



Journal of Applied Sciences

ISSN 1812-5654

science
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Adsorption of Palm Oil Carotene and Free Fatty Acids onto Acid Activated Cameroonian Clays

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Abstract: The adsorption of carotene and free fatty acids from crude palm oil by local clay, activated with various concentrations of sulphuric acid (0.5, 1 and 2 M) was investigated. Kinetic studies of the adsorption of carotene and of free fatty acids at 65, 80 and 90°C, showed that the time required attaining adsorption equilibrium decreases as the temperature increases, regardless of the adsorbent used. Clay activated with 1 M sulphuric acid solution was the most efficient local clay for the adsorption of carotene and of free fatty acid and it compared favourably with the industrial clay used as reference. The bleaching efficiency of local clay was correlated to the surface area of the adsorbents. It was found that the Freundlich equation is applicable to the adsorption isotherms of carotene from palm oil. The Brimberg model used to determine the activation energy of the adsorption process gave the values, 82 ± 12 , 72 ± 11 , 74 ± 11 and 37 ± 6 kJ mol⁻¹, for industrial adsorbent, 0.5, 1 and 2 M activated clays, respectively.

Key words: Acid activated clay, carotene adsorption energy, free fatty acids, Freundlich isotherm, palm oil

INTRODUCTION

Palm oil is a flesh fruit fat with a distinctive orange-red colour, due to its high content of carotenoids. Palm oil being a major source of vegetable fats is used extensively in cooking, cosmetics and in the manufacture of soap. Crude palm oil is found to contain pigment likes carotenes and impurities like free fatty acids. When processing vegetable oils, the bleaching operation is an important step intended to remove pigments and other unwanted constituents such as those of mucilaginous character and other volatiles (Christidis *et al.*, 1997). Many types of adsorbent have been tested for the removal of pigments from vegetable oil (Kamga *et al.*, 2000; Falaras *et al.*, 2000; Topallar, 1998; Proctor and Snyder, 1988; Kheok and Lim, 1982). Adsorption materials used nowadays throughout the world by vegetable oil refiners are mainly activated montmorillonite clays. Christidis and Kosiari (2003) showed that removal of β -Carotene from crude maize oil with acid activated low grade bentonite from Cyprus is a chemical adsorption process. The isotherm they obtained was of the Freundlich type. None of the above studies mentioned the adsorption of free fatty acids during the decolourisation process. Moreover other authors pointed that the

bleaching process led to and increased of the free fatty acids content of the vegetable oil (Habile *et al.*, 1992; Boki *et al.*, 1992; Nnandozie *et al.*, 1989). More recently (Bike Mbah *et al.*, 2005), we show that acid activated clay from Cameroon could be used successfully for the adsorption of pigments and free fatty acids of shea butter. The high value of the activation energies obtained indicated that the adsorption of shea butter pigment was of a chemical nature. It is the purpose of this contribution to study the mechanism of the simultaneous adsorption of carotene and free fatty acids of palm oil, by means of kinetics, with determination of activation energy and construction of the adsorption isotherm.

MATERIALS AND METHODS

Palm oil used for this research was the olein portion of fractionated palm oil provided by SOCAPALM. Co (Cameroon). The physicochemical characteristic of the crude fat was: Acid index 12.34, Peroxyde value 96 meq kg⁻¹, Absorbance at 445 nm 1.975.

Adsorbents used were activated clays and an industrial adsorbent. The industrial adsorbent was obtained from Engelhard Co (Netherlands). The clays were extracted from aggregates of soil collected at Kaélé which

Table 1: Adsorbent characteristics

Characteristic	Natural clays	A0.5M	A1M	A2M	EN
SiO ₂	47.82	51.16	53.42	56.54	64.04
Al ₂ O ₃	22.31	21.45	20.99	19.52	8.23
Fe ₂ O ₃	9.14	8.28	6.98	5.31	2.43
MnO	0.05	<LD	<LD	<LD	<LD
MgO	1.84	1.09	0.96	0.76	1.05
CaO	1.39	0.42	0.32	0.28	3.95
Na ₂ O	0.55	0.17	0.18	0.14	0.35
K ₂ O	0.95	0.80	0.76	0.77	0.65
TiO ₂	0.98	1.06	1.12	1.18	0.67
P ₂ O ₅	0.08	0.07	0.08	0.07	0.06
LOI	15.36	15.34	15.48	15.28	18.53
Total	100.47	99.84	100.29	99.85	99.96
Mass balance (%)	100.00	92.00	88.00	83.00	ND
Specific surfaces areas (m ² g ⁻¹)	110.90	143.60	168.00	202.00	329.80
Mean pore diameter (nm)	3.17	3.05	2.70	2.54	2.80

LD: Lower than the detection limit, ND: Not Determined

is a locality in the far north province of Cameroon (latitudes 10° and 10°15' North and longitudes 14°10' and 14°35' East). The mineral composition of the natural clays was: smectites 74.4, kaolinite 7.7, quartz 15.4 (Nguetnkam *et al.*, 2005). Other adsorbent characteristic are presented in Table 1.

The extraction of the argillaceous fraction was made by gravimetric sedimentation. A sample of soil (200 g) was placed in a beaker and to this was added 200 mL of distilled water. The mixture was then placed in an ultrasound water bath for 25 min and transferred thereafter into a sedimentation vessel of 1500 mL volume. Distilled water was added up to 1200 mL. The mixture was then stirred for few minutes and left to stand for 8 h. After this time, the mixture located a higher of 10 cm from edge of the sedimentation vessel was collected by siphon. According to Stokes law this mixture should contain the argillaceous fraction whose particles size is lower than 2 µm. The process of agitation-rest-siphon was repeated several times. The mixture of clay obtained was placed in an oven at 105°C until completely evaporation of water.

The procedure of activation was carried out according to the method described by Vincente-Rodriguez *et al.* (1996). The clay sample (50 g) was introduced into a beaker and 250 mL of sulphuric acid (analytical grade) solution added; three different concentrations of sulphuric acid solution were used, that is 0.5, 1.0 and 2.0 M. The mixture was homogenized from time to time at ambient temperature using a glass rod for 3 h. At the end of this period, the mixture was washed several times with distilled water until the silver nitrate test for sulphate ion was negative.

Nitrogen adsorption-desorption isotherms at 77 K were recorded on a step-by-step automatic home-built setup (Laboratoire Environnement et Minéralurgie; Nancy, France). Specific Surfaces Areas (SSA) were determined from adsorption data by applying the

Brunauer-Emmet-Teller (BET) equation. The error in the determination of SSA was estimated as ±1 m² g⁻¹. Pore size distributions were calculated on the desorption branch using the numerical integration method of Barrett-Joyner-Halenda, assuming slit-shaped pores.

For the adsorption experiment, 5 g of palm oil was placed in a stoppered conical flask held in a shaking (80 cycles min⁻¹) water bath thermostated at a predetermined temperature, that is 65±1, 80±1, or 90±1°C. When the content had reached the required temperature, usually not more than 15 min, a known amount of adsorbent was added to the flask, which was then shaken for the desired time. For the kinetic studies residence time varied between 5 and 75 min. Thereafter, the contents of the flask were filtered through Whatman No. 1 filter paper and the concentration of carotene and free fatty acids in the filtrate determined as described below. The amount of pigment adsorbed was determined by difference between the initial and the final concentration, while the amount of free fatty acids adsorbed was determined by difference between the initial and the final acid value. The amount of adsorbent added varied between 1 and 5% (w/w) with respect to the palm oil. In all cases the adsorbent was previously dried overnight at 105°C. Each adsorption experiment was repeated twice, the results reported are de means of three measurements. The error in the determination of amount of pigment and fatty acids adsorbed was evaluated to 10%.

The evaluation of the amount of pigment removed was made by UV-visible spectroscopy. The sample 0.1 g of palm oil was diluted in 7.5 mL of petroleum ether (analytical grade) and the absorbance of the sample determined at 445 nm using petroleum ether as reference.

The acid value and peroxide value was determined according to the respective AFNOR method (1981).

RESULTS AND DISCUSSION

Determination of clay yield from soil aggregate: The percentage yield of clay from the soil aggregate was 40.3±0.5%. This value lies within the range suggested by Nnandozie *et al.* (1989).

UV-visible spectrum of palm oil: The adsorption spectrum of crude palm oil (result not shown) presents a maximum adsorption band at 445 nm, with shoulders at 420 and 470 nm. The reduction of the optical density to this maximum of absorption was used to follow the decoloration process.

The thermal stability of the palm oil pigment was tested. For this purpose, crude fat was heated at 65, 80 and 90°C for 60 min and the absorbance of the final

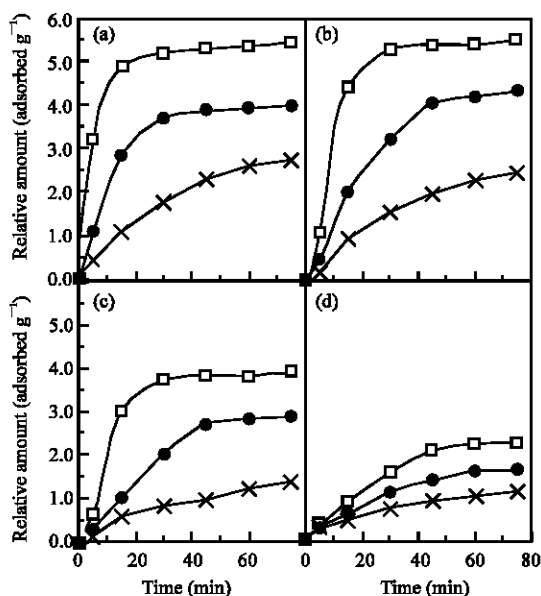


Fig. 1: Kinetics of the adsorption of palm oil carotene at various temperatures, (□) 90°C, (●) 80°C and (×) 65°C, by EN (a), A1M (b), A0.5M (c) and A2M (d) clays

product read at 445 nm. It appears that there is no major change in the pigment concentration since the absorbance remains almost constant through out the heating process.

Kinetics of the adsorption of palm oil carotenes: Figure 1 shows the kinetics of the adsorption of palm oil carotenes at three different temperatures (90, 80, 65°C) by industrial clay (EN, Fig. 1a), the local clay activated with sulphuric acid solution at concentrations of 1M (A1 M, Fig. 1b), 0.5M (A0.5 M, Fig. 1c) and 2M (A2 M, Fig. 1d). A clay dosage of 3% w/w oil was used for the kinetic studies. It is evident from these results that the time required to reach the adsorption equilibrium decreases as the temperature increases, regardless of the adsorbent used. It was observed indeed that at 65°C the time required to reach the adsorption equilibrium is 80 min for all the adsorbents used. At 80°C this time reduce to 30 min for EN clay, 45 min for A0.5M and A1M clays and finally 60 min for A2M clay. At 90°C the time require for the adsorption equilibrium is 20 min, 30 min and 50 min for EN, A0.5M and A1M and A2M clays, respectively. This observed reduction correlates well with the enhancement of oil viscosity with decreasing temperatures reported by Langmaack and Eggers (2002). When the viscosity of the oil is high, there will be a slowing down of transport mechanisms due to decreasing diffusion rates of pigment

molecules to the surface of the adsorbent. Other authors attributed the increase in adsorption rate with temperature to the activation of more adsorption sites by heat (Achife and Ibenesi, 1989).

It was also observed that the amount of pigments adsorbed increased with the temperature independent of the adsorbent used. However the clays had different adsorbing capacities. The difference in the bleaching efficiency of local clays can be attributed to their structure. Preliminary tests showed that natural clays were ineffective in the adsorption of palm oil pigment. A0.5M clay had a better performance compared to natural clay; this can be explained by the increase in surface area and pores volumes during acid leaching (Yebra-Rodrigues *et al.*, 2003; Nnandozie *et al.*, 1989; Achife and Ibenesi, 1989). In effect A0.5M had a greater surface area (143.6 m² g⁻¹) than natural clay (110.9 m² g⁻¹). The efficiency of A0.5M clay is lower than that of A1M clay; this is due to the fact that during acid leaching with 0.5 M sulphuric acid not all of the adsorption sites were liberated because of the weak concentration of the acid solution. Although A2M clay have greater surface area (202.0 m² g⁻¹) than A1M (168.0 m² g⁻¹) and A0.5M (143.6 m² g⁻¹) clays it had the lowest bleaching efficiency. This poor performance of A2M clay can be attributed to the collapse of the crystalline structure of the clay with the formation of silicium and aluminium oxide during the severe acid leaching (Nguetnkam *et al.*, 2005; Christidis *et al.*, 1997; Kheok and Lim, 1982). Preliminary studies with silicium and aluminium oxide showed that there was an insignificant amount of pigment adsorbed from palm oil. The evolution of the bleaching efficiency of clays with the increases of acid concentration of the acid solution used for clay leaching is similar to those obtained by Biké Mbah *et al.* (2005).

Estimation of activation energy: According to Brimberg (1982) the speed of discoloration of vegetable oils is given by the equation $\ln(C/C_0) = -k(t)^{0.5}$ where t is the time of contact between the adsorbent and oil, C the concentration of the pigments at time t, C₀ the initial concentration of the pigments and k the rate constant. According to the Beer-Lambert law the absorbance is proportional to the concentration of the pigments in the oil, therefore the equation of Brimberg can take the form $\ln(A/A_0) = -k(t)^{0.5}$ where A is the absorbance of the oil bleached at time t and A₀ the absorbance of crude oil. From this equation the linear regression between $\ln(A)$ and $(t)^{0.5}$ is a straight line whose slope is equal to k. The values of the rate constant k for palm oil decolourised with various clays at three different temperatures are

Table 2: Rate constants and activation energies for the adsorption of palm oil carotenes on various adsorbents at different temperatures

Adsorbent	Rate constant at various temperatures (k min ⁻¹)			Activation energy (kJ mol ⁻¹)
	90°C	80°C	65°C	
EN	0.339±0.026	0.139±0.011	0.045±0.004	82±12
A0.5M	0.149±0.011	0.041±0.006	0.023±0.003	72±11
A1M	0.199±0.015	0.072±0.011	0.031±0.005	74±11
A2M	0.045±0.007	0.030±0.004	0.018±0.003	37±6

given in Table 2. It is can be deduced from this table that the rate constants vary from 0.018 min⁻¹ for A2M to 0.339 min⁻¹ for EN. For all the clays used, the smallest rate constants were obtained at 65°C. This is in conformity with the results obtained in the kinetics of discoloration according to which, at low temperature, the adsorption of the pigments of the palm oil is very slow.

The activation energy can be deduced from these values of k using the Arrhenius equation $k = k_0 \exp(-E_a/RT)$ where k is the rate constant, k₀ the Arrhenius constant, E_a the activation energy, R the perfect gas constant and T the absolute temperature. From this equation the linear regression between ln(k) and 1/T is a straight line whose slope is equal to -E_a/R. The values of the activation energy obtained for each adsorbent used are also reported in Table 2. These values indicate that the adsorption of palm oil carotenes on the various clays used is probably a chemical adsorption process. This result is in agreement with that found by Christidis and Kosiari (2003) for the adsorption of β-carotene from maize oil.

Figure 2 shows the variation in the amount of free fatty acid adsorbed with time at 90°C. Adsorption equilibrium is attained at about 40 min for EN clay and at about 60 min for the activated clays. It can be seen that the industrial adsorbent EN clay, is the most effective adsorbent for free fatty acid, followed by A1M, A0.5M and A2M activated clays, respectively. The range of acid concentrations used to treat the clays therefore has a significant influence on their adsorption capacities with respect to the adsorption of free fatty acids. The results presented here on the adsorption of free fatty acids are not in agreement with the results reported in previous works. Indeed, it is generally found or admitted in the literature that the acid value of vegetable oils increases during discoloration (Boki *et al.*, 1992; Habile *et al.*, 1992; Nnandozie *et al.*, 1989). This difference could be related to either the nature of the adsorbents, or to the temperatures at which the experiment was performed. The works cited in the literature were generally completed at temperatures higher than those implemented in this research.

Evolution of peroxide value: The peroxide value for palm oil was determined in the course of discoloration at 90°C.

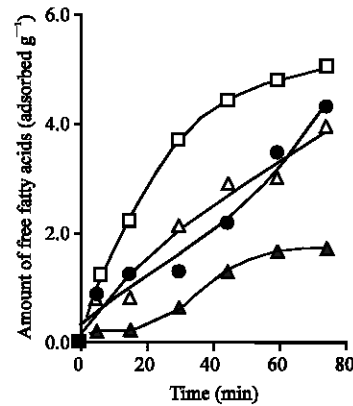


Fig. 2: Kinetics of free fatty acid adsorption by the various adsorbent at (□) 90°C, (◇) EN, (●) A1 M activated clay, (Δ) A0.5 M activated clay and (▲) A2 M

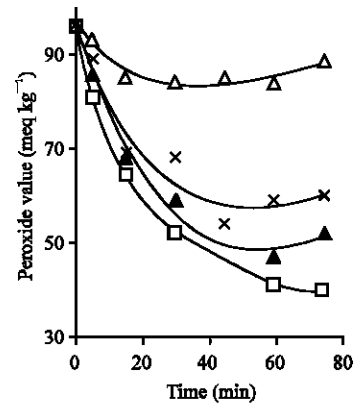


Fig. 3: Evolution of peroxide value with time. (◇) EN, (▲) A1M, (×) A0.5M and (Δ) A2M, clays

Fig. 3 shows that during discoloration, the products of oxidation are also eliminated. It appears that the adsorbents which are effective in the adsorption of the pigments and free fatty acids are also those which are effective in the destruction of peroxide. The order of effectiveness is the same. This result is in agreement with that of Kheok and Lim (1982), but in disagreement with the results obtained by other authors (Nnandozie *et al.*, 1989).

Adsorption isotherms of carotene: The kinetic study has shown that the required temperature and time to reach adsorption equilibrium are 90°C and 30 min, respectively. These parameters were selected to build the adsorption isotherms. The relative amount of pigment adsorbed per gram of adsorbent X and the concentration of pigment at equilibrium X_e are obtained by the following equations: $X = ((A_0 - A)/(A_0)) / m$ and $X_e = A/A_0$ where A₀ and A are

Table 3: Parameters of Freundlich equation for the adsorption of palm oil carotenes

Adsorbent	n	λ	Correlation coefficient
EN	0.94±0.47	0.020±0.01	0.93
A0.5M	1.94±0.97	0.016±0.008	0.94
A1M	1.299±0.64	0.018±0.009	0.97
A2M	0.262±0.13	0.340±0.17	0.99

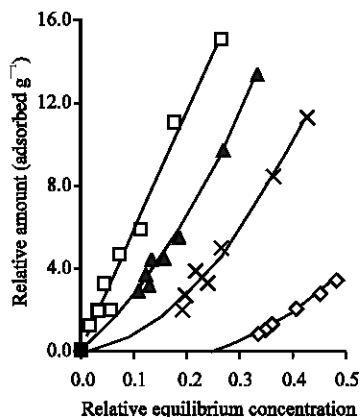


Fig. 4: Adsorption isotherms of carotene on the various adsorbents. (◇) EN, (▲) A1M, (×) A0.5M and (Δ) A2M, clays

the optical densities of the crude and decolourised palm oil, respectively and *m* is the amount of adsorbent used. The adsorption isotherms obtained are presented in Fig. 4. It is observed that the amount of pigments adsorbed per gram of adsorbent increases according to the amount of clay used.

Modeling of the isotherms: The models frequently used to represent the adsorption isotherms of pigments from vegetable oils or from solvents are the Langmuir and Freundlich equations (Christidis and Kosiari, 2003; Kamga *et al.*, 2000; Boki *et al.*, 1992; Achife and Ibenesi, 1989; Sarier and Güler, 1988). Thus, we tested these two equations with our experimental data. The correlation coefficients for Langmuir equation were 0.004, 0.626, 0.664 and 0.900 for EN, A0.5M, A1M, A2M clays, respectively. It was therefore deduced that the Langmuir equation does not fit our experiment data.

The equation of adsorption of Freundlich can be given by the equation:

$$\log(X/m) = \log(\lambda) + (1/n)\log(Xe)$$

where, λ is the constant reflecting the measurement of the capacity of adsorption and *n* the constant reflecting the affinity of the pigments for the adsorbent. *X/m* is the relative amount of pigments adsorbed per gram of adsorbent and *Xe* the relative amount of pigment at

equilibrium. The values of the correlation coefficients obtained (Table 3) show that the Freundlich equation is applicable to the adsorption of palm oil carotenes by clays.

CONCLUSIONS

Adsorption of carotene and free fatty acids from crude palm oil by local clay, activated with various concentrations of sulphuric acid (0.5, 1 and 2 M) was investigated. The kinetic study of discolouration showed that the adsorption of the pigments increased with temperature. The most effective adsorbents for discolouration were clays EN and A1M followed by clays A0.5M and A2M. An optimal effectiveness of local clay seemed to be obtained when it was activated with solution of sulphuric acid of 1 M concentration. The most efficient adsorbents for the adsorption of the pigments were also those which gave the best results for the adsorption of free fatty acids and in the elimination of peroxides.

After physicochemical analysis, it appeared clearly that discolouration not only makes it possible to give an attractive colour to the palm oil, but also to have stable oil and of good quality. Indeed, free fatty acids are adsorbed on clays and peroxides contained in raw oil are destroyed during the process.

The high values of the energies of activation determined according to the model of Brimberg suggest that the adsorption of palm oil pigments on various clays is probably a chemical process. The adsorption isotherms obtained follow Freundlich equation for the adsorption of pigments from palm oil.

The improvement of the quality of palm oil obtained after discolouration, show that activated local clay can be used for palm oil bleaching.

show that acid activated clay from Cameroon could be used successfully for the adsorption of pigments and free fatty acids.

ACKNOWLEDGMENT

The authors are grateful to Dr. F. Villiéras (LEM-INPL Nancy, France) for the surface area determination of the clays sample and for fruitful discussions.

REFERENCES

- Achife, E.C. and J.A. Ibenesi, 1989. Applicability of the Freundlich and Langmuir adsorption isotherms in the bleaching of Rubber and Melon seed oils. *J. Am. Oil Chem. Soc.*, 66: 247-253.

- AFNOR (French Association of Norm), 1981. Fat materials, oleaginous grains and derivatives. Collection of French Norms. 2nd Edn., AFNOR, Paris (France), pp: 438.
- Bike Mbah, J.B., R. Kamga, J.P. Nguetnkam and J. Fanni, 2005. Adsorption of pigments and free fatty acids from shea butter on activated Cameroonian clays. *Eur. J. Lipid Sci. Technol.*, 107: 387-394.
- Boki, K., M. Kubo, T. Wada and T. Tamura, 1992. Bleaching of alkali-refined vegetable oils with clay minerals. *Ibid*, 69: 233-236.
- Brimberg, U.I., 1982. Kinetics of bleaching of vegetable oils. *J. Am. Oil Chem. Soc.*, 59: 74-78.
- Christidis, G.E., P.W. Scott and A.C. Duhnam, 1997. Acid activation and bleaching capacity of bentonites from the islands of Milos and Chios. *Aegan. Applied Clay. Sci.*, 12: 329-347.
- Christidis, G.E. and S. Kosiari, 2003. Decolorization of vegetable oils: A study of the mechanism of adsorption of β -carotene by acid activated bentonite from Cyprus. *Clays Clay Miner.*, 51: 327-333.
- Falaras, P., F. Lezou, G. Seiragakis and D. Petrakis, 2000. Bleaching properties of alumina-pillared acid activated montmorillonite. *Clays Clay Miner.*, 48: 549-556.
- Habile, M., J.P. Barlow and M. Hole, 1992. Adsorptive bleaching of soybean oil with Non-Montmorillonite Zambian clays. *J. Am. Oil Chem.*, 69: 379-383.
- Kamga, R., G.J. Kayem and P.G. Rouxhet, 2000. Adsorption of gossypol from cottonseed oil on oxide. *J. Colloid Interface Sci.*, 232: 198-206.
- Kheok, S.C. and E.E. Lim, 1982. Mechanism of palm oil bleaching by montmorillonite clay activated at various concentrations. *J. Am. Oil Chem. Soc.*, 59: 129-131.
- Langmaack, T. and R. Eggers, 2002. On the bleaching kinetics of vegetable oils - experimental study and mass transfer-based interpretation. *Eur. J. Lipid Sci. Technol.*, 104: 98-109.
- Nguetnkam, J.P., R. Kamga, F. Villieras, G.E. Ekodeck, A. Rawafitianamaharavo and J. Yvon, 2005. Assessment of the surface area of silica and clay in acid-leached clay material using concepts of adsorption on heterogeneous surfaces. *J. Colloid Interface Sci.*, 289: 104-115.
- Nnandozie, N.N., T.A. Arowolo and H.J. Akpan, 1989. Quality of Nigerian palm oil after bleaching with local treated clays. *J. Am. Oil Chem. Soc.*, 66: 218-222.
- Proctor, A. and H.E. Snyder, 1988. Adsorption of lutein from soybean oil on silicic acid II. Kinetics. *J. Am. Oil Chem. Soc.*, 65: 761-763.
- Sarier, N. and Ç. Güler, 1988. β -carotene adsorption on acid activated montmorillonite. *J. Am. Oil Chem. Soc.*, 65: 776-779.
- Topallar, H., 1998. Bleaching kinetics of sunflowerseed oil 1998. *J. Am. Oil Chem. Soc.*, 75: 531-533.
- Vincente-Rodriguez, M.A., M. Suarez, J. de Dios Lopes-Gonzalez and M.A. Banares-Munoz, 1996. Characterization, Surface Area and Porosity Analyses of the Solids Obtained by Acid Leaching of a Saponite. *Langmuir*, 12: 566-572.
- Yebra-Rodrigues, A., J.D. Martin-Ramos, F. Del Rey, C. Viseras and A. Lopez-Galindo, 2003. Effect of acid treatment on the structure of sepiolite. *Clay Minerals*, 38: 353-360.