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A model system for cocomposting hydrocarbon contaminated soil by using water activity and porosity as response variables

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Abstract

Cocomposting of soil is the process of simultaneously stabilising organic materials and degrading toxic compounds foreign to the environment. The fraction of components in cocomposting modifies water activity (a_w), it is therefore important to define the composition of the bulk medium. Water activity and the porosity of the bulk medium were response variables applied to a system for the biodegradation of hydrocarbons in the soil. This work proposes a definition of a model system for cocomposting using hydrocarbon contaminated soil, sugarcane bagasse pith and water. The experimental mixtures were determined according to a simplex centroid design. The results were adjusted to a Scheffé multiple regression model and response surfaces were generated. In order to follow the biodegradation of hydrocarbons and a_w, an appropriate mixture (weight basis) was established at 25% sugarcane bagasse pith, 15% contaminated soil, and 60% water. This mixture was then tested in packed bed bioreactors of both 50 and 864 g, resulting in 40% biodegradation of total hydrocarbons after 150 h of composting. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cocomposting; Soil; Response surface methodology; Porosity; Water activity

1. Introduction

The usual techniques employed for disposal or decontamination of hydrocarbon contaminated soils are landfill disposal, incineration, vapour extraction, and detergent washing. Cocomposting is a recent technique for biodegradation and stabilisation of organic substrates, in order to degrade a toxic compound foreign to the environment. Cocomposting offers significant advantages as it is more controlled than landfill and less costly than incineration [1]. However, cocomposting systems consist of a variety of materials which provide great heterogeneity of physical and chemical properties in mixtures.

The biodegradation of hydrocarbons depends on several factors such as an electron acceptor, oxygen in the case of aerobic systems, water content to permit microbial growth, and presence of substrates which are susceptible to be utilised as a source of carbon and energy [2]. Particularly, significant are water activity (a_w) and porosity (ε_0). Water activity is considered [3] to be proportional to free water that is able to transport soluble nutrients to the biomass, in contrast with moisture which includes all water content (available and non-available) [4]. Porosity can be regarded as providing the transport medium which enhances oxygen and CO_2 transfer through the cocomposting aerobic medium. The quantity of contaminated soil added to the designed mixture to be composted has an important effect on both a_w and ε_0, therefore, the balance of the components in the mixture must first be determined. Response surface methodology (RSM) can be applied in this context in order to show the behaviour of those properties which depend on the composition of the system [5].

The objective of this work was to design a model cocomposting system by using soil contaminated with hydrocarbons, sugarcane bagasse pith (SBP) and water by means of RSM, using a_w and ε_0 as the response variables. The cocomposting system was tested by measuring the hydrocarbon biodegradation.

2. Materials and methods

2.1. Materials

The cocomposting model was composed by combining three fractions: (i) soil contaminated with hydrocarbons sam-

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Nomenclature

η	dependent variable
β_{ijk}	multiple regression coefficient
λ_{ijk}	multiple regression coefficient
x_i	independent variable i
n	number of variables
a_w	water activity
ε_0	porosity
f_w	water fraction
f_b	sugarcane bagasse pith fraction
f_s	contaminated soil fraction

pled from the surrounding areas of an oil-well located in the industrial zone of Cactus, Chiapas, Mexico; (ii) SBP obtained from the sugar mill 'Independencia' in Martínez de la Torre, Veracruz state, Mexico, and (iii) tap water.

The SBP (0.695 mm average size) fraction was blended with the following (g (g dry SBP)$^{-1}$): sucrose, 0.5; dibasic potassium phosphate, 0.28; urea, 0.025; and a solution of mineral salts proposed by Goodhue et al. [6], 5.6 ml; activated sludge, sampled from an aerobic waste water reactor, was added as inoculum, 0.02 g (g mixture)$^{-1}$ and was considered as part of the contaminated soil fraction.

2.2. Cocomposting bioreactors

In order to evaluate the cocomposting system, two packed bed type bioreactors were used: a stainless steel cylindrical column with 0.864 kg capacity and a tandem of 12 glass columns each with 50 g [7]. All materials were packed to a density of 350 kg m^{-3}. Bioreactor and columns were continuously aerated at 2.8 l of air per kilogram of packed wet material per minute. The air was previously saturated [8], and the bioreactors were incubated for 150 h in a temperature controlled chamber [9]. The purpose of the stainless steel — 0.864 kg bioreactor was to obtain natural self-heating profiles due to metabolism, therefore, the on-line temperature of the centre was used as target to heat the chamber and, consequently, the glass columns. The temperature within the chamber was maintained 2–4°C (in average) below the internal temperature in the stainless steel bioreactor. Over the experiment, two 50 g columns were sampled every 24 h and sacrificed to measure a_w and residual hydrocarbons. Each experimental unit was analysed by duplicate. In graphical results, error bars were generated by plotting mean values ± S.D.

2.3. Analytical techniques

The a_w was determined in an Aqua Lab CX-2 equipment. In order to determine the ε_0, a known volume of the mixture was weighed in a test tube compacted to the same apparent density of that used in the experiments. Then, the empty spaces were filled with an oil of known density, resulting in the real density of the mixture [10]. Finally, ε_0 was obtained by computing the difference between real minus apparent density and related to the real density.

Hydrocarbons were measured by extracting with the Soxhlet method with a mixture of hexane:acetone 1:1 (v/v) and determined by gravimetric analysis (EPA 3540) [11]. In order to determine the type of contaminants, the Soxhlet extract was used to obtain hydrocarbon fractions. Extracts were partitioned into fractions by column chromatography [12]. Asphaltene fraction was previously eliminated and quantified by precipitation with *n*-pentane. Aliphatics were eluted with *n*-hexane, aromatics with benzene and polar molecules with methanol:acetone (1:1 v/v). All fractions were measured by gravimetric procedure. The CO_2 was monitored on-line through a spectrophotometric detector of absorption in an IR, Servomex 1505.

3. Application of response surface methodology

3.1. Variable definition

Contaminated soil has a very low water retention capacity (WRC) of 0.25 g water (g dry soil)$^{-1}$, which therefore signifies moisture values below 20% at field capacity. However, in the range of moisture measured in soil (between 17 and 20%), the a_w values (from 0.95 to 0.99) are adequate for microbial growth [13]. Nevertheless, a limited range of moisture can restrict the process because any slight decrease of moisture provokes a drastic diminishment in a_w. In contrast, an increase in moisture causes water leakage which occupies the spaces between the particles and thus diminishes the oxygen transfer to the medium.

The SBP was used as a volume agent to facilitate aeration and to incorporate nutrients and water into the bulk. The SBP has a WRC of 4 g water (g dry SBP)$^{-1}$, which indicates its potential to reach up to 80% moisture without water leakage. The a_w in SBP has a wide range of moisture values, from 40 to 80%, adequate for microbial growth. Activated sludge was added to the experimental mixture as a source of viable microorganisms to enhance hydrocarbon biodegradation in cocomposting [14,15].

The components of the mixture were grouped together to emphasise those which represent the most important fractions. Thus, the sucrose, urea and potassium dibasic phosphate were considered as part of the SBP. The activated sludge was considered as part of the contaminated soil and the mineral salts solution was incorporated to the fraction of water. In this way, three principal fractions were defined: contaminated soil, SBP and water. The response variables, a_w and ε_0, are properties which depend only on the relative quantity of components in the mixture.

3.2. Delimitation of experimental area

Fig. 1 shows the variety of mixtures generated by the above mentioned components. Diagrammed in three phases,

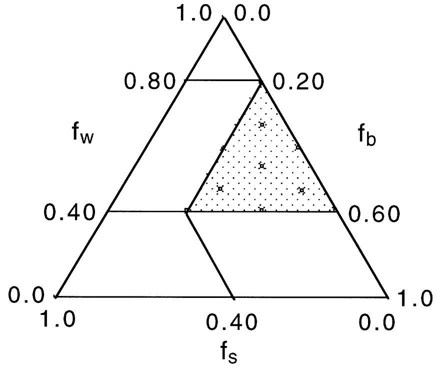

Fig. 1. Three phases scheme for soil–SBP–water. Experimental area (⊡). Water fraction, f_w; SBP fraction, f_b; and contaminated soil fraction, f_s. Experimental points (⊛).

each side of the triangle represents a fraction of each principal component, varying between 0 and 1. There is one set of mixtures which fulfils the necessary requirements to guarantee the water availability and the aeration of the mixture containing the highest quantity of contaminated soil. This restricted operation area is shown in Fig. 1 (shaded) and its limits are

1. Fraction of contaminated soil: from 0.00 to 0.40.
2. Fraction of SBP: from 0.20 to 0.60.
3. Fraction of water: from 0.40 to 0.80.

Mixtures in the resulting area were prepared according to a simplex-centroid design to obtain response surfaces related to a_w and ε_0.

3.3. *Experimental design simplex-centroid type*

The simplex-centroid design was applied to this type of model system to determine the effect of the mixture's components on the defined variables. The proportions of each component in the mixture are not independent of each other [5]. Therefore, components fulfil the following condition:

$$\sum x_i = 1 \tag{1}$$

which in our study case gives

$$f_w + f_b + f_s = 1 \tag{2}$$

For a simplex-centroid design, Cornell [16] proposes that the testing points within the universe of mixtures be those which correspond to the mixtures shown in Table 1 and pointed out in Fig. 1. The statistical model to analyse this type of experimental design has previously been proposed by Scheffé [17], the general equation is the following:

$$\eta = \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n}\sum_{i<j}^{n} \beta_{ij} x_i x_j + \sum_{i=1}^{n}\sum_{i<j}^{n}\sum_{j<k}^{n} \beta_{ijk} x_i x_j x_k \tag{3}$$

In our study case, the response a_w, is defined as

$$a_w = \beta_1 f_w + \beta_2 f_b + \beta_3 f_s + \beta_{12} f_w f_b + \beta_{13} f_w f_s + \beta_{23} f_b f_s + \beta_{123} f_w f_b f_s \tag{4}$$

and for porosity, ε_0, is

$$\varepsilon_0 = \lambda_1 f_w + \lambda_2 f_b + \lambda_3 f_s + \lambda_{12} f_w f_b + \lambda_{13} f_w f_s + \lambda_{23} f_b f_s + \lambda_{123} f_w f_b f_s \tag{5}$$

It is important to note that Eqs. (3)–(5) have no independent term because the response is exclusively a function of the fraction of components in the mixture.

4. Results and discussion

4.1. *Effect of soil, SBP, and water in a_w and ε_0*

Experimental results of both a_w and ε_0 for 10 prepared mixtures are shown in Table 1. In all cases, fraction components (expressed in weight) correspond to the prepared mixtures. Values of a_w varied from 0.884 to 0.983. Since different microorganisms require different a_w ranges to support microbial activity, for example, bacteria in the range of 0.85–0.99 while fungi from 0.6 to 0.9 [3,4], the operation a_w range was considered acceptable. On the other hand, 0 for mixtures varied from 0.599 to 0.748, which are higher and therefore better than those experimentally determined in our original contaminated soil samples (0.463).

The experimental data were adjusted to the Scheffé model by using *Statistical Package for Social Sciences for Windows*'95, SPSST^{TM}, version 7.5. Results are presented in Eqs. (6) and (7) for a_w and ε_0, respectively. The value of the correlation coefficient (R^2) for both cases was 0.999, indicating that the models significantly explain the response for both variables.

$$a_w = 0.99 f_w + 0.71 f_b + 1.25 f_s + 0.32 f_w f_b - 0.50 f_w f_s - 1.05 f_b f_s + 2.01 f_w f_b f_s \tag{6}$$

$$\varepsilon_0 = 0.54 f_w + 0.26 f_b + 2.26 f_s + 1.03 f_w f_b - 2.73 f_w f_s - 5.26 f_b f_s + 11.64 f_w f_b f_s \tag{7}$$

Table 1
Resulting values of a_w and ε_0 in different mixtures (soil–SBP–water) according to a simplex-centroid design

Mixture	Compositions[a]			a_w[b]		ε_0[b]	
	f_s	f_b	f_w	$\bar{x}$	$\sigma\times10^{-3}$	$\bar{x}$	$\sigma\times10^{-2}$
1	0.40	0.20	0.40	0.964	2.12	0.748	1.90
2	0.00	0.60	0.40	0.884	4.24	0.599	3.16
3	0.00	0.20	0.80	0.983	5.66	0.649	1.40
4	0.20	0.20	0.60	0.971	2.12	0.683	0.71
5	0.20	0.40	0.40	0.926	3.54	0.675	2.12
6	0.00	0.40	0.60	0.943	2.12	0.676	0.86
7	0.14	0.33	0.53	0.954	0.70	0.699	0.56
8	0.28	0.26	0.46	0.957	2.83	0.744	0.17
9	0.08	0.26	0.66	0.968	0.00	0.694	1.34
10	0.08	0.46	0.46	0.922	0.71	0.664	0.64

[a] Weight fraction.
[b] $\bar{x}$: Average value; σ: standard deviation.

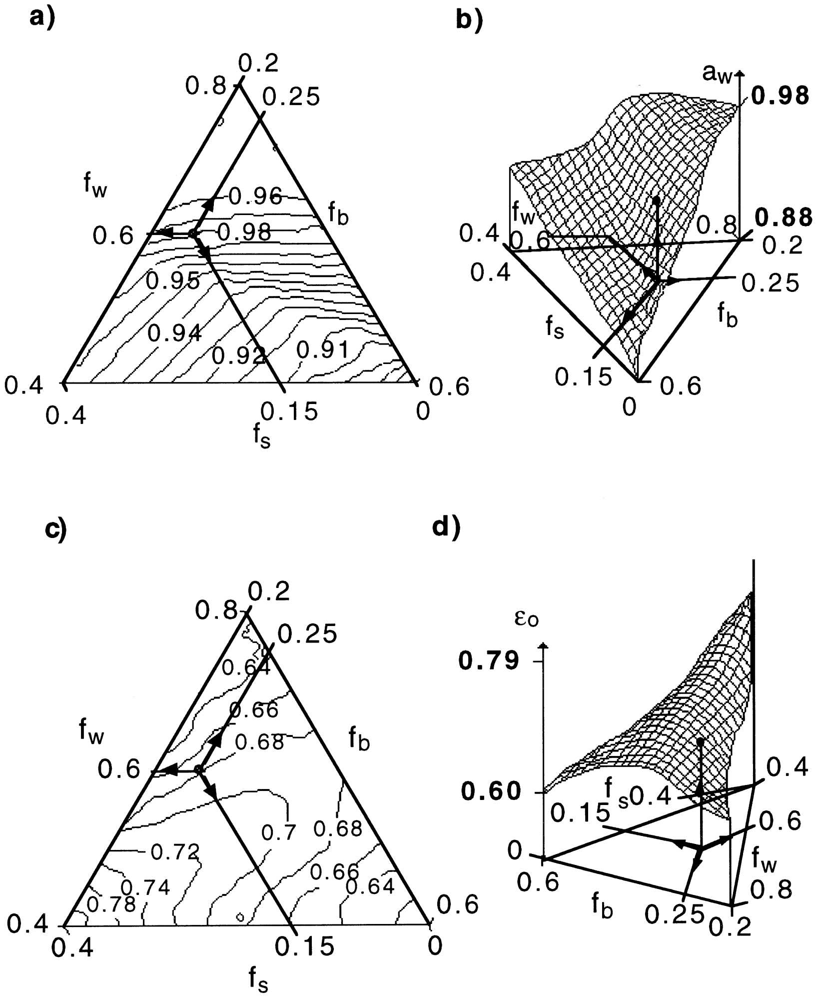

Fig. 2. Contour levels and response surface of a_w (**a** and **b**) and ε_0 (**c** and **d**, respectively). Operation area, (⊗); operation point, (●); water fraction, f_w; SBP fraction, f_b; and contaminated soil fraction, f_s.

The a_w and ε_0 response surfaces were obtained from these statistical models within the experimentation region. The triangular co-ordinates of each composition system was transformed to Cartesian co-ordinates in order to graph the data in the *Surfer Access System* package, version 4.07 for DOS. It was possible since the fraction of the third component values depends of other two fractions, according to Eq. (2).

The contour levels corresponding to a_w are shown in Fig. 2. As observed, the rise in this variable is consistent with the rise in the fraction of water and soil. However, there exists a decrease in a_w which corresponds to the increase in SBP. It is due to the fraction of water retained which also diminishes. The a_w surface response (Fig. 2b) shows a zone of elevated values in which the a_w presents slight variations. This zone is located in the region of high values of the fraction of water and low values of the fraction of SBP. As the fraction of water diminishes the a_w surface shows descent and it is more pronounced by diminishing the fraction of contaminated soil. Fig. 2c depicts contour levels which correspond to the ε_0 of the mixture. As the fraction of water decreases, the ε_0 increases and as such as the fraction of soil present in the mixture is incremented it also increases. In fact, Fig. 2c illustrates that the major change in ε_0 is associated to the variation of water content in the mixture. This is possibly due to SBP swelling which compacts the material by absorbing water.

The ε_0 response surface (Fig. 2d) presents the form of a surface curve throughout its centre. Here, a maximum ε_0 is achieved when the water fraction is minimum (0.40) and the contaminated soil is maximum (0.40). The curvature is more pronounced as the fraction of SBP varies. Furthermore, the surface gradually descends until the fraction of water reaches its maximum value (0.80).

4.2. Cocomposting mixture

The operation point was selected dealing with the following composition: water fraction 0.60, contaminated soil fraction 0.15, and SBP fraction at 0.25. Table 2 shows a detailed composition of the mixture in the selected operation

Table 2
Mixture composition during hydrocarbon contaminated soil cocomposting

Principal component	Component	Subfraction (w/w)	Fraction (w/w)
f_b	SBP	0.14	
	Sucrose	0.07	
	K_2HPO_4	0.003	
	Urea	0.037	0.25
f_s	Contaminated soil	0.13	
	Activated sludge	0.02	0.15
f_w	Water	0.597	
	Mineral salts	0.003	0.60

point indicated in Fig. 2a–d. The mixture in this point had the best combination of high a_w and ε_0 (Fig. 2a and c) while maintains a ratio in weight of approximately 1:1 of SBP to contaminated soil. They were considered as raw materials without added substances. Similar ratios have been used by other authors [13,14,17], in which garden refuse such as leaves and twigs or any compost of different origin were used as agents of volume.

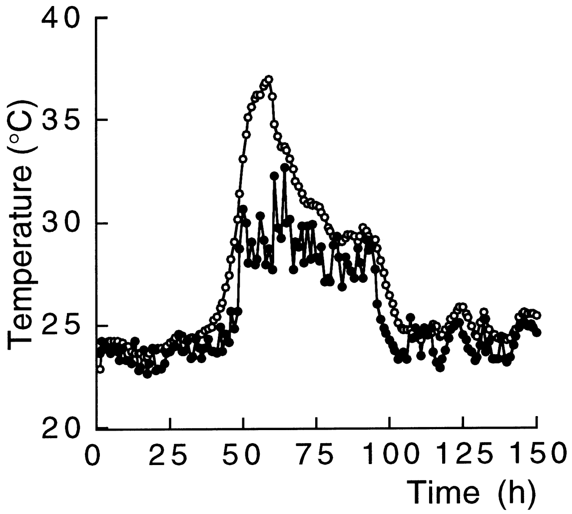

Fig. 4. Evolution of the temperature in the center (○) of the stainless steel bioreactor and in the controlled chamber (●) during cocomposting.

4.3. Evaluation test of the cocomposting mixture

Once the operation point was defined, an evaluation test of the cocomposting system was performed. For a moisture of 62.7 ± 0.46%, the initial a_w was 0.96 ± 0.006 which agrees with the prediction of the multiple regression model (Fig. 2a). Likewise, ε_0 was 0.69 and agrees with prediction of the (Fig. 2c).

The a_w evolution during the time of cocomposting 50 g columns is showed in Fig. 3. The increase in a_w can be associated to the microbial respiratory process. The falling in a_w is possibly due to the loss of water caused by forced air throughout the bioreactor [19]. The temperature profile over the 150 h is depicted in Fig. 4. Stainless steel bioreactor was used to promote natural self-heating, resulting temperature profile was used on-line as target to heat the chamber. Since stainless steel bioreactor and glass columns were incubated into the same chamber, we assure the same temperature profiles in both stainless steel and glass columns. Fig. 5 shows the production of CO_2 during the cocomposting. The greater production observed (between 40 and 85 h) agrees with the temperature profile (Fig. 4). It can be observed that maximum CO_2 production was obtained in the period of high temperature. This also corresponds to the period of greater a_w values, and can be related to sucrose uptake in the mixture.

The initial soil hydrocarbon content was 82,000 ± 1000 ppm constituted by four fractions as follows (in % w/w dry basis): aliphatics, 63.64; polars, 14.61; polyaromatics, 13.7 and asphalthenes, 8.05. The initial concentration of

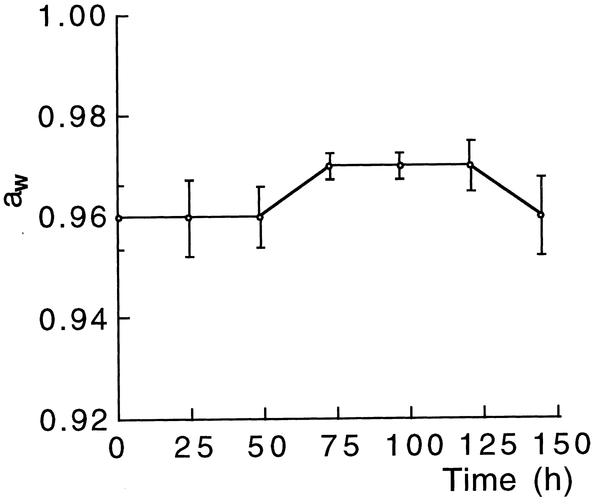

Fig. 3. Water activity (a_w) evolution during cocomposting.

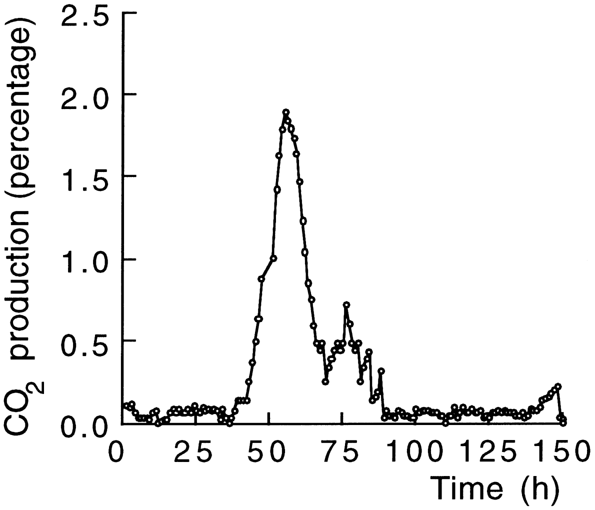

Fig. 5. Evolution of CO_2 during cocomposting.

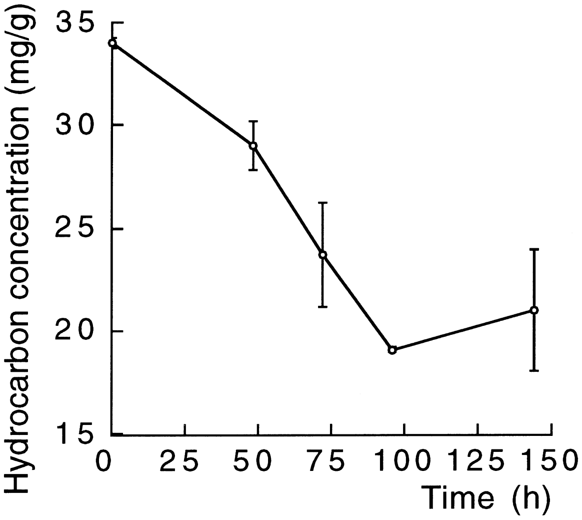

Fig. 6. Hydrocarbon biodegradation during cocomposting.

total hydrocarbons in the mixture was 34,000 ± 1000 ppm of dry matter. A hydrocarbon biodegradation of 38.6 ± 6.1% (w/w) was achieved in 150 h (Fig. 6). Since soil was obtained from a site contaminated for more than 10 years, volatile and leaching fractions were considered absent [15] and only the non-volatile fraction was taken into account.

Comparable values were found by Beaudin et al. [15], when degrading hydrocarbons in contaminated soil in Canada, in which maple leaves and alfalfa were used as the volume agent. Breitung et al. [18], achieved approximately 60% biodegradation of the contaminant in an aerobic cocomposting system with soils contaminated with 2,4,6-trinitrotoluene, and pieces of beet were used as a volume agent. Cassidy and Irvine [20], treated a soil contaminated with diesel by venting, without any volume agent and 22% of the contaminant was degraded.

5. Conclusions

The use of RSM to deal with appropriate values for a_w and the ε_0 in mixtures allows reliable experimental design in cocomposting. It avoids conventional trial and error time consuming methods. Resulting operation zones assure mixtures with a_w and the ε_0 values able to promote microbial activity and therefore hydrocarbon biodegradation in contaminated soil.

Under our experimental conditions, 38.6% of hydrocarbon degradation was observed in 150 h, using a model mixture (15% contaminated soil, 25% SBP and 60% water) containing 34,000 ppm of hydrocarbons coming from the surrounding areas of an oil-well.

Acknowledgements

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