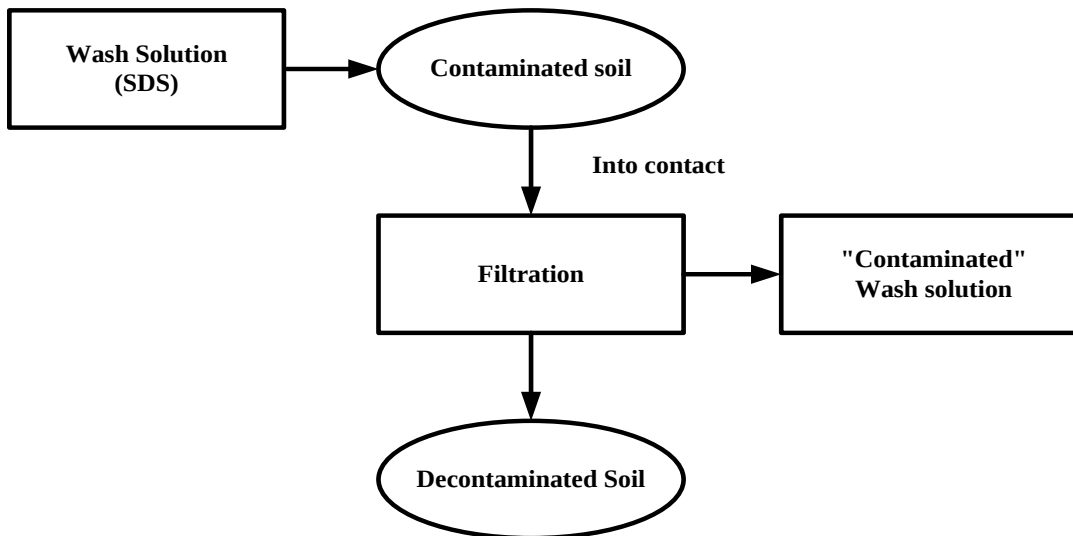


Figure 1: Schematic diagram of the washing process of the polluted solid matrix

Results and discussion

The full factorial design allowed us to perform two-level experiments and the response assessment gives us the residual hydrocarbon content. The peak areas of the 12 experiments performed were measured using the chromatograph to determine the residual hydrocarbon content.

Table 7: Experimental Plan and Answers Obtained

Experiences	Reduced variables			Actual variables			Response
	X ₁	X ₂	X ₃	X ₁	X ₂	X ₃	Y _{exp}
1	-1	-1	-1	0,5	10	50	26,456
2	+1	-1	-1	1	10	50	25,933
3	-1	+1	-1	0,5	60	50	24,223
4	+1	+1	-1	1	60	50	17,600
5	-1	-1	+1	0,5	10	250	30,741
6	+1	-1	+1	1	10	250	35,621
7	-1	+1	+1	0,5	60	250	28,19
8	+1	+1	+1	1	60	250	26,436
9	0	0	0	0,75	35	150	28,970
10	0	0	0	0,75	35	150	26,423
11	0	0	0	0,75	35	150	27,453
12	0	0	0	0,75	35	150	26,450

The different effects are given by the following coefficients:

$$a_0 = 27.0413, a_1 = -1.005, a_2 = -5.5755, a_3 = 6.694, a_{12} = -3.1835, a_{13} = 2.568, a_{23} = -0.2925$$

The factor corresponding to the interactions between the three variables was neglected for the calculation of the optimum. The first-degree mathematical model with interactions representing residual hydrocarbon content is as follows:

$$Y = 27.0413 - 1.0050X_1 - 5.5755X_2 + 6.6940X_3 - 3.1835X_1X_2 + 2.5680X_1X_3 - 0.2925X_2X_3$$

Equation 18 shows the following effects:

- A positive effect (+6.6940) of the variable X_3 corresponding to the particle size fraction of the treated soil. The particle size fraction significantly increases the residual hydrocarbon content. An increase in particle size does not promote good desorption of pollutants to the surfactant.
- A negative effect (-5.5755) of the variable X_2 corresponding to the contact time. A high contact time contributes to a significantly lower residual hydrocarbon content.
- A negative effect (-3.1835) of the interaction X_1 and X_2 respectively corresponding to the concentration of the SDS solution and the contact time. The X_1X_2 interaction significantly decreases the residual hydrocarbon content.
- A positive effect (+2.568) of the interaction X_1 and X_3 respectively corresponding to the SDS concentration and the particle size fraction of the treated soil. This interaction significantly increases the residual hydrocarbon content.
- A negative effect (-1.0050) associated with X_1 is observed. This factor contributes to a decrease in residual hydrocarbon content but not significantly.
- A negative effect (-0.2925) associated with the interaction X_2 and X_3 is noted. This interaction decreases the measured response but not significantly.

This is confirmed by the Pareto diagram below (Figure 2) representing the effects of the variables and their interactions at the 95% confidence level:

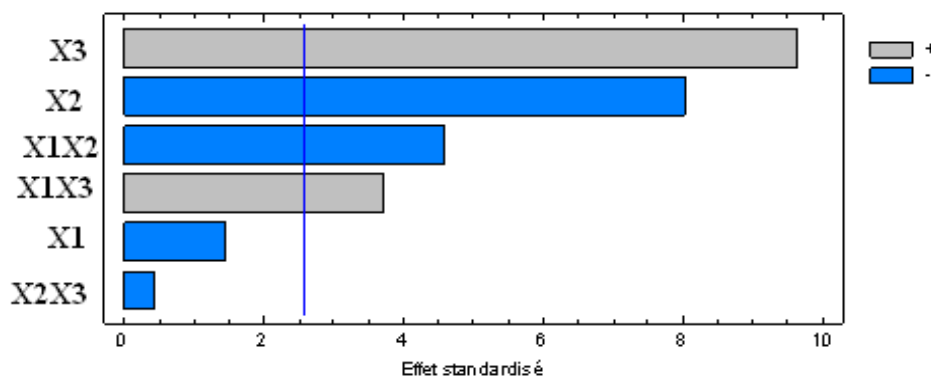


Figure 2: Pareto diagram for the answer

The purpose of our analysis is to reduce or eliminate pollutants from the polluted solid matrix. For this, a factor that contributes to the reduction of residual hydrocarbon content is considered a positive factor. On the other hand, a factor that increases the response is considered a negative factor. This observation shows that the contact time, the SDS concentration, the time / concentration interaction and the time / particle fraction interaction have a positive influence on the response.

Nature and residual hydrocarbon content

The depollution test performed using sodium dodecyl sulphate showed the ability of the latter to remove pollutants from the contaminated solid matrix. The various chromatographic analyzes carried out on the "decontaminated" soil have shown that the residual hydrocarbon contents depend on the experimental conditions.

Table 8: Nature and content of residual aliphatic hydrocarbons ($\mu\text{g/g DM}$)

Nature of residual hydrocarbons (aliphatic)	Residual hydrocarbon content according to the tests							
	E1	E2	E3	E4	E5	E6	E7	E8
Decane (C10)	0,893	0,468	0,436	0,354	0,483	0,775	0,602	0,693
Undecane (C11)	0,641	0,859	0,500	0,044	0,644	0,833	0,892	0,507
Dodecane (C12)	0,927	0,471	0,667	0,711	0	0,805	0,816	0,263
Tridecane (C13)	0,847	0,463	0,383	0,153	0,820	0,798	0,894	0,265
Tetradecane (C14)	0,477	0,892	0,589	0,540	0,651	1,078	0,986	0,827
Pentadecane (C15)	0,590	0,916	0,655	0,960	1,810	1,670	0,918	0,246
Hexadecane (C16)	0,961	0,877	0,748	0,780	1,860	1,030	0,989	0,657
Heptadecane (C17)	0,769	0,532	0,868	0,900	1,009	0,860	0,999	0,939
Octadecane (C18)	0,826	0,929	0,781	0,312	0,859	0,814	0,973	0,903
Eicosane (C20)	0,676	0,856	0,467	0,342	1,077	1,901	1,130	0,902
Tetracosane (C24)	0,946	0,679	0,814	0,164	0,864	0,849	0,813	0,737
Heptacosane (C27)	0,678	0,586	0,648	0,175	0,871	1,447	0,997	0,739
Octocosane (C28)	0,680	0,561	0,527	0,708	0,980	1,400	0,907	1,001

The individual residual aliphatic hydrocarbon content ranged from 0 to 2.001 $\mu\text{g/g DM}$ while it ranged from 4.79 to 65.90 $\mu\text{g/g DM}$ in soil particles $<50 \mu\text{m}$ and 0.91 to 30.70 $\mu\text{g/g DM}$ in soil particles of sizes $<250 \mu\text{m}$.

In soil particles of sizes $<50 \mu\text{m}$, the concentration of alkane at 28 carbons (Octocosane) increases from 65.90 $\mu\text{g/g}$ to a minimum value of 0.527 (E3), which corresponds to a reduction of 99.2%. That of the alkane with 20 carbons (Eicosane) goes from 34.00 $\mu\text{g/g}$ to a minimum concentration of 0.342 $\mu\text{g/g}$ (E4), which corresponds to a reduction of 98.99%. The concentration of Decane goes from 4.79 $\mu\text{g/g}$ to a minimum concentration of 0.354 $\mu\text{g/g}$ (E4), which corresponds to a reduction of 92.60%. The concentration of Dodecane in soil particles of sizes $<250 \mu\text{m}$ increases from 14.10 $\mu\text{g/g}$ of MS to 0 (E5).

In soil particles of sizes $<250 \mu\text{m}$, the concentration of the alkane at 11 carbons (Undecane) increases from 30.70 $\mu\text{g/g}$ to 0.507 $\mu\text{g/g}$, a reduction of 98.35%. That of the alkane with 18 carbons (Octadecane) goes from 3.57 $\mu\text{g/g}$ to 0.814 $\mu\text{g/g}$, ie a reduction of 77.20 and that of Tetracosane passes from 0.91 $\mu\text{g/g}$ to 0.737 $\mu\text{g/g}$, ie abatement of 19.01%.

Table 9: Nature and levels of residual PAHs ($\mu\text{g/g DM}$)

Nature of Residual Hydrocarbons (PAHs)	Residual hydrocarbon content according to the tests							
	E1	E2	E3	E4	E5	E6	E7	E8
Naphthalene	0,819	1,236	1,03	0,672	1,355	1,136	1,014	1,038
Acenaphthylene	0	0	0	0	0	0	0	0
Acenaphthene	1,38	1,098	1,237	0,911	0,896	1,135	1,061	1,117
Fluorene	0,941	0,956	0,473	0,885	0,904	1,075	0,928	0,951
Phenanthrene	1,438	1,985	0,801	0,958	1,242	2,415	1,353	1,136
Anthracene	1,364	1,293	0,986	0,854	1,413	0,965	1,154	1,85
Fluoranthene	0,935	0	1,13	0,924	1,055	0,944	0,933	1,023
Pyrene	0,893	1,038	1,051	0,331	0,895	1,012	0,952	1,496
Benzo [a] Anthracene	-	-	-	-	-	-	-	-
Cchrysene	1,837	2,058	2,039	1,319	1,319	2,262	1,893	2,133
Benzo [b] fluoranthene	0,848	0	1,469	0,352	1,159	2,297	1,348	1,724
Benzo [k] Fluoranthene	0,955	1,096	1,359	0,932	2,01	3,397	1,358	0,935
Benzo [a] pyrene	1,178	1,658	1,034	0,451	-	-	-	-
Indeno [1,2,3-c, d] pyrene	1,276	1,247	1,065	0,661	1,643	1,277	1,535	2,279
Dibenzo [a, h] Anthracene	0,937	1,147	1,653	1,23	2,689	1,381	1,057	-
Benzo [g, h, i] perylene	1,744	2,032	0,807	0,977	2,233	2,065	1,688	2,075

For all tests conducted, PAH concentrations ranged from 0 to 3,397 $\mu\text{g/g DM}$ while they ranged from 3.46 to 103.5 $\mu\text{g/g DM}$ in soil particles of sizes $<50 \mu\text{m}$ and 2.90 $\mu\text{g/g}$ to 21.85 $\mu\text{g/g DM}$ in those of sizes $<250 \mu\text{m}$ before the treatment trial.

In soil particles of sizes $<50 \mu\text{m}$, the concentration of Benzo [a] pyrene increases from 103.50 $\mu\text{g/g}$ to 0.451 $\mu\text{g/g}$ (E4), a reduction of 99.56% and the concentration of Naphthalene passes from 3.46 $\mu\text{g/g}$ to 0.672 $\mu\text{g/g}$ (E4), representing an 80.57% reduction.

In soil particles of sizes $<250 \mu\text{m}$, the concentration of pyrene increases from 21.85 $\mu\text{g/g}$ to 0.895 $\mu\text{g/g}$ (E5), a reduction of 95.90% and that of Acenaphthene from 2.90 $\mu\text{g/g}$ at 0.896 $\mu\text{g/g}$ (E5), a reduction of 69.10%. The content of Dibenzo [a, h] Anthracene in this fraction goes from 8.09 $\mu\text{g/g}$ to 0 (E8).

The pollution control test carried out showed that when the initial concentration of pollutant is low, its mobilization by sodium dodecyl sulphate is difficult.

Some PAHs found in the "clean-up" solid matrix are greater than 2 $\mu\text{g/g}$, considered the standard not to be exceeded when it comes to the individual hydrocarbon content (Ministry of the Environment of the Ontario, 2004). In contrast, the aliphatic hydrocarbon concentrations found in the "cleared" soil are all low and do not pose a threat to the food chain (Mzoughi et al. 2002).

Depollution efficiencies

Residual hydrocarbon contents obtained after treatment and according to the different operating conditions are used to calculate the pollution abatement efficiencies. The depollution efficiencies are generally used to evaluate the efficiency of the applied process. The equation below is used to make this calculation. $Rd (\%) = \frac{Y_{fc} - Y_r}{Y_{fc}} \times 100$

Rd: Depollution Yield

Y_{fc} : Hydrocarbons content in the fraction to be treated

Y_r : Residual hydrocarbons content in the treated fraction.

Table 10: Depollution efficiencies of the eight tests performed

Tests	E1	E2	E3	E4	E5	E6	E7	E8
Rd (%)	90,4	96,0	96,3	97,3	88,8	87,1	89,8	90,4

Decontamination efficiencies (Rd) range from 87.1 (E6) to 97.3 (E4). The yields of the E2, E3, and E4 experiments are greater than 95% considered as the effective abatement rate of the chemical surfactant wash processes of the solid matrices polluted by hydrocarbons (Boivon and Ricour, 2005). The maximum depollution efficiency is 97.3% with a residual hydrocarbon content of 17.6 µg/g DM. The value of the residual hydrocarbons content of 17.6 µg/g is greater than the thresholds of 2 to 10 µg/g defined by the French Environment and Energy Management Agency (ADEME) for the reuse of hydrocarbons cleared land. In order to be able to reuse our polluted soil, it would be necessary to find the optimal conditions which make it possible to reach the thresholds of 2 to 10 µg/g.

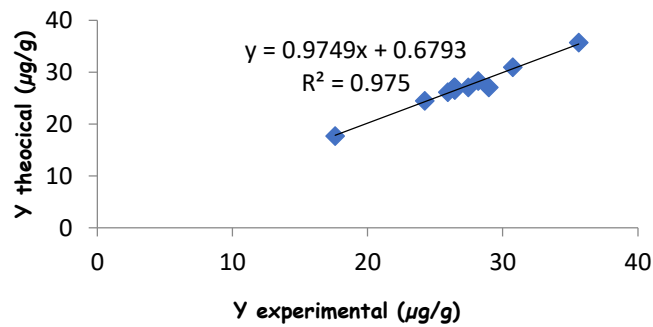
Obtaining these optimal conditions necessarily involves modeling followed by optimization of the residual hydrocarbon content.

Study of the mathematical model

In order to validate the mathematical model studied, it is necessary to compare the theoretical and experimental results (Table 11).

Table 11: Comparison of theoretical results with experimental values

Experiences	Y _{experimental}	Y _{theoretical}	Residues
Ex 1	26,456	26,531	-0,075
Ex 2	25,933	26,141	-0,208
Ex 3	24,223	24,431	-0,208
Ex 4	17,600	17,675	-0,075
Ex 5	30,741	30,945	-0,204
Ex 6	35,621	35,696	-0,075
Ex 7	28,19	28,265	-0,075
Ex 8	26,436	26,644	-0,208
Ex 9	28,970	27,041	1,929
Ex 10	26,423	27,041	-0,618
Ex 11	27,453	27,041	0,412
Ex 12	26,450	27,041	-0,591

**Figure 3:** Regression curve and equation of the response function

The multiple linear correlation coefficient obtained now clearly quantifies the good quality of the fit. The model used can therefore be considered valid (since $R^2 = 0.975$).

Search for optimal conditions

Now that a good quality fit has been achieved, the final step is to look for the optimal conditions for the problem, ie the values of the concentration, the contact time as well as the particle size fraction leading to reduce the residual hydrocarbon content in the polluted solid matrix.

Equation 18 can be deliberately simplified by eliminating the effect of the concentration considered insignificant in the previous analysis (this makes it easier to manipulate this reduced expression while keeping an almost similar quality of fit).

The equation of the model becomes:

$$Y = 27.0413 - 5.5755X_2 + 6.6940X_3 - 0.2925X_2X_3$$

The response surface studied here is three-dimensional (the response and the two variables X_2 and X_3). The graphical representation such as that proposed in FIG. 4 also makes it possible to define the position of the minimum sought.

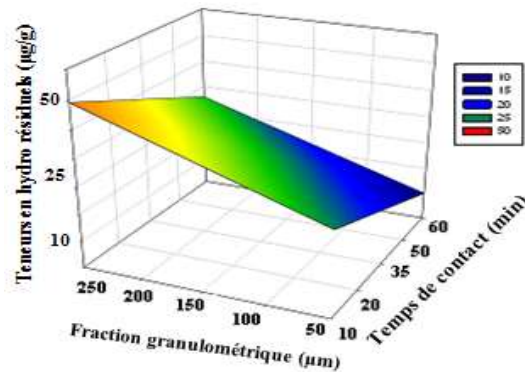


Figure 4: Response Surface

By setting the variable X_1 , it is found that there is an area for which the residual hydrocarbon content is minimal ($10 \mu\text{g/g}$). In this zone, the contact time is high, but the particle size is small.

It appears that the optimal experimental conditions, that is to say those allowing to reduce the residual hydrocarbon content are obtained for the following coded levels:

$$X_1 = 0, X_2 = +1, X_3 = -1.$$

Returning to the initial units, this corresponds to the settings given below:

Table 12: Actual values obtained at optimum

Factor 1:	Concentration of the SDS solution	0,75g/L
Factor 2:	Contact time	60min
Factor 3:	Particle size fraction	50µm

Three experiments carried out concretely by fixing these levels ($X_1 = 0$, $X_2 = +1$, $X_3 = -1$), allowed us to obtain a content of residual hydrocarbons of $10.79 \pm 0.98 \mu\text{g/g}$. This value obtained is close to the average value predicted by the model, that is to say to: $Y_{\text{opt}} \approx 10 \mu\text{g/g}$.

Y_{opt} : Optimum residual hydrocarbon content.

CONCLUSION

The tests carried out according to the experimental plan show that the pollution abatement efficiencies vary from 87.08% to 97.32%. The maximum efficiency (97.32%) of depollution is obtained on soil particles of size $<50 \mu\text{m}$ with a surfactant concentration of 1 g/L and a contact time of 60 minutes. The yield obtained in this condition is certainly higher than 95% considered as the effective abatement rate

of the washing processes of solid matrices polluted by hydrocarbons. However, the residual hydrocarbon content of 17.6 µg/g obtained with this yield is greater than the thresholds of 2 to 10 µg/g defined by the French Environment and Energy Management Agency (ADEME) for the reuse of cleared land. The modeling followed by the optimization enable to obtain the experimental conditions for which the residual hydrocarbon content reaches the threshold of 10 µg/g. This soil treatment method makes it possible to have an interesting yield of pollutant extraction. It could therefore be used for the remediation of soils polluted by hydrocarbons in general and PAHs in particular.

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