American Journal of

Food Technology

ISSN 1557-4571

Academic
Journals Inc.

www.academicjournals.com

OPEN ACCESS American Journal of Food Technology

ISSN 1557-4571
DOI: 10.3923/ajft.2016.92.99

Research Article

Comparison Between Some Common Clays as Adsorbents of Carotenoids, Chlorophyll and Phenolic Compounds from Vegetable Oils

Mona El-Hamidi and Ferial A. Zaher

Department of Fats and Oils, National Research Centre, 33 Bohouth St. Dokki, Giza, Egypt

Abstract

Four different clays were compared for their capacities to adsorb chlorophyll and carotenoids; two major pigments in vegetable oils at 30 and 100°C. The clays used include Fulmont, Tonsil N, Tonsil ACC and a factory grade bentonitic clay. Extracts of chlorophyll and carotenoids were prepared from rocket plant and carrot, respectively. Each extract was then mixed with a refined, bleached and deodorized edible grade sunflower oil giving two oil blends, one rich in chlorophyll, while the other rich in carotenoids. The concentration of each pigment in the oil was adjusted, so that it will have reasonable absorbance(s) at the wave length(s) specific of each pigment. The removal of chlorophyll as well as carotenoids from each of the two blends was then studied using the four types of clays at different clay loadings at 30 and 100°C. The reduction in the oil absorbance at 670 nm due to bleaching was taken as an indicator of the amount of chlorophyll removed by bleaching. Similarly, the reduction in the total of the oil absorbances at three wave lengths being 432, 455 and 480 nm were taken as an indicator of the amount of carotenoids removed. The results have proved that the adsorption of both pigments obeyed Freundlich adsorption equation in case of one clay only being Fulmont. In view of the results obtained, the effects of temperature, clay type and clay load on the removal of each pigment have been explored. In addition, the four types of clays used were compared for their capacity to remove the phenolic compounds which have a beneficial anti-oxidant property. According to the results of this study it can be stated that carotenoids can be adsorbed on the bleaching clays more efficiently than chlorophyll. In addition, the effect of temperature on pigment removal by bleaching is much more pronounced in case of carotenoids compared to chlorophyll. Also, it has been found that bleaching of vegetable oils using Fulmont clay can yield oils of lighter color compared to other clays, while their bleaching using Tonsil ACC clay can yield oils more stable to oxidation.

Key words: Clay, sunflower oil, adsorbent, bleaching, carotenoids, chlorophyll, total phenolics

Received: February 13, 2016 Accepted: March 05, 2016 Published: April 15, 2016

Citation: Mona El-Hamidi and Ferial A. Zaher, 2016. Comparison between some common clays as adsorbents of carotenoids, chlorophyll and phenolic compounds from vegetable oils. Am. J. Food Technol., 11: 92-99.

Corresponding Author: Mona El-Hamidi, Department of Fats and Oils, National Research Centre, 33 Bohouth St. Dokki, Giza, Egypt

Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

The whole world is highly concerned with the increasing consumption rate of food as well as its quality. The quality of edible oil which is an essential component of food is determined by its colour, odour and content of free acids. The oil colour is considered as one of the main parameters that affect their acceptance for human consumption. The color of an edible oil depends on the amount and types of pigments in the oil which in turns depend on the type of original crude vegetable oil and the techniques used for crude oil processing to yield an edible grade oil (Zaher, 1990). Crude vegetable oils derive their color from the pigments which naturally occur in oilseeds such as carotenoids, chlorophylls, xanthophylls, gossypol and gossypol derivatives (Bailey *et al*., 1964; Zaher, 1990; Zaher *et al*., 1991; Megahed, 1991; Patterson, 1992). The two major natural pigments in vegetable oils that cannot be removed during the process of alkali refining are chlorophyll and carotenoids. The removal of these two pigments can be achieved by adsorption bleaching on a suitable clay which depends on the specific affinity between the adsorbent and the adsorbate either dissolved or colloidally dispersed in the oil. Adsorbents used in bleaching are usually materials with high surface activity such as bleaching earths, natural or activated or active carbon (Zaher, 1990; Megahed, 1991; Patterson, 1992). The efficiency of the bleaching process will be thus determined by the type of adsorbent used and the nature of coloring matters in the refined oil, in addition to some other factors, such as the bleaching temperature and the mode of bleaching (Bailey *et al*., 1964; Zaher *et al*., 1991; El-Nomany *et al*., 2014). Thus, the selection of the most suitable adsorbent to bleach a certain oil should be made very carefully in order to achieve the ultimate goal of the bleaching process. Some oils are rich in carotenoids such as palm oil, whereas, some other oils are rich in chlorophyll, such as olive oil (El-Nomany and Zaher, 1987; Siddiqui, 1968; Gonzalez-Pradas *et al*., 1993; Hamn and Hamilton, 2000). Adsorbents which are more selective to carotenoids are thus, more suitable for the first category of vegetable oils while those selective to chlorophyll are more suitable for the other category.

The oil odor on the other hand can develop in edible oils due to the formation of oxidation products and their decomposition products either during processing, storage or use. Phenolic compounds which occur naturally in vegetable oils have a potent power as anti-oxidants which delay oil oxidation and hence improve their odor and shelf life. Phenolic compounds may be removed from vegetable oils during the bleaching process by their adsorption on the bleaching clay. Therefore, selection of the most suitable adsorbent should be made on basis of their efficiency of removing the coloring matters with least effect on the oxidative stability of the oils.

This investigation was proposed to compare four types of adsorbents commonly used for industrial oil bleaching with respect to their power to improve the oil color with least reduction in the oil oxidative stability. Since carotenoids and chlorophyll are the two major pigments generally left in vegetable oils after chemical refining of crude oils, the four clays are to be tested for their efficiencies to adsorb these two types of pigments. Thus, adsorbents more suitable to decolorize oils rich in chlorophyll and those rich in carotenoids can be identified. Those clays will be also compared for their effects on removing the desirable phenolic compounds from vegetable oils during the process of oil de-colorization. Adsorbents which are more efficient to remove carotenoids as well as chlorophyll with the least effect on oil oxidative stability can be then recommended rather than other adsorbents.

MATERIALS AND METHODS

Materials and reagents: The adsorbents used in this study were selected from the mostly common adsorbents used to de-colorize vegetable oils. These include Fulmont, Tonsil Optimum N (Tonsil N), Tonsil ACC (T. ACC) and a Mexican factory grade bentonitic clay (Mexican). The latter type is the one currently used in the industrial bleaching of refined vegetable oils in El-Ayatt Factory, Giza, Egypt. This factory belongs to Cairo Company for Oil and Soap in Egypt which imports this clay from Mexico (Mexican clay). On the other hand, Tonsil N and Tonsil ACC are both produced by Süd Chemie, West Germany. A refined, bleached and deodorized edible grade sunflower oil (SFO) was purchased from local market. All the reagents used were of analytical grade and were purchased from Fisher Scientific, UK. Folin and Ciocalteu's Phenol Reagent (FCP reagent) AR was purchased from Sisco Research Laboratories Pt. Ltd.

Methods

Extraction of chlorophyll and carotenoids: Chlorophyll and carotene pigments were both extracted from their natural sources and then blended with two samples of a refined, bleached and deodorized edible grade sunflower oil (SFO). The carotenoids were extracted from the roots of carrots (*Daucus carota*) whereas the chlorophyll was extracted from fresh leaves of rocket plant (*Eruca sativa*) according to the AOAC (2012).

Extraction of carotenoids: The roots of carrots (*Daucus carota*) were thoroughly washed and then minced in a meat grinder. The ground product was then vigorously stirred for 5 min with a mixture of acetone and n-hexane (1:1, v/v) to which 2 g $MgCO_3$ was added for each 100 g carrot. The residue was allowed to settle and the liquid extract was filtered. The liquid extract was then stirred with distilled water whereby two liquid layers have been formed, a polar and a non-polar layers. The first contained acetone and water while the other contained the carotenoids dissolved in n-hexane, which was then completely evaporated under vacuum.

Extraction of chlorophyll: Fresh leaves of rocket plant (*Eruca sativa*) were cut and ground as given under the extraction of carotenes. The minced product was then stirred with 85% acetone to which 2 g Na_2CO_3 was added for each 100 g rocket, filtered and dried under vacuum.

Blending of each of the two pigments with SFO: Both pigment extracts were blended with SFO to yield two oil blends; one rich in chlorophyll (A), while the other was rich in carotenoids (B). The concentration of each pigment in the oil blends A and B was adjusted so that they will have reasonable absorbance(s) at the wave length(s) specific of each pigment. Chlorophyll absorbs at 670 nm, whereas, carotenoids absorb at 432, 455 and 480 nm. The absorbance of an oil at 670 nm and the sum of its absorbance at 432, 455 and 480 nm are thus, proportional to its content of chlorophyll and carotenoids, respectively.

Bleaching of samples of each of the two oil blends (A) and (B), using the four types of adsorbents: Twenty grams of the oil containing the pigment extract (chlorophyll or carotenoids) was heated to the desired temperature, stirred with the specified load of the clay for 10 min and it was then filtered. The absorbance of the filtered oil was then measured at the wave length(s) specific of each pigment using UV-visible spectrophotometer (UV-160 1PC, UV-visible spectrophotometer, Shimadzu, Tokyo, Japan). The procedures were carried out at 30 and 100°C and it was repeated at each temperature using different clay loads. The oil absorbance(s) after bleaching were recorded each time at the previously mentioned wave lengths.

Investigating the effect of the different clays used on the removal of phenolics during oil bleaching: Four samples of an edible grade SFO, 20 g each, were bleached following the pre-mentioned procedure at 100°C using 1% of each clay, which are the conditions usually used in industrial bleaching. The bleached oil samples as well as the original oil sample (a total of five oil samples) were then tested for their content of phenolic compounds. This has been done through two consecutive steps being the extraction of phenolic compounds from the five oil samples followed by quantitative determination of total phenolics using Folin-Ciocalteu (FC) reagent.

Extraction of total phenolics: The phenolic compounds in each of the five oil samples were extracted using the procedure of Tasioula-Margari and Okogeri (2001). Briefly, 10 mL of n-hexane was added to 10 mL of each oil sample, shook for one minute followed by the addition of 10 mL of MeOH/H_2O mixture (70/30, v/v). The whole mixture was then thoroughly shook in a separating funnel and the lower layer containing the phenolic compounds was then separated. The extraction procedure was repeated twice with another 10 mL MeOH/H_2O mixture. The two extracts were collected and the volume was made up to 25 mL with the same solvent mixture.

Quantitative determination of total phenolics: The method of Singh *et al.* (2002) was used to estimate the percentage of total phenolic compounds in the oil samples using Folin-Ciocalteu (FC) reagent with slight modification according to El-Hamidi and El-Shami (2015). From each of the phenolic extracts, a suitable volume (100 μL) was taken and the volume was brought up to 3 mL with distilled water. Two milliliters of 10-fold diluted FC reagent was then added. After 5 min, 1 mL of 7.5% sodium carbonate solution was added and it was left for 30 min at room temperature before taking spectrophotometric readings. The absorbance was measured at 765 nm using a UV-visible spectrophotometer (UV-160 1PC, UV-visible spectrophotometer, Shimadzu, Tokyo, Japan). A blank was prepared exactly the same way with exclusion of phenolic extracts. The percentage removal of total phenolic compounds using the four different adsorbents were then estimated and compared.

RESULTS AND DISCUSSION

Results of oil bleaching using the four different clays under study: The removal of carotenoids as well as chlorophyll from vegetable oils were followed up according to the reduction in the oil absorbance by bleaching at the wave length(s) at which each of these two pigments absorbs. As previously mentioned, chlorophyll absorbs at 670 nm whereas, carotenoids absorb at 432, 455 and 480 nm. The absorbance

Table 1: Adsorption constant and exponent constant in case of pigment adsorption on Fulmont clay

	At 30°C			At 100°C		
Pigments	Adsorption constant (k)	Exponent constant (n)	Correlation coefficient (R^2)	Adsorption constant (k)	Exponent constant (n)	Correlation coefficient (R^2)
Chlorophyll	$10^{1.0942}$ = 12.4222	0.2456	0.9819	$10^{1.1374}$ = 13.7214	0.2341	0.9614
Carotenoids	$10^{1.4447}$ = 27.8419	0.5412	0.9531	$10^{1.769}$ = 58.7489	0.8011	0.873

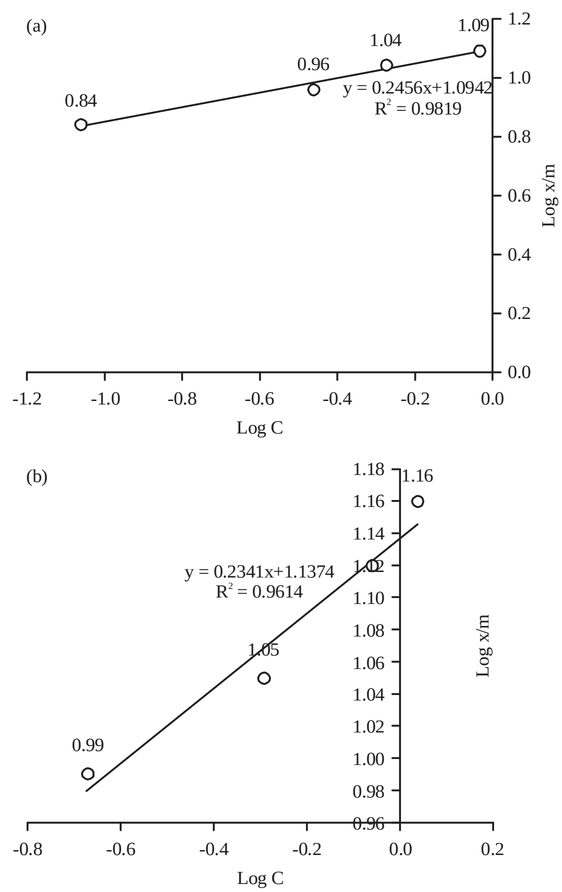

Fig. 1(a-b): Adsorption isotherm of chlorophyll on Fulmont clay at (a) 30°C and (b) 100°C

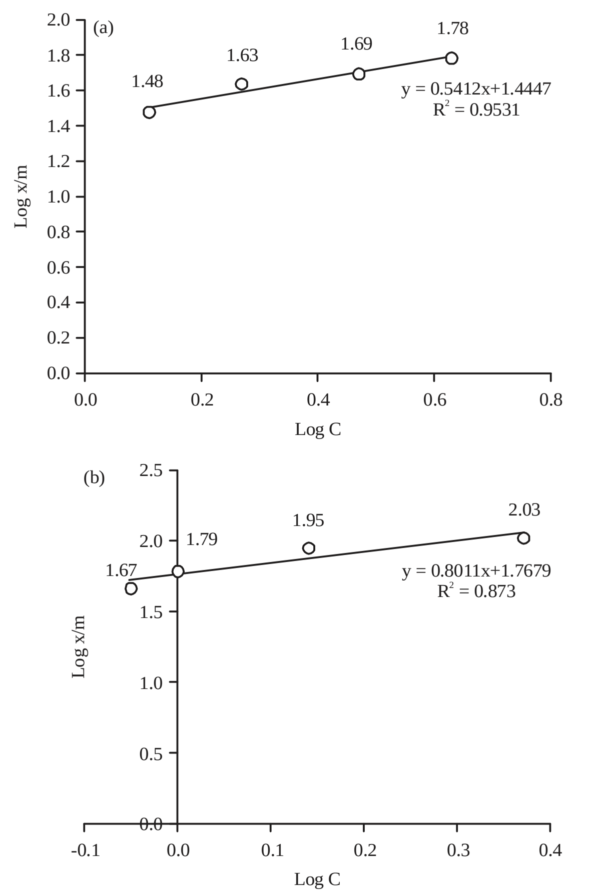

Fig. 2(a-b): Adsorpthon isotherm of carotenoids on Fulmont clay at (a) 30°C and (b) 100°C

of an oil at 670 nm and the sum of its absorbances at 432, 455 and 480 nm are thus, proportional to its content of chlorophyll and carotenoids, respectively. The adsorption of pigments on bleaching clays is supposed to obey Freundlich adsorption equation, $x/m = kC^n$ in which m refers to the load of the adsorbent g/100 g oil, while C refers to the concentration of the pigment after bleaching and x refers to the difference between its concentration before and after bleaching, R and C, respectively (Patterson, 1992). In this equation k is referred to as the adsorbent constant, while n is another constant called the exponent constant. According to Freundlich equation; the plotting of log (x/m) on the Y axis against log C on the X axis will yield a straight line, whose slope is equal to n and its intercept with the ordinate equals log k (Megahed, 1991). However, it has been reported that adsorption of colouring matters on some types of adsorbents does not follow that equation (Gutfinger and Letan, 1978; Megahed, 1991; El-Nomany *et al*., 2014).

It is clear from the results presented in Fig. 1(a-b) and 2(a-b) that the adsorption of chlorophyll as well as carotenoids on Fulmont clay obeys Freundlich equation. A summary of the results is listed in Table 1. However, the results obtained in this study concerning the removal of chlorophyll and carotenoids on the other three clays used in this study were not in

Table 2: Derived correlations between percentage removal of chlorophyll (y) and percentage of clay used (x) and the correlation coefficient (R^2)

Clay types	Correlation at 30°C	R^2	Correlation at 100°C	R^2
Tonsil ACC	$y = -76.567x^2+194.01x-31.464$	0.999	$y = -22.003x^2+113.97x-6.6061$	0.997
Mexican	$y = -46.6x^2+129.51x-24.82$	0.979	$y = -63.159x^2+164.53x-28.416$	0.999
Fulmont	$y = -34.12x^2+106.14x+13.35$	0.999	$y = -28.27x^2+103.61x+14.836$	0.999
Tonsil N	$y = -8.2073x^2+59.167x+1.5364$	0.862	$y = -88.711x^2+184.37x-27.473$	0.998

Table 3: Derived correlations between percentage removal of carotenoids (y) and percentage of clay used (x) and the correlation coefficient (R^2)

Clay types	Correlation at 30°C	R^2	Correlation at 100°C	R^2
Tonsil ACC	$y = 56.033x^2-43.429x+13.566$	0.984	$y = -259.21x^2+417.83x-80.356$	0.994
Mexican	$y = 3.7189x^2-4.7839x+1.9718$	0.9948	$y = -10.804x^2+81.266x-31.848$	0.9869
Fulmont	$y = -50.637x^2+134.06x+0.0176$	0.978	$y = -60.207x^2+102.62x+48.454$	0.942
Tonsil N	$y = -0.162x^2+2.3642x+0.3797$	0.979	$y = 39.097x^2-43.984x+14.507$	1

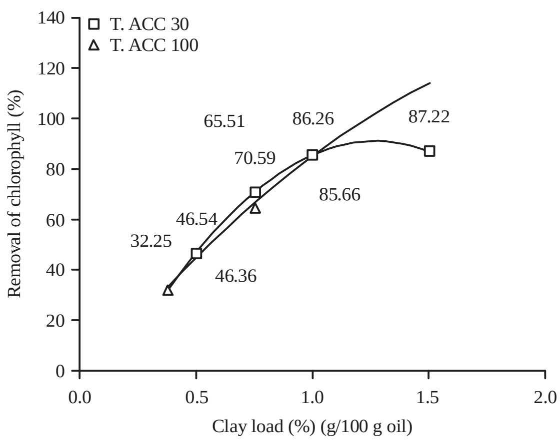

Fig. 3: Percentage removal of chlorophyll by adsorption on Tonsil ACC clay using different clay loads

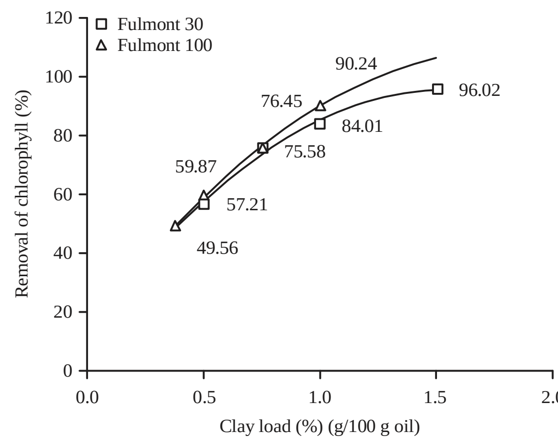

Fig. 5: Percentage removal of chlorophyll by adsorption on Fulmont clay using different clay loads

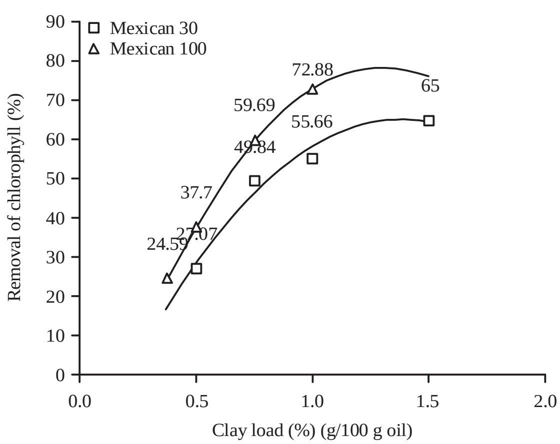

Fig. 4: Percentage removal of chlorophyll by adsorption on Mexican clay using different clay loads

agreement with Freundlich adsorption equation. This has been similarly reported with some types of clays (Gutfinger and Letan, 1978; El-Nomany *et al*., 2014).

Therefore, the efficiencies of the four clays to adsorb these two pigments from vegetable oils were studied and compared according to their percentage removal by bleaching using each clay. The results of bleaching at 30 and 100°C using the four clays are graphically represented in Fig. 3-10. The correlations obtained by fitting the data in these figures which show the effect of clay load on the percentage removal of each of the two pigments are listed in Table 2 and 3.

These equations have been then utilized to estimate the percentage improvement in pigment removal due to the increase of the oil temperature from 30-100°C during the bleaching process using different types of clays at different loads. The obtained results of such estimations are graphically represented in Fig. 11-14. It is quite clear that the temperature is a much more controlling variable in case of carotenoids as compared to chlorophyll and it varies greatly according to the type of clay used in bleaching. For example, the increase in the temperature effects an increase in the percentage removal of

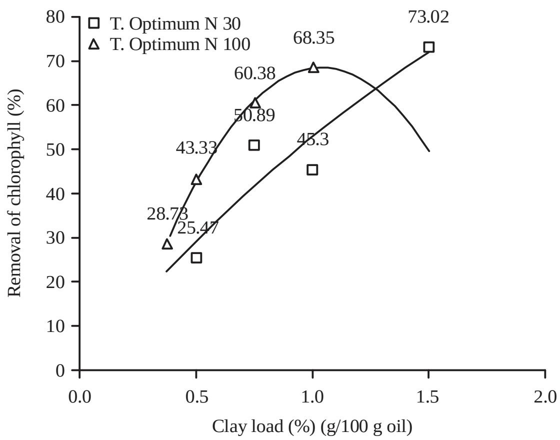

Fig. 6: Percentage removal of chlorophyll by adsorption on Tonsil Optimum N clay using different clay loads

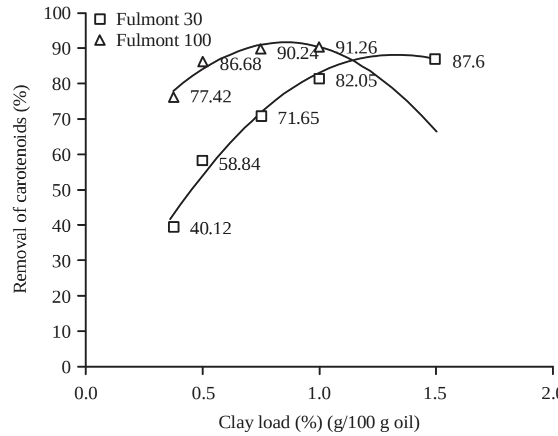

Fig. 9: Percentage removal of carotenoids by adsorption on Fulmont clay using different clay loads

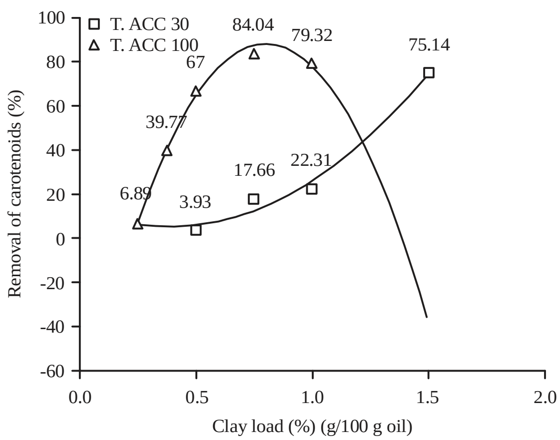

Fig. 7: Percentage removal of carotenoids by adsorption on Tonsil ACC clay using different clay loads

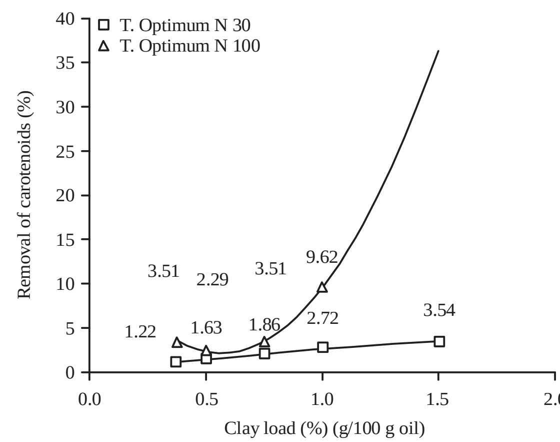

Fig. 10: Percentage removal of carotenoids by adsorption on Tonsil Optimum N clay using different clay loads

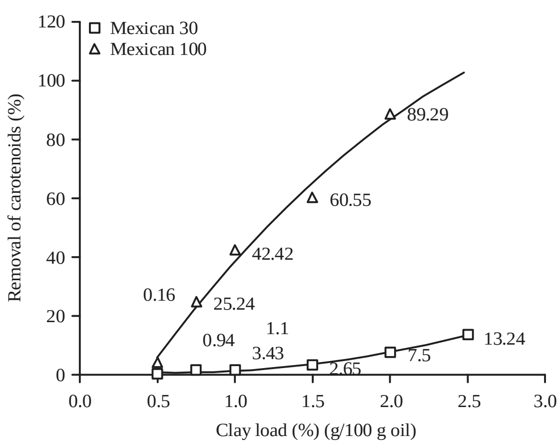

Fig. 8: Percentage removal of carotenoids by adsorption on Mexican clay using different clay loads

carotenoids equivalent to 3718, 234, 210 and 5 folds by bleaching using 1% of Mexican clay, Tonsil N, Tonsil ACC and Fulmont clay respectively. However, in case of chlorophyll, such increase in temperature effects an increase in percentage removal equivalent to 35.8, 35.85, 5 and 2.6 folds only for the same clays in the same order. It appears also that the role of temperature as a controlling variable differs according to the clay load used. At lower clay loads, the effect of increasing the temperature on improving the adsorption efficiency is more pronounced in case of Mexican clay and Tonsil ACC while the reverse is true in case of the other two clays; Tonsil N and Fulmont clay. In view of the pre-mentioned results, it is highly recommended to increase the temperature during the bleaching of oils rich in carotenoids such as palm oil especially when the clay load used is low. However, the increase in the

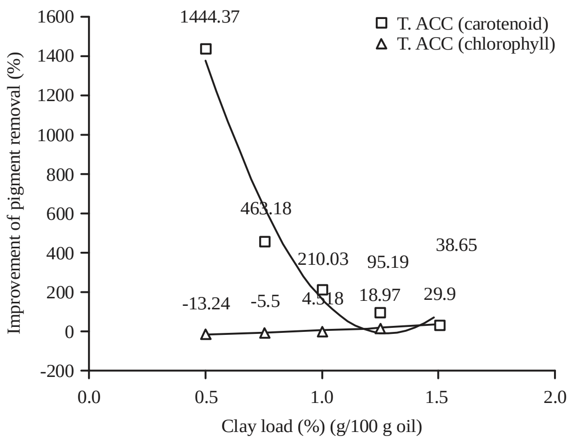

Fig. 11: Percentage improvement of pigment removal by increasing the adsorption temperature from 30-100°C using different clay of Tonsil ACC clay

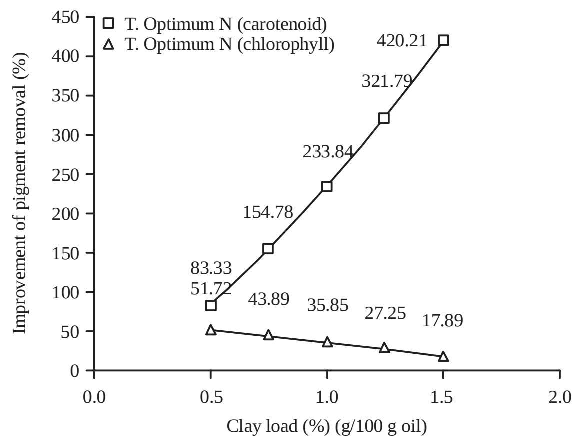

Fig. 14: Percentage improvement of pigment removal by increasing the adsorption temperature from 30-100°C using different clay of Tonsil Optimum N clay

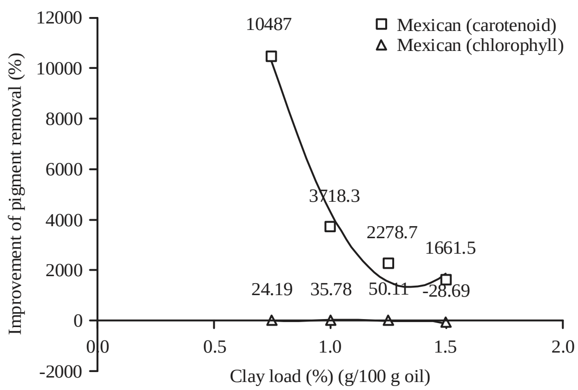

Fig. 12: Percentage improvement of pigment removal by increasing the adsorption temperature from 30-100°C using different clay of Mexican clay

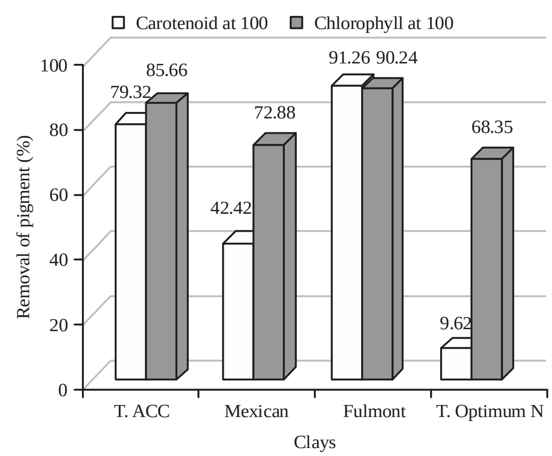

Fig. 15: Percentage removal of chlorophyll and carotenoids using 1% of each of the four types of clays at 100°C

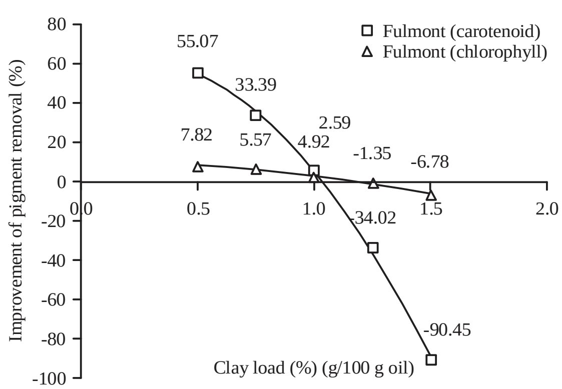

Fig. 13: Percentage improvement of pigment removal by increasing the adsorption temperature from 30-100°C using different clay of Fulmont clay

bleaching temperature of oils rich in chlorophyll such as olive oil will not effects an appreciable improvement in the removal of this pigment. Hence, it is not recommended to heat such oils during the bleaching process as to reduce energy consumption and hence the running cost of the bleaching process.

The capacities of the different clays to adsorb chlorophyll as well as carotenoids at 100°C using 1% clay which are the conditions usually adopted in the oil and soap industrial bleaching are compared in Fig. 15. Fulmont clay seems to have the greatest power to remove both types of pigments whereby the percentage of their removal using this clay was over 90%. The adsorption power of other clays decreases in the following order: Tonsil ACC>Mexican>Tonsil N. The effect of clay type on pigment removal is more pronounced in case

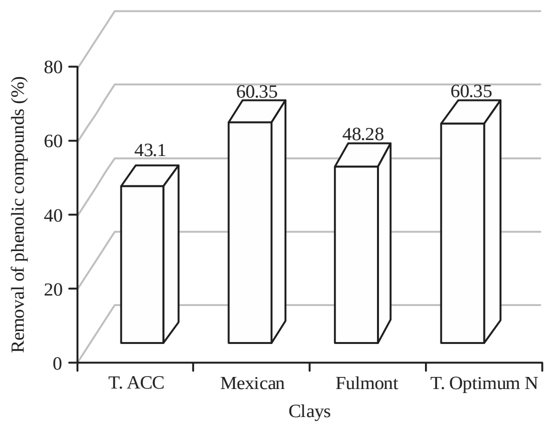

Fig. 16: Percentage removal of phenolic compounds of SFO using 1% of each of the four types of clays at 100°C

of carotenoids compared to that in case of chlorophyll. The percentage of carotenoids removal using Fulmont clay was 91.3% compared to 9.62% only using Tonsil N. Thus the latter type of clay, Tonsil N is not recommended to bleach oils rich in chlorophyll.

Effect of clay type on the removal of phenolic compounds: The four types of clays are compared for their effect on removing phenolic compounds from vegetable oils (SFO) during their bleaching in Fig. 16. It can be seen that the removal of phenolic compounds from vegetable oils (SFO) is least using Tonsil ACC clay followed by Fulmont clay. Mexican clay and Tonsil N have almost the same power to remove phenolic compounds. Hence, it is expected that oils bleached using Tonsil ACC will be the most stable against deteriorative oxidation during their use or storage. However, they are slightly darker than those bleached using Fulmont clay.

CONCLUSION

According to the results of this study it can be stated that carotenoids can be adsorbed on the bleaching clays more efficiently than chlorophyll. In addition, the effect of temperature on pigment removal by bleaching is much more pronounced in case of carotenoids compared to chlorophyll. Also, it has been found that bleaching of vegetable oils using Fulmont clay can yield oils of lighter color compared to other clays, while their bleaching using Tonsil ACC clay can yield oils more stable to oxidation.

REFERENCES

AOAC., 2012. Official Methods of Analysis of AOAC International, Volume 1. 19th Edn., AOAC International, USA., ISBN: 9780935584837.

Bailey, A.E., D. Swern and K.F. Mattil, 1964. Bailey's Industrial Oil and Fat Products. 3rd Edn., John Wiley and Sons, New York, ISBN: 9780470041253, Pages: 1103.

El-Hamidi, M. and S.M. El-Shami, 2015. Scavenging Activity of different garlic extracts and garlic powder and their antioxidant effect on heated sunflower oil. Am. J. Food Technol., 10: 135-146.

El-Nomany, H.M. and F.A. Zaher, 1987. Cottonseed oil pigment contents as affected by miscella refining and oil storage. Seifen Ole Fette Wachse, 113: 74-75.

El-Nomany, H.M., O.A. Megahed and F.A. Zaher, 2014. Comparison between different types of adsorbents. Part 1: Efficiency of decolourizing cottonseed and soybean oils. Trans. Egypt. Soc. Chem. Eng., 40: 1-15.

Gonzalez-Pradas, E., M. Villafranca-Sanchez and A. Gallego-Campo, 1993. Influence of the physical-chemistry properties of an acid-activated bentonite in the bleaching of olive oil. J. Chem. Technol. Biotechnol., 57: 213-216.

Gutfinger, T. and A. Letan, 1978. Pretreatment of soybean oil for physical refining: Evaluation of efficiency of various adsorbents in removing phospholipids and pigments. J. Am. Oil Chem. Soc., 55: 856-859.

Hamn, W. and R.J. Hamilton, 2000. Edible Oil Processing. Sheffield Academic Press, UK.

Megahed, O.A., 1991. Evaluation of some common adsorbents and local activated clays as bleaching agents. M.Sc. Thesis, Cairo University, Giza, Egypt.

Patterson, H.B.W., 1992. Bleaching and Purifying Fats and Oils: Theory and Practice. AOCS Press, Champaign, IL., ISBN-13: 9780935315424, Pages: 242.

Siddiqui, M.K.H., 1968. Bleaching Earth. 1st Edn., Pergamon Press, London, ISBN-13: 9780080127385, Pages: 96.

Singh, R.P., K.N.C. Murthy and G.K. Jayaprakasha, 2002. Studies on the antioxidant activity of pomegranate (*Punica granatum*) peel and seed extracts using *in vitro* models. J. Agric. Food Chem., 50: 81-86.

Tasioula-Margari, M. and O. Okogeri, 2001. Isolation and characterization of virgin olive oil phenolic compounds by HPLC/UV and GC-MS. J. Food Sci., 66: 530-534.

Zaher, F.A., 1990. Bleaching of cottonseed oil. I. Evaluation of the efficiency of various adsorbents. Seifen Ole Fette Wachse, 116: 813-816.

Zaher, F.A., A. Amin and B.S. Girgis, 1991. Suitability of some Egyptian clay deposits as decolorizing agents for edible oils. AMSE., 7: 19-30.