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The Environmental Impact of Polycyclic Aromatic Hydrocarbons: Mechanism of Extraction by Bio-Surfactant in a Microwave

Haroun Ali Adannou[1,2*], Nayaou Kadidja Kamane[1], Samba Koukouare Prosper[1,2], Dorim Ngarbaroum[1,2], Allaramadji Ngarmadji Constant[3], Abdel-Hamid Mahamat Ali[1], Simon Ngos III[2]

[1]Department of Chemical Engineering, Higher National Institute of Petroleum of Mao, Mao, Chad
[2]National Higher School of Engineering of Maroua, University of Maroua, Maroua, Cameroon
[3]Faculty of Exact and Applied Science, University of N'Djaména, N'Djaména, Chad
Email: *harounali100@gmail.com

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Abstract

In N'Djaména, the use and marketing of certain hydrocarbons does not comply with any standard in force or with regulations provided for this purpose. Their evaporation and unregulated release into the wild significantly affects the ecosystem. The present work consists in developing a method of extraction from sediments polluted by bio surfactant (rhamnolipid) assisted by microwaves. The goal here is to look for the presence of polycyclic aromatic hydrocarbons in polluted sediments. The rhamnolipid used consists of mono-rhamnolipids and di-rhamnolipids, its emulsion index is 64.66% and is composed of saturated and unsaturated fatty acids having carbon numbers ranging from 12 to 18. We used the microwave micellar extraction process. It was made by keeping the concentration values fixed at 0.15 g/L and the power at 400 W and more. We observed a positive interaction of the rhamnolipid concentration factors and the power of the microwave to obtain the optimal conditions at the time of 50 S, at the concentration of 0.16 g/L and at the power of 443 W for a rate of optimal extraction of 0.91%. Chromatographic analysis by GC-MS of the optimum extracts allowed us to identify twelve (12) C10 to C43 n-alkanes and eight (8) PAHs. It emerges from this analysis that the rhamnolipid extracts seven (7) Polycyclic Aromatic Hydrocarbons in equivalent proportions while the tween 80 extracts only four (4) Polycyclic Aromatic Hydrocarbons with a high proportion (80.02%) of benzo [a] antracene.

Keywords

Marketing, Polycyclic Aromatic Hydrocarbons, Rhamnolipid, Benzo [a]

Antracene and Microwaves

1. Introduction

The production, processing, transport and use of crude oil generates waste consisting mainly of hydrocarbons and entails pollution risks (accidental and chronic) for the environment, which can influence the ecological balance and sometimes lead to the destruction of the ecosystem and even human health [1] [2]. Among the multitudes of hydrocarbons there are types which have at least two fused benzene rings called Polycyclic Aromatic Hydrocarbon. They are more than a hundred existing in the environment. Some have alkyl groups, halogens, or sulfur, nitrogen and oxygen atoms in their structure. Of these compounds, sixteen (16) are defined as priorities by the United States Environment Agency (US EPA). They have 2 to 6 benzene rings and are the most frequently searched for and analyzed in environmental risk studies because they are recognized as environmental pollutants and are known by their carcinogenic and/or mutagenic characteristics [3]. In addition to their characteristics, PAHs have a very marked hydrophobic property [4] depending on the chemical structure of the metabolites formed and lead to a decrease in the response of the immune system, thus increasing the risk of infection [5] and adsorbing more readily on particulate matter [6]. Pollution by these products is one of the most pronounced and dangerous forms of pollution [7]. These hydrocarbons are present daily in our environment and are found in the various compartments of the ecosystem [8]. Some of them (PAHs) have moderate toxicity, with common effects: their repeated or prolonged inhalation leads to manifestations such as headache, dizziness [9]. In high concentrations, they also cause disorders of the nervous system and the digestive system. PAHs are part of Persistent Organic Pollutants (POPs) because they are characterized by their Toxicities; their Persistances in the Environment, their Bioaccumulation in Living Tissues, and their Long Distance Transport. They are biologically active molecules which, once absorbed by organisms, undergo transformation reactions under the action of enzymes leading to the formation of epoxides and/or hydroxy derivatives. However, what are the sources of exposure of PAHs?

The main sources of potential exposure are: food (fruits, vegetables, grilled meats [10]; (which is not lacking throughout our cities); coal tar, bitumen, pitch, asphalt, mineral oils, automobile exhaust fumes, industries All along the asphalted roads and even inside the districts and peripherals one can notice several exposures of the sellers of hydrocarbons on the sly and non-compliant hydrocarbon sales points is the major source of PAH exposure for non-smokers (70% of exposure). Studies carried out in different countries have shown that the amount of PAH ingested varied from 1.2 to 5 µg/day [11]. The combustion of fuels and fossil fuels is the major anthropogenic source of carbon dioxide (CO_2) emissions, the main greenhouse gas responsible for climate change. For example, 1 liter of gasoline produced, on combustion, 2.34 kg of CO_2 and 1 liter of diesel produced, on combustion, 2.61 kg of CO_2 [12] [13]. The IARC (International Agency for Research on Cancer, 1983) indicates that the most potentially carcinogenic PAHs are benzofluoranthene, benzo [a] pyrene, benzo [a] anthracene, dibenzo [a, h] anthracene and indeno [1,2,3-cd] pyrene. The mutagenic and carcinogenic powers of PAHs appear after 4 cycles, and are particularly marked for PAHs at 5 and 6 cycles [14].

Many methods of extracting PAHs from sediments have been developed. The first methods used are: Soxhlet extraction and reflux extraction. Unfortunately, it is less effective. In recent years, new extraction techniques have been developed to reduce the volume of extraction solvents and the extraction time, such as supercritical fluid extraction (SFS) [15], fluid extraction under pressure (EFSP) [16], microwave assisted extraction (MEAM) [17], micellar extraction (EM) [18] and microwave assisted micellar extraction (EMAM) [19]. The use of surfactant solutions can also be used as solvents [20] and have found a large number of applications in analytical chemistry [21], and as suitable solvents for hydrophobic species [22]. In this case, they can replace the toxic organic solvents used in the other methods. It is this latter technique that is called microwave assisted micellar extraction. It cuts extraction hours to minutes, reduces the volume of extraction solvent, and uses surfactants instead of toxic solvents. These types of surfactants produced by microorganisms, called biological surfactants or biosurfactants, have the same surfactant properties as their synthetic counterparts, but have the advantage of being biodegradable and non-toxic [23]. They see their use more and more in the depollution of polluted oil sites and in the control of pollution by hydrocarbons [24] [25]. There are several types of biosurfactants but the most widely used is rhamnolipid which is a glycolipid biosurfactant produced by microorganisms from Pseudomonas aeruginosa strains [26]. Its environmental use is currently considered the largest market for biosurfactants because of their environmental compatibility. Rhamnolipids can be used in the bioremediation of soils, sediments and rivers polluted with hydrophobic compounds and heavy metals [27]. They improve the degradation of chlorinated hydrocarbons, alkanes, n-paraffins and polycyclic aromatic compounds when incorporated into the medium [28] and are used in hydrocarbon extraction processes [29]. Their effectiveness is as much as a 0.2% solution in rhamnolipids allows a removal of 23% to 63% respectively of light and heavy hydrocarbons [30].

2. Materials and Method

2.1. Materials

- The sediment and the culture broth of rhamnolipid

Pretreated sediment samples and rhamnolipid culture broth were provided to us by the Industrial and Bioresource Chemistry Laboratory (LCIB) of ENSAI.

- The microwave oven

The KOG-360 brand microwave oven modified and adapted to the electronic laboratory of ENSAI was used, this microwave has a maximum power of 800 W and a frequency of 2450 MHz (magnetron). The inside of the microwave has a fast 900 rpm agitation system and perforated to pass the cooling flow. The entire installation is inerted.

- Solvents

The analytical solvents used in this work are hexane and ethyl acetate.

- Statistical analysis software

The statistical analysis of the results was done using the STATGRAPHIC Centurion16.1.11 software which is a statistical software.

- Chromatographic analysis apparatus

The chromatographic analysis was carried out with an HP6890 gas chromatograph coupled to an HP5973 mass spectrometer (GC-MS) (Agilent) equipped with an MDN 12 column (Supelco) having the characteristic 30 m × 250 μm × 0.25 μm. MS detection is performed in SIM (Single Ion Monotoring) mode with the aim of reducing interfering products and increasing the detection limit.

2.2. Method

The general methodology of the work is represented by the following figure (**Figures 1-3**):

- Extraction of rhamnolipid

The extraction of rhamnolipid from the culture broth is carried out according to the method described by [31].

Figure 1. Photograph of the microwave used.

Figure 2. Photograph of the GC-MS device.

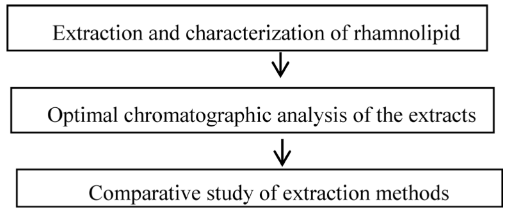

Figure 3. General method of work.

- Characterization of the extracted rhamnolipid and analysis of thin layer chromatography

It is carried out according to the method described by Bhat *et al.*, (2015) [32].

- Emulsifying activities

The emulsifying capacity of the extracted biosurfactant was determined according to the method described by Batista *et al.* (2006) [33].

Composition of fatty acids

The method described by Rosana *et al.* (2009) [34] was used to determine the fatty acid composition of the extracted biosurfactant.

Characterization of hydrocarbons present in polluted sites

It is carried out according to the method described by Grimalt and Albaigés (1987) [35].

Fractionation of hydrocarbon extracts

The different fractions of the hydrocarbons were obtained by the method described by Moreda *et al.* (1998) [36].

Analysis by gas chromatography coupled to a mass spectrometer

The temperature program used is that described by Regonné *et al.* (2017). This program goes from 40˚C to 320˚C (2 min), with a heating rate of 6˚C/min.

Extraction

The extraction of the hydrocarbons was carried out according to the method described by Gulmini *et al.* (2010) [37].

3. Result and Discussion

Our work gave several results consistent with the literature search. Several experiments were carried out in order to meet one of the objectives of modeling extraction kinetics, which is nothing more than the study of the influence of time on an extraction process. In this article, this study of the influence of time on the microwave micellar extraction process consists of a kinetic modeling of the extraction of total n-alkanes and total PAHs. It was done by keeping the concentration values fixed at 0.15 g/L and the power at 400 W and by varying the time from 20 s to 90 s with a step of 10. We have thus studied several models and that of Hervas presents the best approach of which we present the kinetic parameters in **Table 1**. The parameters of **Table 1** allowed us to choose the best concentration, the best time and the best power in order to allow a rapid extraction carried out in a single step following first order kinetics. Before responding to the expected results there were several steps as mentioned on the methodology. First, we carried out the analysis of the rhamnolipid mixture by thin layer chromatography. The result obtained is in the following figure (**Figure 4** & **Figure 5**).

The UV spectrum revealed two distinct yellow spots on the TLC sheets. According to Noramiza *et al.*, (2015) [38], the appearance of yellow spots on the TLC plate or sheet indicates that the biosurfactant extracted is glycolipid rhamnolipid, thus confirming the work of Schenk *et al.*, (1995) [39] and Arino *et al.* (1996) [40]. Its fatty acid composition reveals carbon numbers ranging from C_{12} to C_{18}. This result is consistent with what WEI *et al.*, 2005 [41] said, we observed that for fatty acids in general, C_{18} acids have priority with a percentage of 43.27% followed by C_{12} acids., C_{16} and C14 respectively by 26.53%, 19.54% and 10.67%.

Regarding the ability to form and stabilize emulsions for the application of a bio-surfactant, the results obtained show that the extracted biosurfactant emulsifies kerosene with an emulsifying stability of 64.66%. The effectiveness of this biosurfactant is comparable to that of synthetic surfactants Tween 80 and SDS which is 80% and 78% with petroleum, thus proving their potential environmental application.

For the characterization of the hydrocarbons present in the polluted sites, the composition in n-alkanes extracted from the first fractions of the hydrocarbon extract were injected into the GC-MS at a volume of 1 µl and the chromatograms were obtained.

The identification of PAHs in our sample was made by correspondence of the Kovats Indices between the standard mixture of PAHs and those of the sample. Depending on the structures of the extraction solvents and the nature of the sediment, we have adopted several extraction methods.

Microwave-assisted micellar extraction of hydrocarbons allowed after screening to rank the factors according to their importance or to see their interaction. However, it allowed us to observe the interactions that exist between our three selected factors (the irradiation time (X_1), the concentration of rhamnolipid (X_2) and the power of the microwave (X_3)) in order to determine the experimental field.

Table 1. Kinetics parameters models.

Model	K (s^{-1})	C_0 (µg E/g MS)	R^2
Hervas	0.055	0.91	0.99

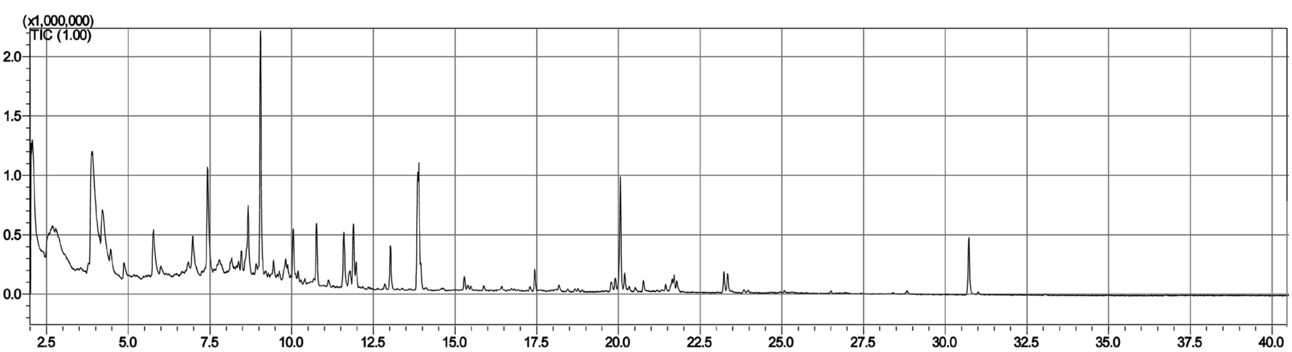

Figure 4. Chromatogram of rhamnolipid lipid fraction.

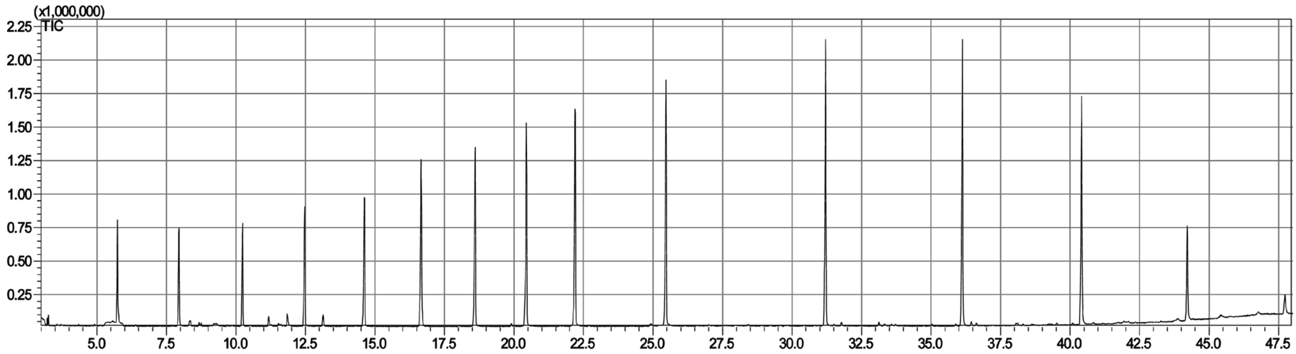

Figure 5. Chromatogramme du standard de n-alcanes.

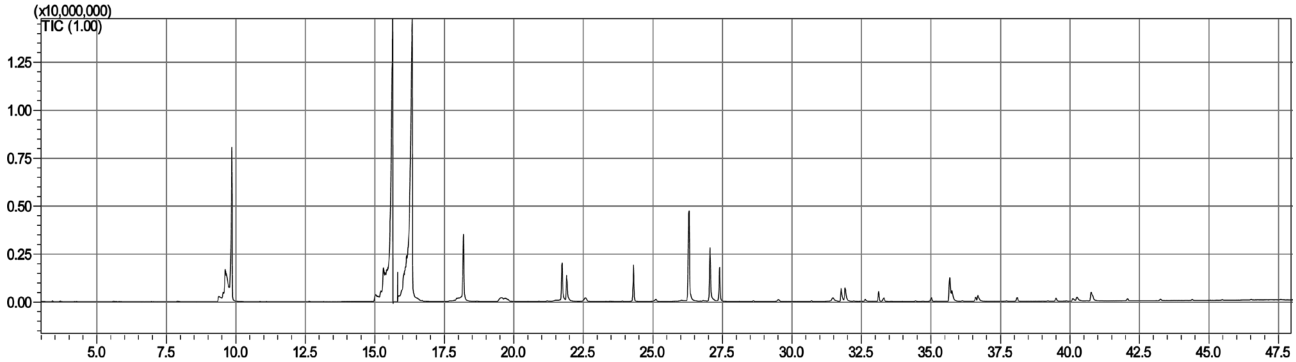

Figure 6. Chromatogram of the n-alkane standard.

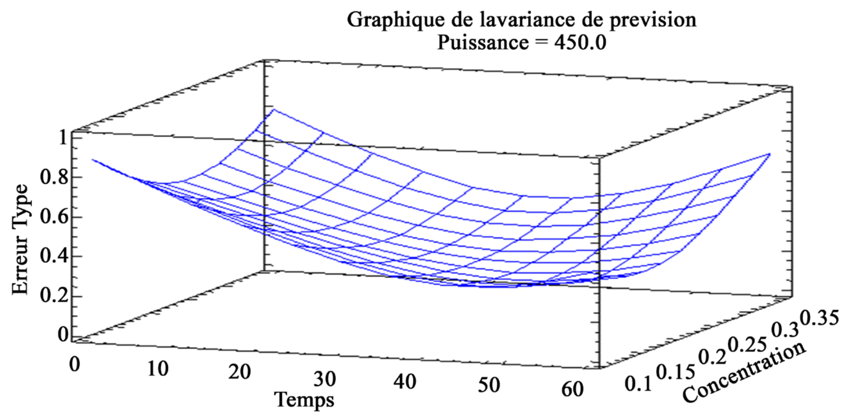

Figure 7. Analysis of variance forecast.

For the acquisition of the response surfaces we have the following figure (**Figure 6** & **Figure 7**) which gives us the analysis of the forecast variance.

When the microwave power is constant and the irradiation time and the concentration of rhamnolipid vary, there is a curvature phenomenon that takes place, the extraction rate increases with the simultaneous increase of these two parameters then decreases to increase further.

- The irradiation time (X_1) is favorable to the extraction rate. The longer the time increases, the more easily the rhamnolipid penetrates into the sediment in order to dissolve the hydrocarbons in the aqueous phase. This is what increases the rate of extraction;

- The concentration of rhamnolipid (X_2) is unfavorable to yield. The more the concentration increases, the more the yield decreases significantly. Because the increase in the concentration of rhamnolipid makes the medium saturated so that the rhamnolipid hardly penetrates into the polluted matrix;
- The power of the microwave (X_3) is also unfavorable to performance. The more the power increases, the more the efficiency decreases. In fact, the power of the microwave depends on the temperature of the compounds to be extracted, the higher it is, the more the temperature increases, then there is degradation of the extracted hydrocarbons;
- The interaction time of irradiation and concentration of rhamnolipid (X_1X_2) is positive. The simultaneous increase of these factors increases the hydrocarbon content insignificantly.
- The interaction time of irradiation and microwave power (X_1X_3) is negative. The simultaneous increase in these factors decreases the hydrocarbon content insignificantly. Their effect is negligible or even zero;
- The interaction of rhamnolipid concentration and microwave power (X_2 X_3) is positive. This interaction increases the hydrocarbon content significantly.

Regarding the experiment on the optimization of the extraction of hydrocarbons in the sediments, the centered composite plane was used to determine the optimal level of the various factors mentioned above, namely the irradiation time (X_1), the concentration of the rhamnolipid solution (X_2) and the power of the microwave (X_3).

We observe that the lowest extraction efficiency is 36% and the highest efficiency is 90%. The optimum values of hydrocarbon extraction are observed at the irradiation time (X_1) of 60 seconds, at the concentration (X_2) of 0.15 g/L and at the microwave power (X_3) of 400 W.

The mathematical model used and which presents the best approach is that of Hervas *et al.* (2006).

Model from Hervas *et al.* (2006).

The kinetic mechanism proposed by Hervas *et al.* (2006) was used for the extraction process under equilibrium conditions. It's a top notch model.

$$c(t) = c_0\left(1 - \mathrm{e}^{-kt}\right)$$

Or $c(t)$: concentration of hydrocarbons in the medium (solvent) at time *t*;

t: irration time (s);

c_0: concentration of the compounds extracted at equilibrium (μg E/gMS);

k: effective diffusion coefficient (s^{-1}).

The accessible quantities have been determined experimentally. The transfer coefficient *k*, the equilibrium contents c_0 and the initial extraction rates Vi are identified from the experimental results.

The R^2 of the Hervas model is 0.99, so the model is validated. The extraction follows the kinetics of the first, that is to say that the extraction is fast it is carried out in one step.

Later, for the application starting from the model equation, we adopted this equation:

$$Y = -3.36 + 0.031X_1 + 14.37X_2 + 0.01X_3 - 0.00017X_1^2 - 0.0075\,X_1X_2 - 0.000029X_1X_3 - 53.59\,X_2^2 + 0.0085\,X_2X_3 - 0.000011X_3^2$$

where X_1 is the time, X_2 the concentration and X_3 the power.

We were able to observe thus:

- A positive effect of the irradiation time (X_1) is observed. This factor contributes to an increase in the hydrocarbon content;
- A positive effect of the concentration of rhamnolipid (X_2) is observed. This factor contributes to an increase in the hydrocarbon content significantly;
- A positive effect of the microwave power (X_3) is observed. This factor contributes to an increase in the hydrocarbon content;
- A quadratic negative effect of the irradiation time (X_{12}) is observed. If we increase the time too much, it will put the extraction rate at a disadvantage. Thus, there is a phenomenon of curvature.
- A negative effect of the interaction time of irradiation and concentration of rhamnolipid (X_1X_2) is observed. This interaction decreases the hydrocarbon content if we simultaneously increase these two factors. Thus, there is a phenomenon of curvature;
- A negative effect of the interaction time of irradiation and microwave power (X_1X_3) is observed. This interaction decreases the hydrocarbon content when they are varied simultaneously. Thus, there is a phenomenon of curvature;
- A quadratic negative effect of the concentration (X_{22}) is observed. If we increase the time too much, it will significantly disadvantage the extraction rate. Thus, there is a phenomenon of curvature.
- A negative effect of the interaction of rhamnolipid concentration and microwave power (X_2X_3) is observed. This interaction decreases the hydrocarbon content when they are varied simultaneously. Thus, there is a phenomenon of curvature;
- A quadratic negative effect of microwave power (X_{32}) is observed. If we increase the time too much, it will significantly disadvantage the rate of extraction. Thus, there is a phenomenon of curvature.

From these results, we observe that the most dominant factor is the concentration with a positive effect. Its effect is 463 times greater than that of time and 1437 times greater than that of potency. The interactions of the factors have very negligible effects. The interaction of concentration and power is positive and the other two interactions are negative. All quadratic effects are negligible. The quadratic effect of focus is 315,235 times that of time and 6304 times that of power.

When the microwave power is constant and the irradiation time and the concentration of rhamnolipid vary, there is a curvature phenomenon that takes place, the extraction rate increases with the simultaneous increase of these two parameters then decreases after reaching a plateau.

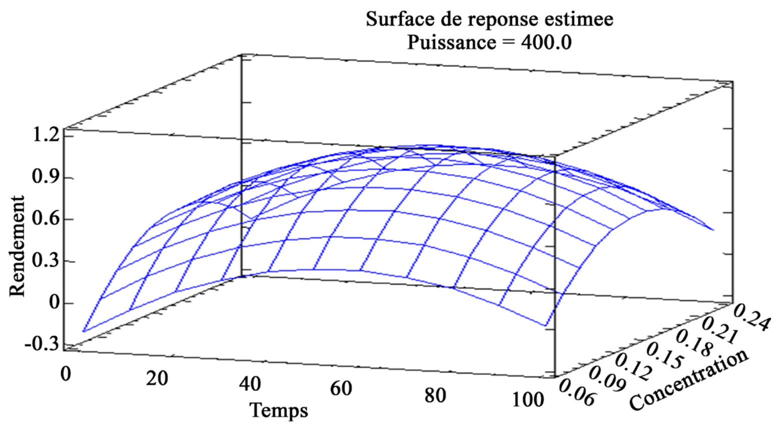

Figure 8. Surface analysis of the estimated responses.

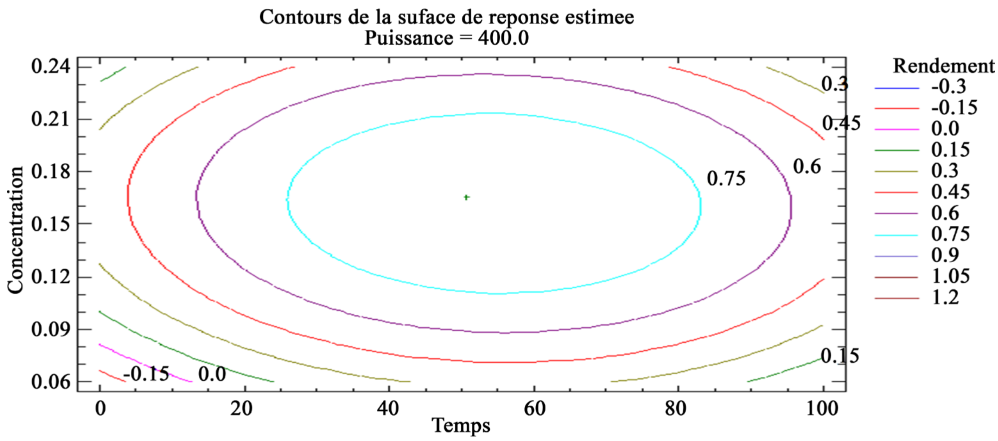

Figure 9. Iso response curve.

The iso response curve is represented by the following figure (**Figure 8** & **Figure 9**).

This curve shows us the optimal zone which is represented by the blue circle with an extraction rate of 0.75.

Finally, the comparative study of the extraction methods was based on the content of the n-alkanes extracted and on the content of the PAHs extracted.

Regarding the content of n-alkanes extracted, rhamnolipid extraction is superior to Tween 80 extraction and reflux extraction. This result is explained by the fact that rhamnolipid also contains alkanes, which is why it was able to extract enough.

And for PAHs, reflux extraction is an optimized technique for PAH extraction. This is why the extracted PAHs are proportional. The PAH extracts by rhamnolipid are also proportional, this is explained by the structure of the latter and its affinity with the extracts. Tween 80 on the other hand does not extract enough PAHs and in a non-proportional way.

4. Conclusions

Pollution from petroleum and petroleum products has become a matter of serious environmental concern around the world, as from its extensive use as a source of energy, it is transported and distributed on a large scale in the biosphere by leaks or exhausts. Petroleum hydrocarbons enter the environment through accidents, spills, industrial releases, or products of commercial or domestic use [42] [43]. These hydrocarbons are mixtures that are complex in their composition and molecular structure. They are made up of a variety of chemicals such as LPGs, gasoline, gas oil, kerosene, fuel oil, heavy fuel oil and lubricating oil etc. [44] [45]. By depositing on the ground or by circulating in the layers of the atmosphere, these hydrocarbons are sources of several problems linked to greenhouse gases, to the destruction of the ozone layer, to the attainment of health. of humans and the imbalance of the viable ecosystem.

For our present study on a method of extracting hydrocarbons from sediments by the biosurfactant (rhamnolipid) assisted by microwave, it is first a question of specifying these hydrocarbons which are Polycyclic Aromatic Hydrocarbons. Then, it emerges that the concentration of rhamnolipid is the most determining parameter in relation to the irradiation time and the power of the microwave. The interaction between rhamnolipid strength and microwave power was positive. Thus, the optimal microwave extraction conditions were determined with the respective values: 50 s for the time, 0.16 g/L for the concentration of rhamnolipids and 443 W for the power. All of these optimal conditions resulted in a maximum extraction rate of 0.91%. Microwave assisted rhamnolipid extraction follows first order kinetics. The model proposed by Hervas *et al.*, which is a first order kinetic model best describes the mechanism of this process with an R^2 of 0.99. GC-MS chromatographic analysis of the optimum extracts allowed us to identify 12 C10 to C43 n-alkanes and 8 PAHs. It emerges from this analysis that the rhamnolipid extracts seven (7) PAHs in equivalent proportions while the tween 80 extracts only four (4) PAHs with a high proportion (80.02%) of benzo [a] antracene.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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