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Optimization of adsorption parameters of carotenoids from palm oil on montmorillonite clays for using in mask face

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Abstract

The adsorption of carotenoids from palm oil on montmorillonite clays from Maroua in the Far North Region of Cameroon was carried out by optimisation of some parameters. The physicochemical characterization of carotenoids was performed by determination of absorbance using the UV-Visible Spectrophotometer and making High Performance Liquid Chromatography. The amount of carotenoids adsorbed was determined by making the difference in optical density before and after adsorption. In order to determine the magnitude of adsorption from a reduced number of experiments, the centered composite design was adopted through three factors which can influence the adsorption: time (15 - 45 min), temperature (25 - 65 °C) and the concentration (20 – 50 mg.L^{-1}). Of these three independent variables, the concentration was the factor which had a greater influence on the response surface and the iso-response of the adsorption (about 84%), while temperature influenced the least (i.e. around 0.77%). The optimum amount of carotenoids adsorbed was 1.76 mg.g^{-1} for the contact time values of 30 minutes and the initial concentration of 35 mg.L^{-1}. The coefficient of determination, the absolute analysis of the mean deviation, the bias factor and the accuracy factors made it possible to validate the model.

Keywords: adsorption, carotenoids, clays, optimization.

Résumé

L'adsorption des caroténoïdes de l'huile de palme sur les argiles en provenance de Maroua dans la région de l'Extrême Nord au Cameroun a été effectuée. L'absorbance a été effectuée grâce au Spectrophotomètre UV-Visible et qualifiée par Chromatographie Liquide Haute Performance. La quantité de caroténoïdes adsorbée est déterminée en faisant la différence de densité optique avant et après adsorption. Afin de déterminer la grandeur d'adsorption à partir d'un nombre réduit d'expériences, le plan composite centré a été adopté à travers trois facteurs pouvant influencer l'adsorption : le temps (15- 45 min), la température (25 – 65 °C) et la concentration (20 – 50 mg/L). De ces trois variables indépendantes, la concentration est le facteur qui a une plus grande influence sur la surface de réponse et d'iso réponse de l'adsorption (soit environ 84%), alors que la température influence le moins (soit environ 0,77%). L'optimum de la quantité de caroténoïdes adsorbée est de 1,76 mg/g pour les valeurs de temps de contact de 30 minutes et de concentration initiale de 35 mg/L. Le coefficient de détermination, l'analyse absolue de la déviation moyenne, le facteur de biais et les facteurs des exactitudes ont permis de valider le modèle.

Mots clés *:* adsorption, argiles, caroténoïdes, optimisation.

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PART 1. SCIENTIFIC RESEARCH

Introduction

Carotenoids are hydrocarbon compounds mainly synthesized by plants. They are responsible for the intensity of the yellow, orange and red colours of many plants and vegetables. They have antioxidant properties due to the presence of a system of conjugated double bonds in the molecule[1,2]. Carotenoids have been the subject of numerous scientific studies in the food industry, mainly because most of these are precursors of vitamin A[3,4,5]. Among the many plants rich in carotenoids, there is palm oil which contains an average of 700 ppm.[6,7]. However, these carotenoids are highly sensitive to light and oxygen, a clay support would limit these effects. Clays are minerals with large specific surface areas, chemical inertness and excellent rheological properties[8]; for these properties they are much use as mask face to improve the general state of skin and can be better by adding the antioxidants properties of carotenoids. The Maroua town in the Far north Region of Cameroon is full in montmorillonite clay with their large specific area suitable for a best adsorption[9,10]. On the other hand, the optimal adsorption conditions can be defined through the experimental designs. The experimental plans make it possible to best organize the tests that accompany scientific research. They are applicable to many disciplines from the moment one searches for the link that exists between a measurement of interest, y, and variables, x_i. With the experience plans we get the maximum information with the minimum experiences. To do this, mathematical rules must be followed and a rigorous approach adopted[11].

Results and Discussion

Figure 1 and 2 present absorption spectrum of palm oil in petroleum ether

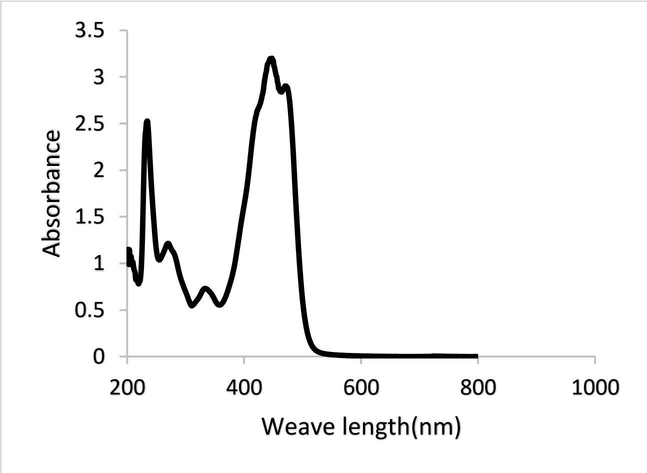

Fig. 1. Absorption spectra of extract of palm oil in petroleum ether.

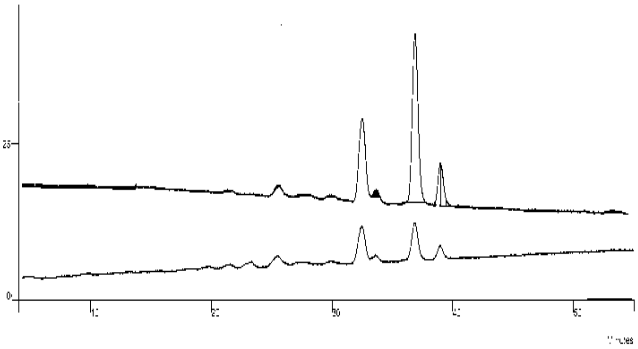

Fig. 2. High Performance Liquid Chromatography analysis of carotenoids from palm oil before (———) and after adsorption (—).

In the absorption spectrum, the carotenoids peaks were clearly visible (416 nm, 439 nm and 467 nm).
The identification and quantification of individual carotenoids in the extracts of palm oil were performed by HPLC before and after adsorption show that a quantity was adsorbed as shown on the difference of intensity of peak. Otherwise, this analyse confirm the three main carotenoids obtain in adsorption.

The main experimental and theoretical responses of the experimental design are presented in Table 1 below for the absorption of carotenoids from palm oil on Maroua clay

Table 1. Effect of different factors on the absorption of carotenoids from palm oil on Maroua clay.

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N°	Coded values			Amount adsorbed			
	X_1	X_2	X_3	Observed	Calculated	difference	Y %
1	-1	-1	-1	1.200	1.279	0.079	64.320
2	1	-1	-1	1.200	1.308	0.108	64.320
3	-1	1	-1	0.990	1.068	0.078	53.064
4	1	1	-1	1.200	1.251	0.051	64.320
5	-1	-1	1	1.632	1.670	0.038	58.317
6	1	-1	1	1.730	1.740	0.010	61.819
7	-1	1	1	1.652	1.632	0.020	59.031
8	1	1	1	1.846	1.855	0.009	65.964
9	-1.68	0	0	1.535	1.473	0.062	58.769
10	1.68	0	0	1.749	1.686	0.063	66.962
11	0	-1.68	0	1.749	1.652	0.097	66.962
12	0	1.68	0	1.600	1.572	0.028	61.257
13	0	0	-1.68	1.000	0.855	0.145	38.286
14	0	0	1.68	1.671	1.692	0.021	63.975
15	0	0	0	1.692	1.699	0.007	64.779
16	0	0	0	1.693	1.699	0.006	64.818
17	0	0	0	1.692	1.699	0.007	64.779

From this table, it can be noted that variations in temperature, time and the initial carotenoids concentration had an influence on the experimental response observed. The results obtained show overall that there was no significant difference between the quantities adsorbed experimentally and the quantities adsorbed theoretically, the small differences observed was due to the variation in the physicochemical conditions of the medium.

More particularly, the combinations of the three parameters with maximum concentrations gave the largest adsorbed quantities, while the combinations with the minimum concentrations presented the least adsorbed quantities. These observations were made both for the calculated values and for the observed values.

1- Regression coefficient and model proposal

The regression coefficient for the empirical model given by the centered composite matrix was determined. The amount of carotenoids adsorbed (µmol/g) was defined by the following model:

$$Y= 1.699 + 0.063X_1 – 0.024X_2 + 0.249X_3 – 0.042X_1^2 + 0.038X_1X_2 + 0.010X_1X_3 – 0.031X_2^2 +0.043X_2X_3 – 01.51X_3^2$$

This model shows that of the three independent variables, the carotenoids concentration was the factor that most influenced the amount of carotenoids adsorbed

Taking the linear factors, we see that time and concentration influenced positively on the adsorption, while temperature influenced negatively.

When we take the quadratic effect of the factors did not have a significant effect, unlike interactions which had a significant effect.

The influence levels of the different factors to better visualize (through the percentages) the contribution of the different independent variables on the quantity of carotenoids adsorbed is presented in Figure 3.

It appears from this figure that the concentration was the factor which influenced mainly on the adsorbed quantity (about 84%), while the temperature influenced the least (about 0.77%). This observation, which confirms the previous results, is in line with the observed values.

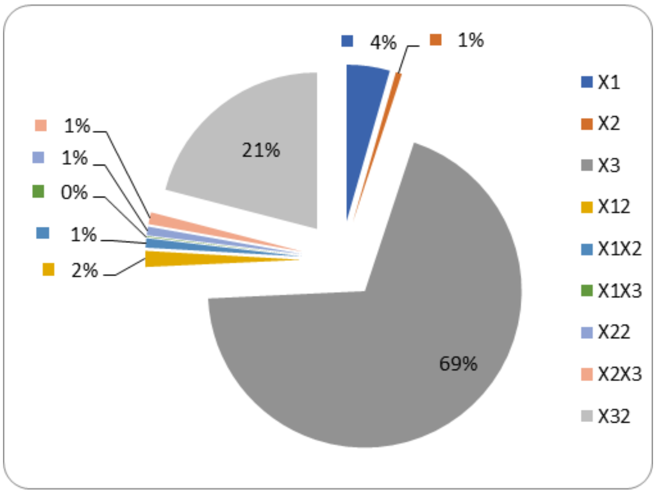


Fig. 3. Contribution of the different factors on the quantity adsorbed.

2- Validation of the model

The calculation of the coefficient of determination (R^2) for the proposed model gave 94.58% and 87.62% after adjustment. This result shows that the proposed model can be accepted, because for a good fit of a model, according to Joglekar and May[12], the coefficient of determination R^2 should be at least equal to 0.80. The plot shown in Figure 4 giving the relationship between the experimental response and that generated by the model confirms the agreement of the model.

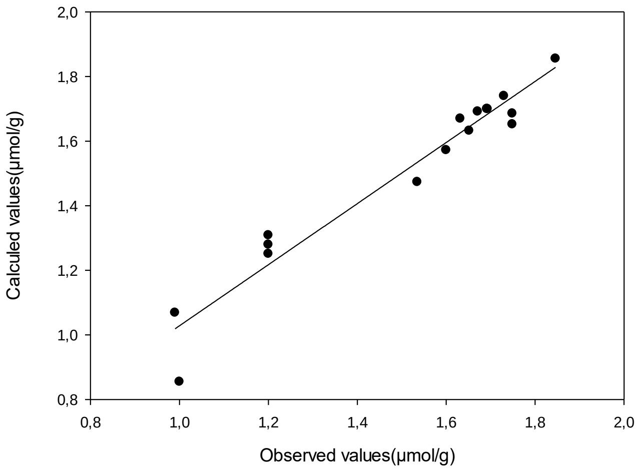


Fig. 4. Comparison of experimental and theoretical values for the quantity of carotenoids adsorbed.

In addition, the absolute mean deviation analysis (AADM) gave a value of 0.01. This value close to 0 confirms that the model can be used to generate the response surface curves and explain the action of the different independent variables having a significant effect on the studied response; because according to Bas and Bayac[13] , the value for the AADM must be between 0 and 0.2.

The determination of the bias factor (B_f) gave a value of 1.006. This result shows that the proposed model can be accepted, because according to Dalgaard and Jorgesen[14] , this value must be less than or equal to 1.20.

The determination of the accuracy factors ($A_{f1},2$) gave the values of 1.1 and 1.01 for $Af1$ and A_{f2} respectively. This result shows once again that the proposed model can be accepted; because according to Dalgaard and Jorgesen[14] , this value must be greater than or equal to 1.

3- Analysis of variance

Statistical analysis for the four factors studied leads to the following variance analysis table:

Table 2. Analysis of variance for the quantity of carotenoids adsorbed on Maroua clay.

Source	Total square	DDL	Square average	Ratio F	Probability
X_1	0.054	1.000	0.054	5.570	0.050
X_2	0.008	1.000	0.008	0.790	0.404
X_3	0.846	1.000	0.846	86.580	**0.000**
X_1^2	0.020	1.000	0.020	2.070	0.193
X_1X_2	0.012	1.000	0.012	1.200	0.310
X_1X_3	0.001	1.000	0.001	0.090	0.778
X_2^2	0.011	1.000	0.011	1.100	0.329
X_2X_3	0.015	1.000	0.015	1.530	0.256
X_3^2	0.256	1.000	0.256	26.230	**0.001**
Total trip	0.068	7.000	0.010		
Total (corr.)	1.262	16.000			

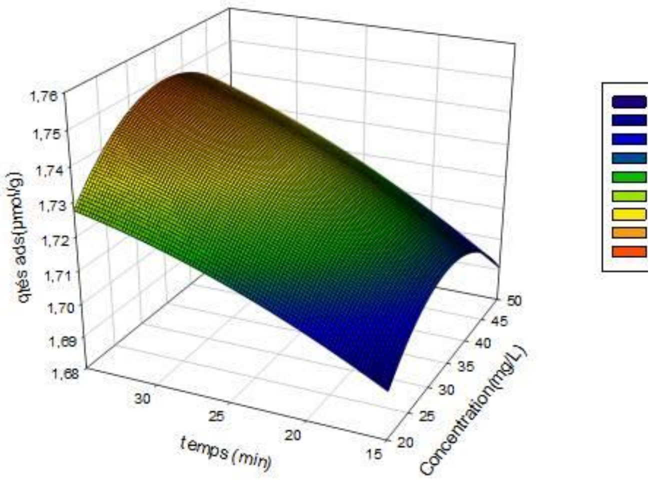
From this table, it appears that the concentration of carotenoids (X_3) had a highly significant effect on the quantity of carotenoids adsorbed (p = 0.0000). The signs of the coefficients observed on the mathematical model showed that these factors had antagonistic effects on the observed response. The increase in the carotenoids concentration indeed contributed to the increase in the amount of carotenoids adsorbed, on the other hand the increase in temperature and time had a negative effect on the response.

Furthermore, it can be noted that the quadratic effect of the initial concentration ($X_3 * X_3$) also had a significant influence on the amount of carotenoids adsorbed (p = 0.00014).

4- Optimization of the parameters for adsorption

The optimum amount of carotenes adsorbed was 1.76 $mg.g^{-1}$ for the values of contact time of 30 minutes, temperature of 11 ° C and initial concentration of 35 $mg.L^{-1}$. This optimal value shows that carotene was strongly retained on montmorillonite by comparing to the initial solution of carotene and HPLC analysis.

The response surface and the iso-response curve are represented in Fig. 5 from the equation of the model previously established. Note that the temperature changed until reaching the peak around 35 °C; to maximize the amount of carotenoids adsorbed, the initial concentration of carotenoids should be high.



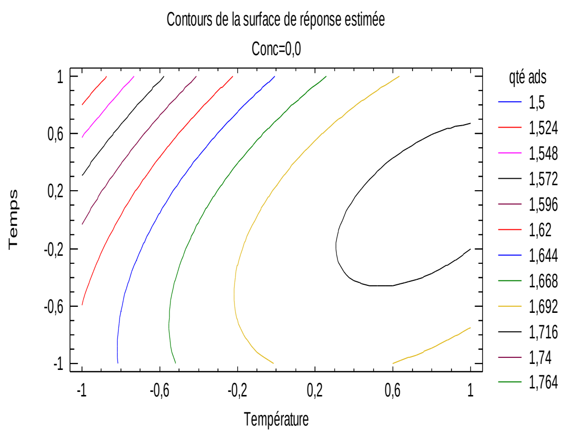


Fig. 5. Response surface (a) and iso response (b) for the adsorbed carotenoids Y.

Conclusions

The facial mask with both antioxidant properties of carotenoids from palm oil and adsorbent properties of clays have been formulate. The centred composite experimental plan used to optimize some parameters shows that of the three independent variables which are time, temperature and initial concentration, the concentration is the factor which has a great influence on the adsorption. The higher the initial concentration is, the greater the quantity is adsorbed. Others share, the temperature influences the least according to the response and iso-response surfaces. The coefficient of determination, the absolute analysis of the mean deviation, the bias factor and the accuracy factors made it possible to validate the model.

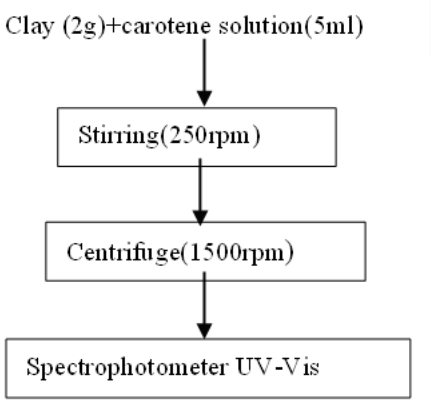
Implication for industry

By knowing the importance of carotenoids and clay in the cosmetic application; and the optimal condition for adsorption of eachoder, we can formulate in the study condition a cosmetic mask with antioxydants properties and begin industrialisation at few level.

Experimental section

The clays come from a cornfield at Maroua in the Far North region of Cameroon and was characterise as montmorillonite by Ngomo et al.[9,10]; and the palm oil was produced by SOCAPALM in the littoral region (Cameroon); adsorption was done in batch:

To know the quantity of adsorb carotenoids, we made the difference before and after adsorption by reading on spectrophotometer UV-vis (Perkin-Elmer (Lambda EZ 210) double beam UV-Visible Spectrophotometer equipped with a Xenon lamp at 450W. The excitation wavelengths were: 416, 439 and 469 nm.) ;



$$q_t = \frac{(C_0 - C_t)V}{m}$$

q_t : adsorbed quantity (mg/g) ; **C_0** and **C_t** initial concentration and at time t (mg/L) ; **V** volume of adsorbent (L) ; **m** weight of adsorbent (g)

The nature of carotenoids was obtained on HPLC Varian Prostar analytique + C_{30} Phase mobile: MeOH + MTBE (Fisher Scientific).

In order to be able to adjust several polynomial models it is possible to use a very classic experiment plan, of the centred composite type.

A centred composite plan is made up of three parts (figure 6):

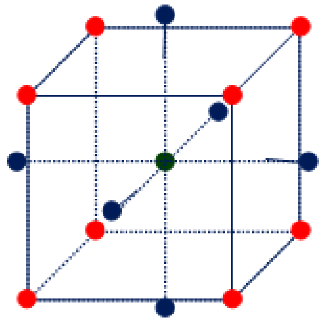


Fig. 6. Composite plan centred for 3 factors.

- N_f number of experimental points of a factorial plan at two levels, complete or fractional.

- $N_\alpha = 2k$ number of points located on the axes of each of the factors studied at a distance α from the center of the experimental domain

- N_0 number of points in the center of the domain

The total number of tests N was calculated using the formula:

$N = \mathbf{N_f} + \mathbf{N_\alpha} + \mathbf{N_0} = 2^{k-r} + 2k + n_0$

Where 2^k is the number of trials for a full factorial design, r is a function of the number of trial reductions for a fractional factorial design. For example, r = 1 for halving the number of trials. In general, r = 0 for k ≤ 4

The number of tests at center n_0 and the parameter α are chosen in accordance with the properties desired for the plan.

The parameter α makes it possible to define the tests in addition compared to the factorial plan. When using coded values, α defines the position at the axial point relative to the center. Ultimately, each factor will take the following coded values: -1 for the low level, +1 for the high level, 0 in the center, -α and + α.

With 3 factors and 3 tests at the center, our experience matrix will be made up of 17 experiences. The multiplicity of tests at the center makes it possible to determine the experimental error and to consider that it is the same everywhere in the field experimental.

The previous experiments made it possible to show that the balance was reached around 30 min of contact time, 30 min will be taken as value in the center. A 15-minute step allows us to cover the experimental area hitherto explored.

The objective of this study was to work at almost normal temperature, we took 25 °C for the low value and 65 °C as the high value, which gives 45 °C as the center value. The values used for the concentration were 20, 35 and 50 mg.L^{-1}.

When applying the principle of rotation, the value of α for three factors was 1.682. Value sought at point α = value at center ± step.α (table 3).

The answer was the amount of carotenoids adsorbed per unit mass of clay (qe).

Table 3. Parameters and experimental domain for adsorption.

Factors	Units	Varia-bles	Variation /Levels				
			-α	dawn (-1)	center (0)	top (1)	+α
Times	(min)	X_1	5	15	30	45	55
Tempe-rature	(°C)	X_2	11	25	45	65	79
Concen-tration	mg.L^{-1}	X_3	6	20	35	50	64

The axial points are defined by the regression equation which shows the contribution of the different factors is presented as follows:

$Y = bo + b_1 X_1 + b_2 X_2 + b_3 X_3 + b_{12} X_1 X_2 + b_{13} X_1 X_3 + b_{23} X_2 X_3 + b_{11} X_1^2 + b_{22} X_2^2 + b_{33} X_3^2$

Where b_0 is the center value, b_i is the linear factor, b_{ii} is the quadratic factor and b_{ij} is the interaction factor.

It is important to validate the empirical model obtained. To do this, the experimental responses obtained were compared to those calculated from the mathematical equation of the model; in addition to the coefficient of determination (R^2),

- The Absolute Average Deviation Analysis (AADM) which provides information on the average error of the manipulations was given by the following expression [15,16] :

$$AADM = \frac{\sum_{i=1}^{p}\left(\left|\frac{Y_{i\exp} - Y_{ical}}{Y_{i\exp}}\right|\right)}{p}$$

With: Y_{iexp} the experimental response and Y_{ical} the response calculated from the model for an experiment i; p being the total number of experiments.

The model is validated if: $0 \leq \text{AADM} \leq 0.2$

- The bias factor

The bias factor is given by the expression

$$Bf = 10^{B}$$

With B the bias

$$B = \frac{1}{n}\sum \log\left(\frac{Y_{theo}}{Y_{obs}}\right)$$

The model is validated if $Bf \leq 1.20$

- Factors of accuracy

The accuracy factors are given by the following expressions:

$$Af_1 = 10^{A_1} \qquad Af_2 = 10^{A_2}$$

With the accuracy

$$A_1 = \frac{1}{n}\sum_{i=1}^{n}\left|\log\left(\frac{Y_{théo}}{Y_{obs}}\right)\right|$$

and

$$A_2 = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(\log\left(\frac{Y_{théo}}{Y_{obs}}\right)\right)^2}$$

The model is validated if: $1 \leq Af_{1,2}$

PART 2- KNOW HOW-TRANSFER

The advantages of clays are their excellent adsorbent properties; so, they are widely used as facial mask to improve the general condition of face. When we add carotenoids from palm oil with their antioxidant properties, we obtain the more efficient product antiaging. Now that the parameters for fixing these carotenoids on clays are optimized, we will be able to set up a small production unit of producing a facial mask efficient and less costly because of easiness to make it, the availability and abundance of materials around of us.

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