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Kinetic modeling of hydrodistillation of *Ocimum basilicum* essential oil from the plateau des Cataractes (Congo Basin)

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Abstract

The extraction kinetics of the essential oil of *Ocimum basilicum* by hydrodistillation was studied for modelling its extraction process and optimizing its yield. The oils obtained, analyzed by GC/MS, are mainly composed of methylchavicol, linalool and 1, 8 cineole. Experimental data were fitted into first and second order kinetics for a 2-steps extraction (washing and diffusion) of the phenomenological model, according to the hypothesis used. When the washing step is negligible compared to that of diffusion, the mechanism, which is under kinetic control, admits first order. Considering both washing and diffusion steps, kinetic order became 2, in agreement with the Peleg model. The Monod and Langmuir models, also fitted experimental data. All these models validated by the experimental results with determination coefficients $R^2 > 0,90$ can be used for optimizing the extraction of the essential oil of *Ocimum basilicum*.

Keywords: Extraction, kinetic modeling, phenomenological model, *Ocimum basilicum*, "plateau des Cataractes"

1. Introduction

The genus *ocimum* includes 65-150 species distributed in the tropical and subtropical areas of Asia, Africa and South America with Africa, as the center of biodiversity dispersion [1]. *Ocimum basilicum*, commonly called basil, has considerable economic and cultural importance, particularly as food. Like some species of this genus, the essential oils of *Ocimum basilicum* exhibits many medicinal uses thanks to their antimicrobial, antioxidant properties.

The optimization of natural products extraction such as essential oils depends on the knowledge of fundamental physic phenomena; the way in which oil is released from the vegetable matrix, under the heat effect, for example.

Three techniques are generally used to extract essential oils from aromatic plants with water: water distillation, often called hydrodistillation in the strict sense (HD); steam distillation (SD), using water in the steam-water-distillation or steam-hydrodistillation (SHD), involving water in both vapour and liquid phases [2]; although the meaning of these terms may vary slightly from one author to another [3]. Essential oils can be synthesized and accumulated in different organs of the plant, including the leaves, flowers, seeds, bark and roots. In these organs, the production and storage of essential oils takes place in very specific and varied structures, such as glandular hairs in labiaceae, verbenaceae, gramineae; parenchyma cells modified for piperaceae; coniferous canals for conifers; schizogenetic cavities for myrtaceae, grasses; the lysegous cavities for the rustaceae; oil tubes for umbelliferaceae; resin canals for burceraceae and cistaceae [3]; essential oil cell, in zingiberaceae; secretory hairs, in laureaceae; secretory pockets, in myrtaceae; secretory canals, in asteraceae [4, 5]. Whatever the variant of steam-water-distillation implemented, hot water in liquid or vapor phase releases the essential oil from the structures in which it has been formed; the mixture of water and oil, in the vapor phase, inner the plant matrix released and passes through a condenser to lead a distillate in the liquid phase (water + oil). The essential oil is recovered by gravity.

Different models in the literature explain the mechanism of this process. Milojevic *et al.* [2], and Chan *et al.* [6] in two reviews found a very flexible activity which goes from the simplest models to extremely complex ones, based on natural laws or on empirical intuition.

A very large variety of plant species were studied: *Lavandula officinalis* [7], *Salvia officinalis* [8], *Thymus vulgaris* [9], *Apium graveolens* [10], *Ocimum basilicum* [11], *Mentha piperita* [12], *Eucalyptus grandis* [13], *Eucalyptus cinerea* [14], *Cymbopogon winterianus* [15, 16], *Cymbopogon* spp [17, 18], *Cymbopogon flexuosus* [19], *Cymbopogon citratus* [20].

Most of the models were gathered in two parts: (i) simple models leading to the calculation of the empirical parameters usable in the optimization of the material and the extraction processes without precise kinetic meaning of these parameters [2]; (ii) theoretical models claiming a physical meaning for the parameters used: models based on the solid-liquid partition thermodynamics, with or without mass transfer resistance to the outside, and the desorption kinetics of essential oils from plant matrix [19].

None of these studies were carried out on endemic or acclimatized essential oils in sub-Saharan Africa. A systematic work on the kinetic modeling of the extraction of essential oils from the Congo Basin is underway and this article reports the first results obtained on *Ocimum basilicum* leaves.

2. Material and Methods

2.1 Plant material

The studied samples were collected at random from the harvest of a 3 m by 12 m plot at the Nkama experimental field on the "plateau des Cataractes", Congo.



Fig 1: Basil plants from the Nkama experimental field

2.2 Kinetics of essential oil extraction

In a 2000 mL flask of a hydrodistillation device (fig. 2), 100-150 g of dried *Ocimum basilicum* leaves were distilled with 1200 mL of water, for 150 minutes and the distillate were collected separately every 10 minutes until 60 minutes and every 30 minutes up to 150 minutes. The essential oil was extracted with diethyl ether and the solution dried with sodium sulfate; the essential oil is recovered by evaporating of ethyl ether at the room temperature. If m_2 (g) is the essential oil mass obtained from m_1 g of plant material (dry matter basis), the essential oil content also called extraction yield is noted:

$$Y_t (\%) = (m_2/m_1)100$$

The experiment was carried out with 3 samples collected with the following ratios: (plant material mass)/(distillation water

volume): sample 1: 150 g/1.20L; sample 2: 100 g/1.20 L; sample 3: 147g /1.25L.



Fig 2: Laboratory hydrodistillation device

2.3 Chromatographic analyzes

2.3.1 Gas Chromatography (GC)

The quantitative analysis of the essential oil was carried out on an Agilent gas chromatograph, model 6890, equipped with a DB5 column (20m x 0,18mm x 0,18 μ m). The oven temperature was 50 °C for 3,2 minutes then increased to 300 °C at the rate of 10 °C per minute, that of the injector is 280 °C. This device was equipped with dihydrogen (40 ml/min)/air (450ml/min) flame ionization detector (FID) and its temperature maintained at 280 °C. The flow rate of the carrier gas (Dihydrogen) was 1 ml/minute.

2.3.2 Gas Chromatography (GC)/Mass Spectrometry (MS) Tandem

The qualitative analysis was carried out using an Agilent gas chromatograph, model 7890 coupled to an Agilent mass spectrophotometer, model 5975, equipped with a DB5 column (20 mx 0,18 mm x 0,18 μ m). The oven temperature was 50 °C and remains constant for 3,2 minutes then increases to 300 °C at the speed of 8 °C per minute, that of the injector is 280 °C. Ionization was done by electronic impact at 70 eV. The carrier gas flow rate (helium) was adjusted to 0,9 ml/minute. The mass acquisition was made using a mass scan of m/z: 33-450 uma. The identification of the compounds was carried out by comparison of their mass spectra and their retention indices (RI) with those of the databases [21-23] and those of the LEXVA-Analytique laboratory.

2.4 Modeling the extraction of essential oils

Different ways are used to model extraction of the metabolites from plant matrices: simple laws of formal kinetics, physical laws (Fick's law, Langmuir adsorption isotherm) and empirical intuition [24-25].

The simplest models are those using "black box" principles (input / output). One observes the transfer of matter through a "black box" and derive simple mathematical equations from the model, without claiming a detailed understanding of the process mechanism inside the box.

In the literature, the explanations proposed for the extraction

of metabolite generally take two complementary approaches: (i) the first which considers the diffusion of the metabolite inside the plant matrix as a limiting step in a two-step process (washing/diffusion); it is based on diffusion Fick's law and therefore leads to the diffusion model [26, 27, 28]; (ii) the second which considers the extraction as a desorption of the metabolite from the plant matrix and which is based on Peleg's work [29] has been successively adapted to the extraction of polyphenols by Bucic Kojic *et al.* [30] and of essential oils by Farhana [31]; it is also a two-step process:

desorption and elution, with desorption as a limiting step related to the intra particle diffusion of the solute. These two paths finally lead to the same overall explanation of the extraction phenomenon, namely: a two-step process (washing / diffusion or elution/desorption) taking place on one or two sites (broken cells, intact cells) according to phenomenological approach. Table 1 summarizes the main simple models found in the literature for the essential oil extraction.

Table 1: Overview of the main models used in the study of essential oil extraction

References	Models	Term meaning
Ameneghawon <i>et al.</i> [18]	First order kinetics $dC_t/dt = k (C_0 - C) \ln(C/C_0) = -kt$; $t_{1/2} = 0,693/k \ln(1/(1-y(t))) = kt$	C_t , concentration or mass of oil in plant matrix at time t ; C_0 , initial concentration or mass of oil in plant matrix; k , first order kinetic constant; $y = (C_0 - C) / C_0$: extracted EO ratio
Thanh <i>et al.</i> [20] Sepidar <i>et al.</i> [32]	Second order kinetics $dC_t/dt = k (C_s - C_t)^2 (C_t = C_s^2 kt) / (1 + C_s kt)$ $(1/C_t) - (1/C_s) = kt / C_t = 1/(kC_s^2) + t/C_s$	C_t , concentration of extracted oil at time t (g, L^{-1}); C_s , concentration of extracted oil at saturation (g, L^{-1}); k , second order kinetic constant ($g L^{-1} min^{-1}$); $h = kC_s^2$: initial extraction rate ($g L^{-1} min^{-1}$),
So and Macdonald [24]	So and Macdonald Washing: $C_L^w = C_L^{*w} (1 - \exp(-K_c^w t))$ Diffusion: $C_L^d = C_L^{*w} (1 - \exp(-K_c^d t))$ washing/diffusion $C_L = C_L^{*w} (1 - \exp(-K_c^w t)) + C_L^{*w} (- \exp(-K_c^d t))$	C_L : concentration of extracted oil; C_L^w : concentration of extracted oil (washing step); C_L^d : concentration of extracted oil (diffusion step) K_c^w : kinetic constant (washing step); K_c^d : kinetic constant(diffusion step)
Desai <i>et al.</i> 2014 [19]	Desai $S_t/S_0 = 1 - [F, \exp(-k_1 t)] - [(1-F) \exp(-k_2 t)]$	S_t : mass(t); S_0 : initial mass; k_1 : first fraction kinetic constant (F); k_2 : second fraction kinetic constant ($1-F$),
Milojevic <i>et al.</i> [2]	Milojevic $q_t/q_\infty = f \exp(-k_1 t) + (1-f) \exp(-k_2 t)$	q_p quantity of EO in plant matrix at time t ; q_∞ quantity of EO in plant matrix at time t_∞ ; k_1 et k_2 : kinetic constants (washing and diffusion); f : fraction extracted by washing; $1-f$: fraction extracted by diffusion,
Mejri <i>et al.</i> [33]	Monod $Y_t = Y_{max} [1/(K_m + t)]$ $1/Y_t = (K_m/Y_{max}) (1/t) + (1/Y_{max})$	Y_t : yeild of extracted oil at time t ($g/100g$); Y_{max} yeild at time t_∞ ; Y_{max}/K_m : slope of straight line, K_m : Monod equation parameter,
Babu and Singh [14]	Langmuir $Y_t = Y_{max} t / (b + t)$ $1/Y_t = (b/Y_{max}) (1/t) + 1/Y_{max}$	Y_t : yeild of extracted oil at time t ($g/100g$); Y_{max} : yeild at time t_∞ , $b/Y_{max} =$ slope of straight line; $1/Y_{max}$, ordinate at the origin,
Peleg, [29] Bucic-Kojic <i>et al.</i> [30], Shafaei <i>et al.</i> [34]	Peleg $C_t = C_0 \pm t / (k_1 + K_2 t)$ $t/C_t = k_1 + K_2 t$	C_t : concentration or mass of extracted EO at time t (m_t); C_∞ : concentration or mass of extracted EO at t_∞ (m_∞); $C_0 = 0$: the mass of extracted EO at $t = 0$; k_1 : kinetic first order extraction constant; K_2 , extraction capacity constant,

2.5 Statistical processing

The descriptive statistics and the graphic representations were carried out on Microsoft Excel 2010.

3. Results and Discussion

3.1 Extraction of the *Ocimum basilicum* essential oil

3.1.1 Characterization of the essential oils studied

The very low values of the standard deviation of the oil content and constituent composition of samples studied highlights similitarity of essential oils from Nkama experimental field on the “plateau des Cataractes” in Congo-Brazzaville (Table 2).

The samples of *Ocimum basilicum* studied were rich in essential oil with an average content of $2.36 \pm 0.31\%$ (dry

matter), while, the *Ocimum basilicum* acclimated in sub-Saharan Africa yielded, 1.4-2.2% in Togo [35], 0.96-1.20% in Congo-Brazzaville [36] 0.92% in Nigeria [37], 0.71% in Sierra Leone [37], 0.17-4.25 in Guinea-Conakry [38]. On a global scale, this yield is on average less than 1% with significant variability depending of the climate and the harvest period [1]. It is a monoterpenic essential oil mainly composed of 1,8 cineole ($12.75 \pm 0.01\%$), linalool ($36.09 \pm 0.02\%$), methylchavicol ($40.66 \pm 0.01\%$) and some minors compounds with about 1% of individual content: limonene (0.988%), pinene (1.223%), camphor (1.556%), Only two sesquiterpenes: *trans alpha* bergamotene ($0,932 \pm 0,002\%$) and *alpha* cadinol ($0.789 \pm 0.014\%$), were detected with significant content.

Table 2: Essential oil content and composition of the three samples of *Ocimum basilicum* acclimated on the “plateau des Cataractes” in Congo-Brazzaville

Sample références				OB 01/19	OB 02/19	OB 03/19	Mean ± SD
Essential oil content (%)				2.12	2.16	2.80	2.36±0.31
N°	RT	KL _c	KL _{lit}	Content (%)			
1	11.008	935	932	<i>alpha</i> pinene			
2	11.657	952	946	camphene			
3	12.494	975	969	camphene			
4	12.691	980	974	<i>beta</i> pinene			
5	12.842	984	974	oct-1-en-3-ol			
6	13.054	990	988	myrcene			
7	14.537	1032	1024	limonene			
8	14.730	1037	1026	1.8-cineole			

9	15.081	1047	1032	Z <i>bé</i> ta-ocimene	0.586	0.588	0.584	0.586±0.002
10	15.530	1060	1054	<i>gamma</i> terpinene	0.061	0.061	0.061	0.061±0.000
11	16.026	1075	1067/	<i>cis</i> oxyde de linalol	0.168	0.164	0.167	0.166±0.002
12	16.443	1087	1086	terpinolene	0.105	0.105	0.104	0.105±0.001
13	16.544	1089	1084	<i>trans</i> oxyde de linalol	0.055	0.054	0.055	0.055±0.001
14	17.133	1107	1095	linalol	36.089	36.069	36.117	36.092±0.024
15	18.226	1144	1140	E-myroxyde	0.127	0.124	0.127	0.126±0.002
16	18.690	1159	1141	camphre	1.566	1.565	1.567	1.566±0.001
17	19.348	1181	1162	<i>delta</i> terpinéol	0.193	0.193	0.194	0.193±0.001
18	19.640	1191	1174	A terpinène-4-ol	0.213	0.213	0.213	0.213±0.000
19	20.341	1214	1195	methyl chavicol	40.673	40.657	40.658	40.663±0.009
20	20.873	1233	1223	citronellol	0.217	0.214	0.212	0.214±0.003
21	21.329	1248	1235	neral	0.111	0.109	0.109	0.110±0.001
22	21.605	1258	1249	geraniol	0.322	0.315	0.314	0.317±0.004
23	22.179	1277	1264	geraniol	0.159	0.157	0.156	0.157±0.002
24	25.088	1383	1379	geranyl acetate	0.084	0.083	0.083	0.083±0.001
25	25.135	1385	1374	<i>alpha</i> copaene	0.068	0.067	0.067	0.067±0.001
26	25.477	1397	1385	<i>beta</i> elemene	0.191	0.191	0.190	0.191±0.001
27	26.580	1440	1432	<i>trans alpha</i> bergamotene	0.932	0.930	0.934	0.932±0.002
28	26.997	1456	1444	Z- <i>beta</i> -farnesene	0.050	0.048	0.049	0.049±0.001
29	27.314	1469	1452	<i>alpha</i> humulene	0.063	0.061	0.063	0.062±0.001
30	27.463	1475	1465	Muurola-4(14).5-diene< <i>cis</i> ->	0.056	0.056	0.056	0.056±0.000
31	27.947	1494	1484	germacrene-D	0.228	0.226	0.227	0.227±0.001
32	28.316	1509	1500	bicyclogermacrene	0.062	0.061	0.063	0.062±0.001
33	28.421	1513	1509	<i>alpha</i> bulnesene	0.037	0.036	0.037	0.037±0.001
34	28.732	1526	1513	<i>gamma</i> cadinene	0.298	0.302	0.299	0.300±0.002
35	28.800	1529	1522	<i>delta</i> cadinene	0.095	0.097	0.095	0.096±0.001
36	28.907	1533	1521	<i>beta</i> sesquiphellandrene	0.090	0.093	0.092	0.092±0.002
37	29.263	1548	-	<i>alpha</i> bisabolene	0.228	0.229	0.229	0.229±0.001
38	29.602	1562	1548	elemol	0.185	0.185	0.186	0.185±0.001
39	31.252	1632	-	<i>epi</i> cubenol	0.120	0.119	0.119	0.119±0.001
40	31.873	1659	-	<i>epi alpha</i> cadinol	0.755	0.758	0.762	0.758±0.004
41	32.192	1673	1652	<i>alpha</i> cadinol	0.034	0.057	0.032	0.041±0.014
42	32.249	1675	1652	<i>alpha</i> eudesmol	-	0.039	-	-
				Total	100.001	99.959	99.998	-

RT: retention time; KI_c: Kovat’s Index calculated; KI_{lit}: Kovat’s Index in literature

European sweet basil mainly contains linalool and methyl chavicol, it is very close to Egyptian basil. Basil from the Indian Ocean Islands, Vietnam and Thailand is rich in methylchavicol, while basil from Bulgaria, India, Guatemala and Pakistan is rich in methyl cinnamate. Russia, Java and North Africa produce an essential oil rich in eugenol [1]. The basil acclimatized at Nkama on the “plateau des Cataractes” was of the "European type" with 1, 8 cineole in addition.

3.1.2 Characterization of the extraction curve of *Ocimum basilicum* oil

The yield variation (Y_t) of the extraction of *Ocimum basilicum* essential oil is reported in Table 3 for 3 samples of the Nkama experimental field on the “plateau des Cataractes”.

Table 3: Yield (%) of *Ocimum basilicum* essential oil extracted by hydrodistillation as a function of time t (min)

t (min)	10	20	30	40	50	60	90	120	150
OB1	1.16	1.65	1.93	2.01	2.02	2.09	2.09	2.12	2.13
OB2	1.51	1.80	1.94	2.03	2.1	2.11	2.14	2.15	2.16
OB3	1.64	2.14	2.39	2.54	2.64	2.68	2.74	2.77	2.80
Mean	1.44	1.86	2.09	2.19	2.25	2.29	2.32	2.35	2.36
SD	0.25	0.25	0.26	0.30	0.34	0.34	0.36	0.37	0.38

Figure 3. Represents the extraction curve of the essential oil from sample 1, It is characteristic for a two-period process: washing (step 1)/diffusion (step 2) in the literature for metabolite extraction from plant solid matrices [6].

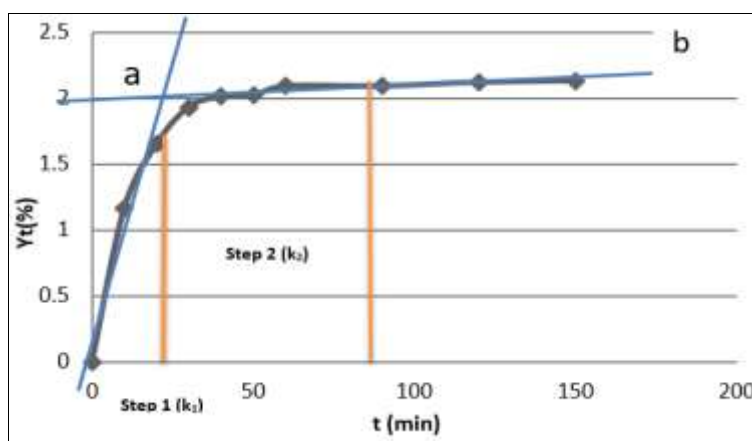


Fig 3: Yield variation of essential oil extraction from the leaves *Ocimum basilicum* dried one week in the open air (OB1),

The first step ($t < 20$ min) with a sharp yield increase corresponding to the rapid washing of the oil from the broken cells (curve a, rate constant k_1), were followed by a longer step with a smaller yield increase ($20 \text{ min} < t < 90$ min (curve b, kinetic constant k_2) corresponding to oil diffusion inner intact cells, and an asymptotic ending of the process ($t > 90$ min). The slope break between lines a and b showed the

change in the mechanism and validated a two-steps process assumption, The maximum extraction yield were estimated at 2.13%, value after 150 min extraction and validated by plotting $1/Y_t = f(1/t)$: a straight line whose ordinate at the origin $1/Y_t (t = \infty)$ allowed to $Y_\infty = 2.17\%$ (figure 4). The extraction ratio at 150 min $(Y_{150\text{min}}/Y_\infty) = (2.13/2.17)100 = 98\%$.

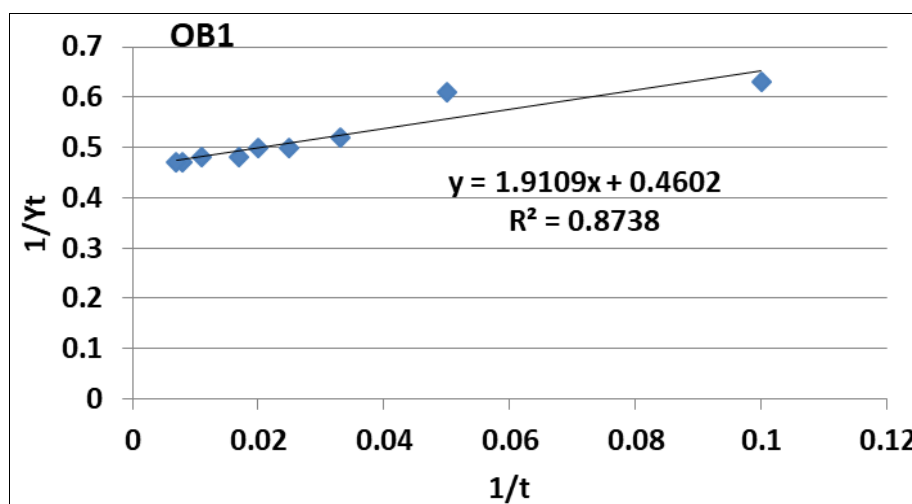


Fig 4: Graphical evaluation of Y_{max} for the sample OB1,

3.2 Test of the first-order kinetic model

With first-order kinetic model, experimental data should fit the following equation:

$$\ln(1/(1-y)) = kt,$$

Values of Y_{max} , (y at 150 minutes), k and validation equations were gathered in table 3 for the 3 samples studied.

Table 3: Values of Y_{max} , of k and expressions of the validation equations

	OB1	OB2	OB3
$Y_{\text{max}} (150 \text{ min})$	2.13	2.16	2.80
$1/Y_t = f(1/t) (R^2)$	$1/Y_t = 1.9109(1/t) + 0.4602 (0.8738)$	$1/Y_t = 2.1772 (1/t) + 0.4444 (0.9902)$	$1/Y_t = 2.7771(1/t) + 0.3308 (0.9924)$
Y_∞	2.17	2.25	3.02
$y = Y_t / Y_{\text{max}} = (t=150 \text{ min})^*$	0.98	0.96	0.93
$\ln (1/(1-y)) = kt (R^2)$	$\ln (1/(1-y)) = 0.0741.t + 0.2867 (0.9359)$	$\ln (1/(1-y)) = 0.0591.t + 0.326 (0.9661)$	$\ln (1/(1-y)) = 0.0328.t + 0.9366 (0.967)$
$k (\text{min}^{-1})$	0.0741	0.0591	0.0328

* Extraction rate

The maximum extraction yield varies from 2.13 to 2.80% leading to extraction ratio of 93-98%, and of kinetic constant values ($k = 0.0328\text{-}0.0741 \text{ min}^{-1}$) which were similar to those already reported in the literature. Amenaghawon *et al*, [18] found $k = 0.045 \text{ min}^{-1}$, for the steam distillation of 100 g lemongrass (*Cymbopogon ssp.*) which they consider as the pseudo first order kinetic constant related to the vapourization step of essential oils in the plant matrix during the extraction process, Tang *et al*, [20] validated this model with a determination coefficient $R^2 = 0.9426$ and a kinetic constant $k = 0.024 \text{ min}^{-1}$ for the steam distillation of 9.5 kg of lemongrass. Mejri *et al*, [33] working on the hydrodistillation of 50 g of *Ruta chalepenis* ($k = 0.0266 \text{ min}^{-1}$ and $R^2 = 0.89$) did not retain this model and move towards more complex alternative models.

3.3 Test of the Peleg model

The Peleg [29] model has been proposed to explain the asymptotic behavior of the evolution of several natural phenomena, including the sorption of certain constituents by plant matrices.

Peleg assumes the following model:

$$Y_t = Y_0 \pm t / (k_1 + K_2 t) \text{ Eq6}$$

with: \pm meaning sorption, adsorption (+) and desorption, (-); C_t : concentration or mass of essential oil extracted at time t (m_t); C_∞ : concentration or mass of essential oil extracted at t_∞ (m_∞); $C_0 = 0$: the mass of essential oil extracted at $t = 0$; k_1 : extraction kinetic constant of first order; K_2 , extraction capacity constant related to equilibrium at the end of the process [29], Eq6 could be re-written in its following linearized form:

$$t/Y_t = k_1 + K_2 t \text{ Eq7}$$

Eq7 is used to validate Peleg model (table 4, figure 5).

Table 4: Data used for the test of the Peleg model for the hydrodistillation of the *Ocimum basilicum* essential oil

t(min)	10	20	30	40	50	60	90	120	150
$t/Y_t(\text{OB1})$	8.62	12.12	15.54	19.90	24.75	28.71	43.06	56.60	70.42
$t/Y_t(\text{OB2})$	6.62	11.11	15.46	19.70	23.81	28.44	42.06	55.82	69.44
$t/Y_t(\text{OB3})$	6.10	9.35	12.55	15.75	18.94	22.39	32.85	43.32	53.57

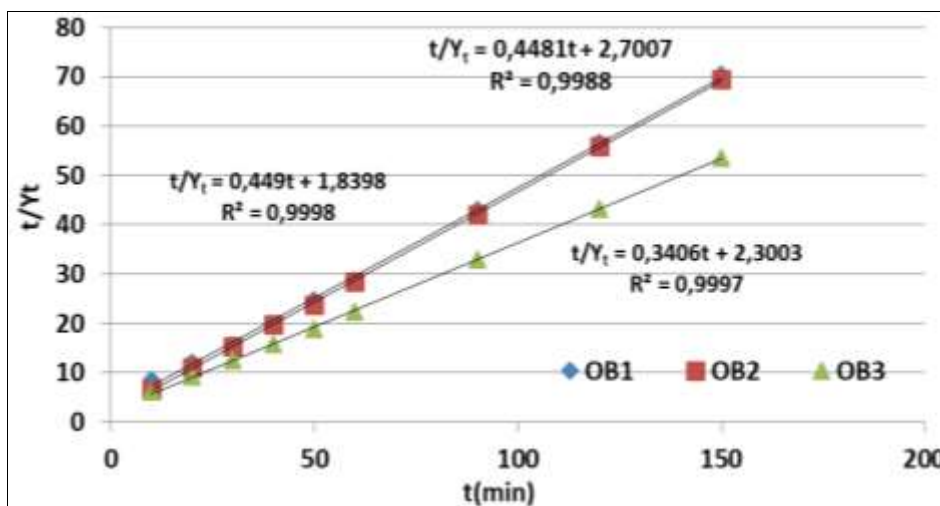


Fig 5: Validation straight lines of the Peleg model for hydrodistillation *Ocimum basilicum* essential extraction

The similarity between $t/Y_t = f(t)$ for the extraction of the *Ocimum basilicum* essential oil leads to straight lines (Fig. 4). With very good coefficients of determination ($R^2 > 0.998$). Thus validating the Peleg model for the extraction of this essential oil. The rate constant k_1 varies from 1.8398-2.7007 $\text{min}\cdot\%^{-1}$ and the extraction capacity constant $K_2 = 0.3406-0.449\%^{-1}$. These constants are to be compared to those calculated by Farhana [16] for the extraction of the essential oil of *Cymbopogon winteranius* ($k_1 = 19.09 \text{ min}$. and $K_2 = 0.0301(\text{g/g})^{-1}$).

3.4 Test of Monod and Langmuir models

These two models are validated by the same linearized equation of $1/Y_t = f(1/t)$.

Monod's model, inspired by Michaelis enzymatic kinetics

leads to following mathematical expression: $Y_t = Y_{\max} [t/(K_m + t)]$ and to its linearized inverse: $1/Y_t = (K_m/Y_{\max}) (1/t) + 1/Y_{\max}$. (table 5, Fig. 6) One obtains a line leading to Y_{\max} and K_m . Y_{\max} were the yield at $t = \infty$ (end of the extraction process) and K_m / Y_{\max} : slope of the line. For the 3 samples studied we obtain straight lines with good determination coefficients ($R^2 = 0.87-0.99$) which allow us to calculate $Y_{\max} = 2.18-3.00\%$ and $K_m 3.761-5.331 \text{ min}\cdot\%^{-1}$.

Table 5: Data used for the test of Monod and Langmuir models for the hydro distillation of the *Ocimum basilicum* essential oil

1/t	0.100	0.050	0.033	0.025	0.02	0.017	0.011	0.008	0.007
1/Y _t (OB1)	0.63	0.61	0.52	0.50	0.50	0.48	0.48	0.47	0.47
1/Y _t (OB2)	0.66	0.56	0.52	0.50	0.48	0.47	0.47	0.47	0.46
1/Y _t (OB3)	0.61	0.47	0.43	0.39	0.38	0.37	0.36	0.36	0.36

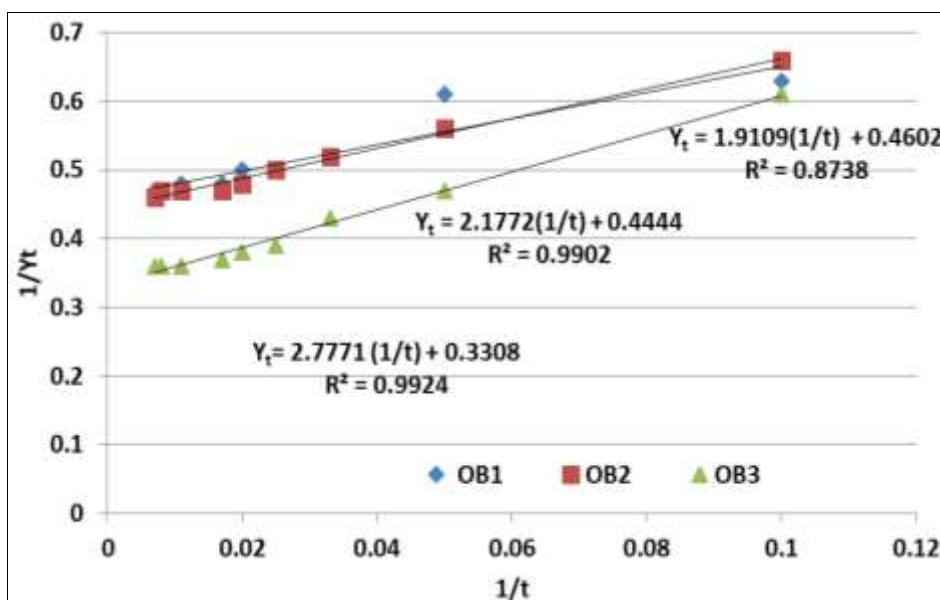


Fig 6: Validation straight-lines of the Monod and Langmuir models for the hydrodistillation of the *Ocimum basilicum* essential oil

These values should be compared with those obtained by Mjeri *et al.* [33] for ($Y_{\max} = 6 - 8 \text{ mL}/100\text{g}$ and $K_m = 56-98 \text{ min},(\text{mL}/100\text{g})^{-1}$) which contains 3 to 4 times more essential oil and which is extracted almost 10 times faster.

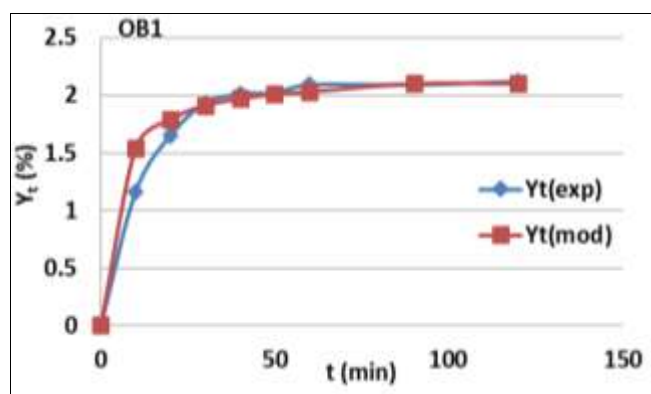
Langmuir's gas adsorption isotherm model is mathematically expressed by the equation: $Y_t = Y_{\max}, t/(b + t)$ with Y_t = yield at time t ; Y_{\max} , the yield at $t = \infty$ and b/Y_{\max} , the slope of the curve at the initial instants, The opposite form: $1/Y_t = (b/Y_{\max})$

$(1/t) + 1/Y_{\max}$ gives a straight line with: slope = b/Y_{\max} and an ordinate at the origin $1/Y_{\max}$ [14]. Fig. 5 represents the straight lines obtained for *Ocimum basilicum* acclimated on the "plateau des Cataractes" which admits the same validation equation as the Monod model: with Y_{\max} which remains unchanged; only K_m becomes b and changes its meaning (Table 5).

Table 6: Parameters and equation of the Langmir and Monod models

Langmuir Model			
Samples	Y_{max}	K_m	Equation
OB1	2.17	4.019	$Y_t = 2.17 [t/(4.019 + t)]$
OB2	2.25	4.898	$Y_t = 2.25 [t/(4.898 + t)]$
OB3	3.02	8.395	$Y_t = 3.02 [t/(8.395 + t)]$
Monod Model			
Samples	Y_{max}	b	Equation
OB1	2.17	4.019	$Y_t = 2.17 [t/(4.019 + t)]$
OB2	2.25	4.898	$Y_t = 2.25 [t/(4.898 + t)]$
OB3	3.02	8.395	$Y_t = 3.02 [t/(8.395 + t)]$

The mathematical expressions of the models obtained are given in table 5. By recalculating the values of Y_t generated by the models with different values of t , we can check the validity of models either by the level of correlation between the experimental values and the values of the model (0.9624) or by superimposing the experimental curve $Y_t = f(t)$ and the curve of the model as indicated by the example of sample OB 1 (fig. 7).

**Fig 7:** Validation of the Langmuir Model for the sample OB1,

4. Conclusion

The extraction of the essential oil of *Ocimum basilicum* occurs according to the phenomenological model proposed by So *et al*, [24] and adapted to essential oils by certain authors [2-15]. The oil behaves like a macro-compound which diffuses into the plant matrix cells which have remained intact during the extraction, dissolves in the extraction solvent which has penetrated into the matrix and exits towards the extraction solvent by gradient effect crossing the solid-liquid barrier, symbolized by a vegetable resistance film. From broken cells, oil is instantly dissolved in the solvent in a rapid washing. The extraction therefore takes place in two steps of different rates characterized by a break in slope on the curve $Y_t = f(t)$; it is formally of second order kinetic. When the washing step is negligible compared to that of diffusion, the mechanism runs with a first order. The rate constant (k) measured is 0.0553 min^{-1} for a maximum extraction yield (Y_{max}) of $2.80 \text{ g}/100\text{g}$ corresponding to an extraction ratio of 93% at 150 minutes. If one considers both the washing and diffusion steps, extraction leads to a second order kinetic and fits the Peleg model, which is a two-parameter model: the kinetic rate constant and the extraction capacity constant). The kinetic data validate the Monod and Langmuir models. All these models fitted by the experimental results with determination coefficients $R^2 > 0.90$ can be used for the modeling and optimization of the extraction of the essential oil of *Ocimum basilicum*.

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