STUDIA UBB CHEMIA, LXI, 2, 2016 (p. 119-126)
(RECOMMENDED CITATION)

ADSORPTION OF PALM OIL CAROTENES ON NATURAL AND ACID ACTIVATED MONTMORILLONITE CLAYS

ORLÉANS NGOMO[a,b,c], JEAN BAPTISTE BIKE MBAH[a*], RICHARD KAMGA[a], RODICA DINICA[c]

ABSTRACT. The adsorption behavior of natural and acid activated Montmorillonite clays from Maroua (Far North region of Cameroon) were studied by batch adsorption method. Carotene adsorption was monitored by measuring the absorbance of the mixture before and after adsorption experiments. The effect of contact time, temperature and initial carotene concentration were analyzed. It was found that the amount of carotene adsorbed increases with contact time and the adsorption equilibrium was attained after 30 min irrespective of the adsorbent used. Temperature has little effect on the adsorption process. The amount of β-carotene adsorbed at equilibrium increased with the initial carotene concentration. Kinetic modeling shows that experimental data follows pseudo-first order, pseudo-second order and intraparticle diffusion models. The line best fit was obtained with the pseudo second order diffusion model. Langmuir, Freundlich, and Temkin isotherms models were used to adjust the equilibrium data. The line best fit was obtained with the Freundlich model. The small values of the Freundlich constants and that of the energy constant of Temkin model revealed that the adsorption of carotene on clays is a physical process.

Keywords*: Montmorillonite, carotene, palm oil, adsorption modelling.*

INTRODUCTION

Crude palm oil is the world's richest natural plant source of carotene in term of retinol. The orange-red color of palm oil is due to the relatively high content of these carotenes. The major carotenes in palm oil are α and β carotenes, which account for 90% of the total carotenes [1].

[a] *Department of Applied Chemistry, National School of Agro-Industrial Sciences, University of Ngaoundere, P.O. Box 455 Cameroon.*
[b] *Department of Chemistry, Faculty of Sciences, University of Yaoundé I, P.O. Box 812 Yaoundé, Cameroon*
[c] *Department of chemistry, Faculty of Sciences, Universitatea "Dunarea de Jos'' din Galati, Str. Domneasca nr. 47. 800 008 Galati, Romania*
[*] *Corresponding author: jbmbahgm@gmail.com / jbmbah@yahoo.fr*

Due to their antioxidant properties, carotenes are usually used in food industries and in cosmetic formulations. It has been found that carotene improves the general aspect of skin [2]. However, carotenes have been considered as undesired compounds in the palm oil refining processes [2, 3, 4]. Adsorption on suitable material has been preferred for the removal of pigments from vegetable oils [5-9]. The most effective adsorbent for pigment removal from vegetable oils are montmorillonite base activated clay and activated carbon [5, 4, 10]. Montmorillonite clay is preferred to activated carbon for the vegetable oil refining due the high cost of the latter adsorbent [3, 4, 9].

The purpose of this work is to study the mechanism of adsorption of palm oil carotenes on natural and activated montmorillonite in hexane. Therefore, kinetic and isotherm data will be fitted with theoretical models.

RESULTS AND DISCUSSION

1. UV-visible Spectrum of palm oil

The absorption spectrum of crude palm oil (Fig. 1) presents a maximum absorption band at 445 nm, with shoulder at 420 nm. The reduction of the optical density to this maximum of absorption was used to follow the adsorption of carotene.

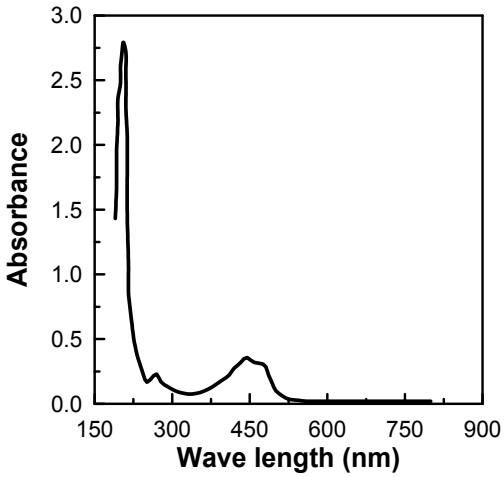

Figure 1. Adsorption spectrum of crude palm oil.

2. Adsorption kinetics

Fig. 2 shows the time evolution of the amount of β-carotene adsorbed on natural clay (a: M0M) and modified clay (b: M0.5M) for different initial concentration of carotenes (20 mg/L, 40 mg/L and 50 mg/L).

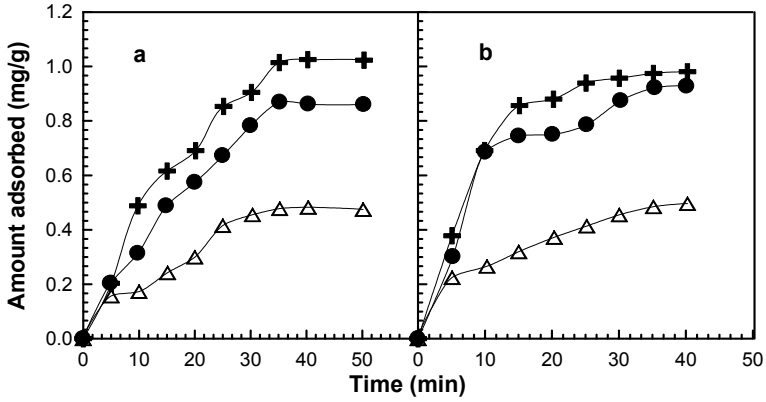

Figure 2. Time evolution of the amount of β-carotene adsorbed on clay for different initial concentrations: 20 mg/L (Δ), 40 mg/L (●) and 50 mg/L (✚). a: M0M, b: M0.5M

It is observed that the amount of carotenes adsorbed increased rapidly with time, and then slowed down for a contact time greater than 30 min. It can also be observed that the amount of carotenes adsorbed increased with the initial concentration, independently of the nature of clay used. This increase is rather fast in the first minutes and is stabilized after a contact time greater than 30 minutes.

At equilibrium, the amount of carotenes adsorbed (table 1) is proportional to the initial concentration for natural clay. This relation of proportionality does not hold after modification of clay.

Table 1. Amount of carotene adsorbed (μmol/g) at equilibrium for different initial concentrations

	Initial concentration (mg/L)		
	20	40	50
M0M	0.89±0.02	1.63±0.03	1.94±0.04
M05M	0.91±0.02	1.73±0.04	1.85±0.04

The effect of the temperature on the adsorption process was studied by carrying out experiments at different temperatures (25, 45 and 65° C). The increase in the amount of carotene adsorbed was less than 2% when temperature increased from 25°C to 65°C (Table 2). Hence temperature has little effect on adsorption kinetics.

Table 2. Amount of carotene adsorbed (µmol/g) at equilibrium for different temperatures

	Temperature (°C)		
	25	45	65
M0M	1.63±0.03	1.67±0.03	1.75±0.04
M05M	1.73±0.04	1.75±0.04	1.77±0.04

The adsorption data were analyzed by using three kinetic models, in particular intraparticle diffusion, pseudo-first order and pseudo-second order models. The respective linear equations of these various models are as follows:

$$q_t = k_{int}\sqrt{t} + \alpha\ ;\ \ln(q_e - q_t) = \ln q_e - k_1 t\ ;\ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q}t$$

where k_{int}, k_1 and k_2 are the respective intraparticle diffusion, pseudo-first and pseudo-second order kinetic constants, q_e and q_t are the respective amount of carotene adsorbed at equilibrium and at time t, α is a constant.

The experimental data follows the pseudo-first model if R^2 of the regression line of $\ln(q_e-q_t)$ as function of t is greater than 0.90. Similarly the experimental data follows the pseudo-second model if R^2 of the regression line of $1/q_t$ as function of t is greater than 0.90. For the intraparticle diffusion model de R^2 for q_t as function of $t^{1/2}$ should be greater than 0.90.

The R^2 values are greater than 0.90 for the three kinetic models, for natural and acid activated clays (Table 3).

Table 3. Kinetic parameters for adsorption of carotene on Montmorilonite

		Clays	
		M0M	M05M
Pseudo first order	k_1	0.07	0.08
	q_e	1.82	1.31
	R^2	0.94	0.92
Pseudo second order	k_2	0.04	0.05
	q_e	2.17	1.81
	R^2	0.91	0.98
Intraparticle diffusion	k_{int}	0.15	0.14
	q_{ei}	0.05	0.05
	R^2	0.97	0.97
$q_{e\ exp}$		1.63	1.73

k_1 (min^{-1}); k_2 ($\mu molg^{-1}min^{-1}$); q_e ($\mu molg^{-1}$), $q_{e\ exp}$ ($\mu molg^{-1}$)

These results show that the experimental data follows the three kinetic models. The amount of carotene adsorbed at equilibrium i.e. q_e, for intraparticle diffusion model is 25 times of magnitude lower than the experimental value

(q_e exp), thus this model is not applicable to the experimental data. The q_e values for the pseudo-first and pseudo-second models are close to the experimental values.

The main steps in adsorption from solution are diffusion from solution to the adsorbent surface, diffusion at adsorbent surface and diffusion inside the pores of adsorbent [2, 10, 11]. The pseudo first order kinetic model assume that the adsorption is a one step elementary reaction; while the pseudo second order kinetic model assumes that the adsorption occurs in two steps; that is diffusion of adsorbate and adsorbate–adsorbent interaction [11, 12]. These results suggest that the adsorbate interaction with clay surface is a quick reaction, and that the diffusion is the limiting step as it has a very small kinetic constant. This explains why this data follows both pseudo first and pseudo second kinetic models.

3. Adsorption isotherms

The isotherms express the amount adsorbed per unit mass of clay (mg/g) as function of the equilibrium concentration in solution (mg/L) (Fig. 3).

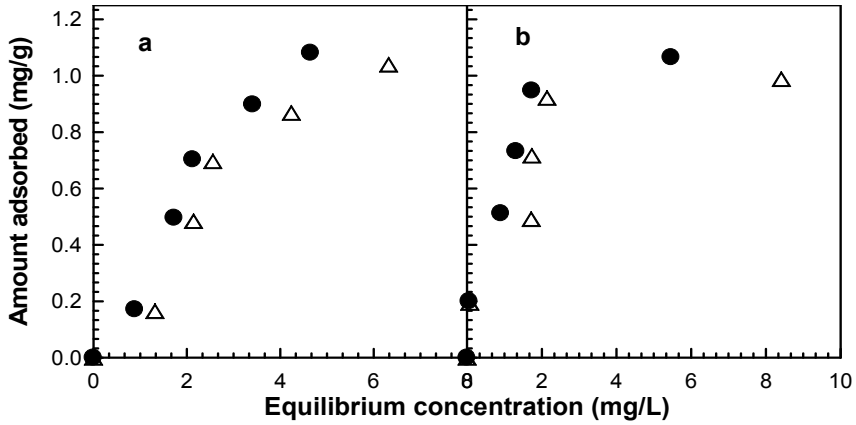

Figure 3. Adsorption isotherms of carotenes on clays at 25°C (Δ) and 45°C (●) a) M0M; b) M0.5M

The isotherms with acid activated clays are characterized by a large increase in the amount adsorbed at low equilibrium concentration, and then followed by a tendency of the formation of a plateau when the concentration is higher. Adsorption isotherms on natural clay are quite different, being characterized by a smaller adsorption in the range of low concentration, while almost a linear increase is observed in the range of higher concentration. Temperature has little effect on the adsorption isotherms; this is in accordance with the results of kinetics experiments.

In order to optimize the design of an adsorption system to remove the carotene from solution, it is important to establish the most appropriate correlations of the equilibrium data with theoretical models. Using different adsorption models to analyze adsorption isotherm data is also an interesting approach to have more information on the carotene-clay interaction. The most usually used isotherm models have been tested in the present study [13, 14, 15]. The respective linear equations of Langmuir, Freundlich and Temkin are:

$$\frac{C_e}{q_e} = \frac{1}{K_L b} + \frac{1}{b} C_e \quad ; \quad q_e = B\ln A + B\ln C_e \quad ; \quad \ln(q_e) = \ln K_F + \frac{1}{n}\ln C_e$$

where C_e is the concentration of carotene at equilibrium; q_e and q_m are the amount of carotene adsorbed per gram of adsorbent at equilibrium and at the monolayer, K_L is the Langmuir constant related to adsorption energy; K_F is a Freundlich constant, indicative of the adsorption capacity of the adsorbent; n_F is a constant indicative of adsorption intensity; B is the Temkin constant indicative of adsorption energy and A is the Temkin isotherm constant.

The results of the application of these equations to the adsorption of carotene on natural and acid activated clays are presented in table 4. Most of the R^2 values exceeded 0.90. However Freundlich isotherm suits the experimental data better than the other 2 models. This suggests that the surface heterogeneity of clay play a major role in the carotene adsorption. Similar results were reported in the literature for adsorption of phenol on different adsorbents [2, 10, 16].

Table 4. Langmuir, Freundlich and Temkin isotherm parameters

		Clays			
		M0M		M05M	
T (K)		298	318	298	318
Langmuir	K_L	0,32	0,61	0,56	0,38
	R_L	0,07	0,04	0,04	0,06
	b	0,24	1,37	1,35	1,32
	R^2	0,90	0,95	0,90	0,97
Freundlich	K_F	0,09	0,26	0,47	0,85
	1/n	0,40	0,54	0,84	2,13
	R^2	0,96	0,96	0,95	0,96
Temkin	A	1,31	1,41	7,91	56,90
	B	0,41	0,84	0,31	0,20
	R^2	0,98	0,99	0,91	0,90

b (µmol/g) ; B (J/mol)

All the n_F value of the Freundlich equation were lower than 1, indicating that carotene molecules are unfavorably adsorbed by clays [16]. This is in accordance with the small value of K_L the Langmuir equilibrium constant. This is also in agreement with the monolayer capacity q_m. The

poor values of the Temkin energetic constant B, shows that carotene are loosely bound to adsorbent surface. The overall analysis of the isotherm parameters shows that the adsorption of carotene on clays at temperatures lower than 60°C is a physical phenomenon. Therefore the clay–carotene material is suitable for cosmetic application.

CONCLUSION

Adsorption of carotene from hexane solution on natural and acid activated clays was studied at different initial concentrations (20 mg/L, 40 mg/L and 50 mg/L) and at different temperatures (25°C, 45°C and 65°C). It was observed that the amount of carotene adsorbed increased with an increase in the initial carotene concentration. Temperature and acid activation have limited effects on the adsorption process. Kinetic studies reveal that diffusion of the adsorbate is the limiting step. Freundlich isotherm fitted the experimental data better than Langmuir and Temkin isotherm. Adsorption of carotene on clays at 25°C was found to be a physical process.

EXPERIMENTAL SECTION

Palm oil was provided by SOCAPALM Co (Cameroon). The standard β carotene used as reference for the calibration curve was purchased from Sigma-Aldrich Ltd. It is a dark red compound of chemical formula $C_{40}H_{56}$ and molecular weight of 536.89 g/mol. A LAMBDA 35, UV visible spectrophotometer was used for carotene analysis. Calibration was performed by measuring the absorbance of a series of standard β- carotene solution at 450 nm. A 1 cm optical path quartz cell was used and hexane was used as reference.

Clay materials used in the present study were sampled in Maroua of the far north region of Cameroon. Clay fraction (<2 μm) was obtained by sedimentation. Monmorillonite was identified as the main clay mineral of the sample.

Acid activation was carried out by mixing clays and 0.5M analytical grade HCl solution for 24 hours at room temperature (≈25°C); the solid to liquid ratio was 1:10w/w ratio. Upon activation, the clay was washed several times with distilled water until negative test of Cl^-. The resulting slurry was filtered under vacuum. The acid activated clay was dried in an oven at 105°C for 8 hours and crushed in an agate mortar.

An initial solution of carotene was made by mixing 2 g of palm oil with 40 mL of hexane (analytical grade). Samples of this initial solution were further diluted drop wise to have the desire initial concentration of carotene. Carotene solutions with initial concentrations of 20, 40 and 50 mg/L were then prepared.

Adsorption of carotene on clay fraction was studied using batch experiments. A fixed amount of dry adsorbent (0.2 g) and 5 mL of β- carotene solution were placed into caped erlenmeyer flasks (100 mL). The flasks were agitated with a magnetic agitator (250 rpm) at the desired temperature for a predetermined contact time. After centrifugation at 1500 rpm, the absorbance of carotene solution was measured at 450 nm. The amount of carotene adsorbed per gram of adsorbent, was calculated according to the mass balance equation as follows:

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

where C_0 and C (mg/L) are initial and final concentrations of carotene; V is the volume of the carotene solution used and W is the mass of dry adsorbent used (g).

ACKNOWLEDGEMENTS

Orléans Ngomo is very thankful to the AUF "Eugen Ionescu" program for providing the fellowship.

REFERENCES

1. Y.M. Choo, S.C.Yap, C.K. Ooi, A.S.H. Ong, S.H. Goh, *Elaeis*, **1997**, *3*: 309.
2. B.J. Nde-Aga, R. Kamga and J.P. Nguetnkam, *Journal of applied Sciences*, **2007**, *7,* 2462.
3. M. Rossi, M. Gianazza, C. Alamprese, F. Stanga, *Food Chemistry*, **2003**, *82*, 291.
4. J.B. Bike Mbah, E. Ngah, M. Praisler, R. Kamga, *International Journal of Biosciences*, **2013,** *3*, 15.
5. A.L. Ahmad, C.Y. Chan, S.R. Adb Shukor, M.D. Mashitah, *Chemical Engineering Journal*, **2009,** *148*, 978.
6. E. Sabah, M. Cinar, M.S. Celik, *Food Chemistry*, **2007**, *100*, 1661.
7. J.B. Bike Mbah, R. Kamga, J.P. Nguetnkam, J. Fanni, *European Journal of Lipid Science and Technology*, **2005**, *107*, 387.
8. G.E. Christidis and S. Kosiari, *Clays and clay Minerals*, **2003**, *51*, 327.
9. P.A.M. Mourao, P.J.M. Carrott, M.M.L. Ribeiro Carrott, *Carbon*, **2006**, *44*, 2422.
10. A. Proctor and C. Palianiappan, *Journal of the American Oil Chemists' Society*, **1990**, *67*, 572.
11. W. Plazinski, J. Dziuba, and W. Rudzinski, *Adsorption*, **2013**, *19*: 1055.
12. F.C. Wu, R.L. Tseng, S.C. Huang, R.S. Juang, *Chemical Engineering Journal,* **2009,** *151*, 1.
13. W. Plazinski, J. Dziuba, W. Rudzinski, *Adsorption,* **2013,** *19,* 1055.
14. A. Derylo-Marczewska, A.W. Marczewski, S. Winter, D. Sternik, *Applied Surface Sciences,* **2010**, *256,* 5164.
15. J. Febrianto, A.N. Kosasih, J. Sunarso, Y.H. Ju, N. Indraswati, S. Ismadji, *Journal of Hazardous Materials*, **2009**, *162*, 616.
16. B.H. Hameed, *Colloids and Surfaces A: Physicochemical Engineering Aspect,* **2007**, *307*, 45.