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Reuse of discarded deactivated bleaching earths in the bleaching of oils

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RESUMEN

Reutilización de tierras decolorantes desactivadas desechadas para la decoloración de aceites.

Tierra decolorante desechada, fue empleada, tras su reactivación para decolorar aceites de girasol, soja y maíz. La eficiencia de la tierra decolorante reactivada fue comparada con la de la virgen activada. La tierra reactivada ácida (pH 2,5-3) tuvo ligeramente mayor contenido en silicona que la tierra virgen o la reactivada neutra. Los mejores resultados en el color de los aceites de girasol y maíz fueron obtenidos cuando se emplearon niveles del 1 y 2% de tierra reactivada neutra (pH 6-7). La tierra ácida reactivada, usada al 2% consiguió una mayor reducción del color del aceite de soja, que una misma dosis de tierra virgen (pH 3). Ambas tierras reactivadas redujeron el índice de peróxidos, hierro, dienos conjugados y jabón de los aceites, mientras que hicieron aumentar la acidez y los trienos conjugados. Además, estas tierras reactivadas determinaron mayores descensos en los periodos de inducción del aceite que la tierra virgen. Las tierras reactivadas podrían ser usadas durante 5 ciclos para la decoloración de aceites de soja y girasol y durante más de 6 ciclos con aceite de girasol.

PALABRAS-CLAVE: Activación de tierra decolorante usada - Reciclado de tierras decolorantes desactivadas - Tierras decolorantes desactivadas y desechadas.

SUMMARY

Reuse of discarded deactivated bleaching earth in the bleaching of oils.

Discarded bleaching earth was used after its reactivation for the bleaching of sunflower, soybean and corn oils. The efficiency of reactivated bleaching earth was compared to the efficiency of virgin activated bleaching earth. Acid reactivated earth (pH 2.5-3) had a slightly higher content in silicone than virgin activated or neutralized reactivated earths. The best results in the color of sunflower and corn oils were obtained when neutralized earth (pH 6-7) was used at 1 and 2 % levels. Acid reactivated earth used at 2 % achieved a higher reduction in soybean oil color than virgin earth (pH 3) at the same dosage. Both reactivated earths reduced peroxide value, iron, conjugated dienes and soap, while they increased acidity and conjugated trienes. Furthermore, these reactivated earths determined higher decrements in the oil induction period than virgin earth. Reactivated earth could be used for 5 cycles for the bleaching of soybean or corn oils and for more than 6 cycles for sunflower oil.

KEY-WORDS: Activation of spent bleaching earth - Discarded deactivated bleaching earth - Recycling of deactivated bleaching earth.

1. INTRODUCTION

Bleaching is recognized as one of the most important steps in edible oil processing (Mag, 1990; Micheal et al., 1992). According to Brimberg (1982), Young (1987), Abul Kalam and Joshi (1988), and Topallar (1998), bleaching is used daily in refining practices and aims not only at the removal of coloring bodies, pigments, etc., but also at the removal of residual amounts of phospholipids, mucilage, oxidized tri – or partial acyl – glycerols, metal traces in ionizable and non – ionizable (complexed) forms, and soap traces which survived the washing of the neutralized oil. Waldmann and Eggers (1991) reported that montmorillonite is the starting material for all activated bleaching clays. While Segers (1992) cited that the bulk of natural bleaching earths consists of complex silicates with aluminum ions.

Kaufmann (1968) and Hoffmann (1989) reported that bleaching earths are subdivided into two groups: the naturally active clays form one group, and the highly active clays form another. Waldmann and Eggers (1991) mentioned that to make clay suitable for bleaching purposes, montmorillonite is subject to acid treatment, which replaces cations by protons and partially dissolves the original crystal structure. On the other hand, many other processes for the regeneration of bleaching earth have been patented (Abul Kalam and Joshi, 1988). Anderson (1996) suggested that spent clay can be used as asphalt additive, replacement for plastic parts in refractories, in cement manufacturing, soil stabilizers and road foundation. In Egypt, spent bleaching earth is not used in any manufacturing, so this discard causes some problems for the environment.

According to The Chamber of Food Industries, Egyptian Industries Federation (The Egyptian Industry Ministry, 2002a), the production volume from oils and fats in 2001/2002 was about 650.000 tons. On the other hand, all activated bleaching earths are imported to Egypt from China, Germany and Indonesia. The percentage of activated bleaching earth used for oil bleaching ranges from 1 to 2 % of the oil weight. Therefore, the imported amounts from activated bleaching earth to Egypt ranged from 6500 to 13000 tons in 2001/2002 for bleaching the entire 650.000 tons. Respectively, the price of imported activated bleaching earth is about $500.00 per ton (The Egyptian Industry Ministry, 2002b). Hence, if discarded deactivated bleaching earth can be reused (after reactivation) for oil bleaching, it will reduce the imported amount of activated bleaching earth and it will also reduce the

production cost of oils at about 3.25 – 6.5 million dollars per year. Therewithal, the reactivation cost of spent bleaching earth in this study is very low.

The purpose of the present research was to reuse spent bleaching earth (discarded deactivated bleaching earth) after its bleaching in the oil bleaching process and to reduce the production cost of oils as well as to reduce environmental pollution from this waste by reusing it in a beneficial manner and, at the same time, to reduce imported amounts of activated bleaching earth to Egypt.

2. MATERIALS AND METHODS

2.1. Materials

Neutralized sunflower and soybean oils were brought from the Cairo Oils and Soaps Company (Aiat factory, Giza, Egypt) while neutralized corn oil was supplied by the Egyptian Company for Starch and Glucose (Cairo, Egypt). These oils were used as substrates in the bleaching tests.

Virgin activated bleaching earth (as a reference) was obtained from the Cairo Oils and Soaps Company (Aiat factory, Giza, Egypt), which was imported from Germany (Table I).

A discarded deactivated bleaching earth was also taken from the Cairo Oils and Soaps Company (Aiat factory, Giza, Egypt), which contained 40 % oil and 10.5 % moisture. It had a repulsive odor.

N – hexane (60 – 80°C) and some materials used for the reactivation of discarded deactivated bleaching earth were brought from the EL-Gomhoria Company for Pharmaceutical (Cairo, Egypt).

2.2. Methods

Determination of physical and chemical properties of the oils used in this study

Acidity (%) as oleic acid, peroxide value (eq. O_2 / Kg oil), iron (ppm), phosphorus (ppm) and soap (ppm) in sunflower, soybean and corn oils were performed according to the methods described in the A. O. C. S. (1997), while conjugated dienes and trienes (absorbance $E^{1\%}_{1\ cm}$ at 232 and 270 nm, resp.) were estimated according to the methods found in the FAO / WHO (1970) by using U.V.– Vis. Spectrophotometer, Model Labomed, 120-02. The color of oils was measured by Lovibond tintometer, Model E, using 5.25 inch cell following the method reported in the A.O.C.S. (1993).

The per cent color reduction was calculated using the equation of Krishnan (1975).

Determination of chemical composition of virgin activated and reactivated bleaching earths

Silicone (SiO_2), aluminum (Al_2O_3), iron (Fe_2O_3), sodium (Na_2O), calcium (CaO), potassium (K_2O) and magnesium (MgO) in each of the virgin activated and reactivated bleaching earths were measured according to the methods reported by Jackson, (1967) and Loranz, et al., (1980) by using Atomic Absorption Spectrometers (Perkin-Elmer 372 and Perkin-Elmer 3300).

The moisture content in both virgin activated and reactivated bleaching earths was determined using an electric oven at 105°C for 3 hrs. while their pH values were estimated using pH Meter HI-9321

Table I

Effect of reactivation of discarded deactivated bleaching earth on its chemical composition

Minerals compounds (%)	Virgin activated bleaching earth (pH = 3)	Reactivated bleaching earths	
		(pH =2.5 – 3.0)	(pH = 6 - 7)
Silicone [SiO_2]	68.3	68.8	66.9
Aluminum [Al_2O_3]	16.4	16.2	17.3
Iron [Fe_2O_3]	3.9	3.8	3.9
Sodium [Na_2O]	0.4	0.4	0.5
Calcium [Ca O]	1.2	1.3	1.3
Potassium [K_2O]	0.5	0.5	0.6
Magnesium [Mg O]	1.3	1.3	1.4
Characters Moisture(%)	10.0	10.0	10.0
pH value (10 % suspension in distillated water)	3.0	2.5 – 3.0	6 – 7
Particle size passing through 200 mesh (74 micron) sieve (%)	85	85	85

(Hanaa Instruments) according to the method described by Anthony and Ogugua (1988).

Determination of oxidative stability of the bleached oils

The determination of the oxidative stability of the bleached oils was performed according to the method described by Tsaknis et al., (1999) using Metrohm Rancimat 679 at 100°C with an air flow of 20 L / h.

Reactivation of discarded deactivated bleaching earth

About 500 gr. of spent bleaching earth was milled and soaked in 2 liters n-hexane (60–80°C) for 24 h at room temperature to remove the residual oil and also to obtain defatted spent bleaching earth. Defatted deactivated bleaching earth was reactivated using several procedures (Patent, 2002). After that, the resultant reactivated bleaching earth was acidic or neutral. The reactivated bleaching earth was dried in an electric oven at 105°C to reach a moisture content of about 10 ± 1 % and pulverized to a fine powder in pestle and mortar to its original particle size (about 85 % reactivated bleaching earth passing through 74 micron sieve 200 mesh). The reactivated bleaching earths were analyzed and tested for bleachability.

The bleachability test for reactivated bleaching earth

The reactivated bleaching earth was tested for bleachability by using the method described by Rolando (1991) with some modifications as follows: Different dosages from reactivated bleaching earth (1.0, 1.5 and 2.0 % from the oil weight) were separately added to each of neutralized sunflower, soybean and corn oils at a temperature of 95 ± 1°C and the mixture was stirred at 250 rpm for 30 min under vacuums (25-30 mm/Hg) in a Rotary evaporator. After that, the mixture (the hot oil and reactivated bleaching earth) was cooled at 50 ± 1°C and filtered through filter paper Whatman n° 1 to separate the clay from the bleached oil and at the same time to return this discard for reusing it in the oil bleaching after its activation. The bleached oils were analyzed for their physical and chemical properties. Virgin activated bleaching earth was used for bleaching the oils (as a reference) according to the method described above.

3. RESULTS AND DISCUSSION

Bleaching clay performs not only color removal, but also the removal of trace metals, adsorption of phospholipids and soap, and decomposition of oxidation products such as peroxides (Nnadozie et al., 1989; Hui, 1996).

3.1. Effect of reactivation of discarded deactivated bleaching earth on its chemical composition

Bleaching clay is a general term for a clay-like substance, water containing aluminosilicates containing various proportions of magnesium, calcium and iron (Waldmann and Eggers, 1991). The effect of activation on the chemical components of the reactivated bleaching earth is evident from the results presented in Table I. It can be noted that acid reactivated bleaching earth (pH 2.5-3) had a slightly higher amount of silicone and a lower content of aluminum (68.8 and 16.2%, resp.) than neutralized reactivated bleaching earth (pH 6–7) which were 66.9 and 17.3%, respectively. These differences are closely related to the variation in pH value. These results are the same as those found by Kheok and Lim (1982) who reported that the initial increase in bleaching ability with increasing sulfuric acid addition is due to net charges in the clay. Also, the results showed that silicone was the main mineral present, followed by aluminum for virgin activated and reactivated bleaching earths but at different levels. Also, the results shown that the contents of other minerals in acid reactivated bleaching earth (pH = 2.5–3) were somewhat equal to those obtained in virgin bleaching earth (pH = 3) but they were slightly higher than those found in the neutralized reactivated bleaching earth (pH = 6–7). These data agree with those recorded by Kheok and Lim (1982) who pointed out that the activation of montmorillonite with mineral acids dissolve some impurities such as aluminum, ferrous and ferric iron and magnesium.

The other parameters pertaining to moisture, pH value and particle size of reactivated bleaching earth are somewhat similar to those found in virgin activated bleaching earth. According to Hoffmann (1989), the moisture content of bleaching earth is generally 10%.

3.2. Effect of pH value of virgin activated and reactivated bleaching earths on the color of bleached oils

Figure 1 and Table II give the changes in color and total color of sunflower, soybean and corn oils treated separately with either virgin activated or reactivated bleaching earths (which had different pH values). From these data, it can be found that the bleaching of sunflower oil with neutralized reactivated bleaching earth (pH = 6-7) produced a reduction of 82.4% in the total color compared to those obtained by acid reactivated bleaching earth (pH = 2.5–3) and virgin activated bleaching earth (pH = 3) which were 74.4

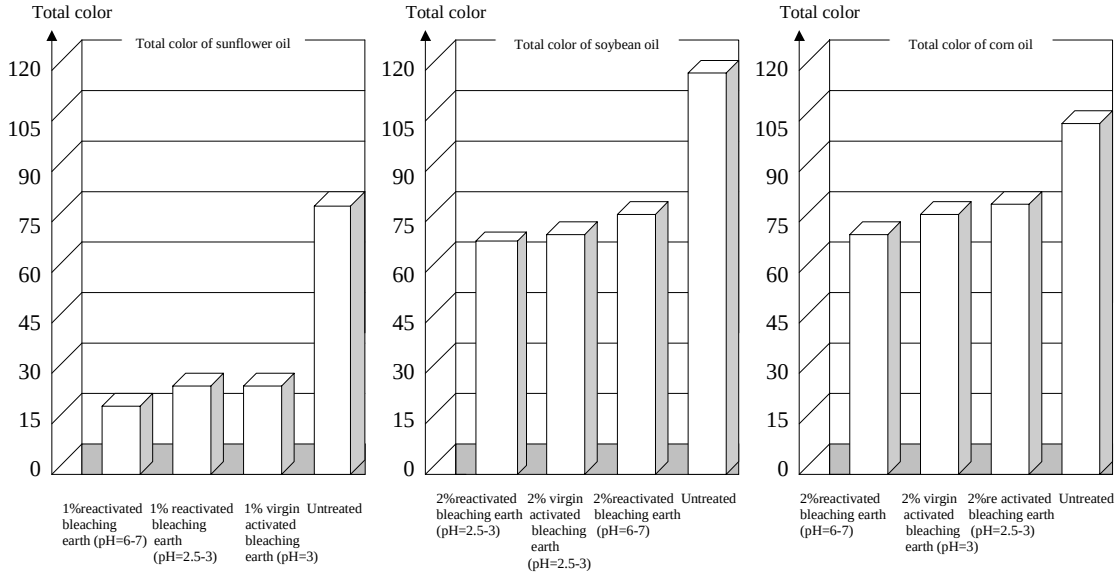

Figure 1
Effect of pH value of reactivated bleaching earth on total color of sunflower, soybean and corn oils.

and 74.5%, respectively. These values are similar to those mentioned by Hoffmann (1989).

Also, the data showed that acid reactivated bleaching earth (pH = 2.5-3) produced a higher reduction in the color of soybean oil than that done by neutralized reactivated bleaching earth (pH = 6 – 7). These differences are perhaps related to the fact that acid reactivated bleaching earth is more effective in color reduction of the oil, containing a high content of chlorophyll, than neutralized reactivated bleaching earth. These data are in agreement with the findings of Hoffmann (1989), who cited that oils (which have a high content of chlorophyll) treated with acid activated bleaching earth have a much lower residual color than do those treated with an earth of natural activity.

According to Loncin (1970) and Hui (1996) from 5 – 20 % reduction in the red color of soybean, canola and palm oils occurred during the bleaching with acid activated bleaching earth, so a breakdown occurs in chlorophyll and carotene. The increase in adsorption activity of clays after acid treatment is explained to be due to the weakness of the Si-O bonds in the clay structure.

The results displayed in Table II show that neutralized reactivated bleaching earth (pH = 6 – 7) produced a high reduction of about 33.7 % in total color of corn oil during the bleaching compared to acid reactivated bleaching earth (pH = 2.5 – 3) which gave a low reduction in the total color (24.2 %) at the same dosage (2%). These results are similar to those recorded by Boki et al. (1991) and Hui (1996) who revealed that differences in physical and chemical properties of activated carbons cause differences in activity for reducing color.

From the aforementioned results, it can be clear that neutralized reactivated bleaching earth (pH = 6 – 7) was more effective in reducing the color of sunflower and corn oils than acid reactivated bleaching earth (pH = 2.5 – 3). On the other hand, the most effective in the reduction of soybean oil color was the acid reactivated bleaching earth (pH = 2.5 – 3), so the pH value of reactivated bleaching earth plays an important role in bleaching efficiency.

3.3. Effect of dosages of virgin activated and reactivated bleaching earths on color of the bleached oils

The quantity of activated bleaching earth required for oil bleaching depends on the quality of the oil, activity of the earth and process conditions, and is normally between 0.5 and 2.0 per cent of the oil weight (Brimberg, 1982; Hoffmann, 1989). From the data listed in Table III, it can be seen that the highest reduction in total color of sunflower oil was observed after bleaching with 2 % neutral reactivated bleaching earth (pH 6 – 7). On the other hand, 1 % of neutral reactivated bleaching earth (pH 6 – 7) produced a reduction in total color (Total color = 12.5) similar to that obtained with 2 % from the same bleaching earth (Total color = 8.0). These results are better than those obtained with either acid reactivated bleaching earth (pH 2.5 – 3) or virgin activated bleaching earth (pH 3) at the same dosages. It is also clear that 2 % acid reactivated bleaching earth (pH 2.5 – 3) used for the bleaching of soybean oil produced a high reduction in total color (Total color = 60.0) compared with that obtained by

Table II

Effect of pH value of virgin activated and reactivated bleaching earths on color of the bleached oils

Parameter	Color of neutralized sunflower oil (Before bleaching)				Color of neutralized soybean oil (Before bleaching)				Color of soybean oil treated with 2% reactivated bleaching earth					Color of neutralized corn oil (Before bleaching)				Color of corn oil treated with 2%reactivated bleaching earth				
	Y	R	B	Total color Y+ 10(R+B)	Y	R	B	Total color Y+10 (R+B)	Y	R	B	Total color Y+ 10 (R+B)	Color Reduc-tion (%)	Y	R	B	Total color Y+ 10 R+B)	Y	R	B	Total color Y+10 (R+B)	Color reduction (%)
Reactivated bleaching earth (pH = 2.5-3)	20	5.1	zero	71	35	6.5	1.0	110	20	4.0	Zero	60	45.4	35	6.0	zero	95	20	5.2	zero	72	24.2
Reactivated bleaching earth (pH= 6-7)	20	5.1	zero	71	35	6.5	1.0	110	20	4.4	0.2	66	40.0	35	6.0	zero	95	20	4.3	zero	63	33.7
Virgin activated bleaching earth (pH = 3)	20	5.1	zero	71	35	6.5	1.0	110	20	4.1	0.1	62	43.6	35	6.0	zero	95	20	4.9	zero	69	27.4

Note: Y = Yellow ; R = Red; B = Blue

Table III

Impact of dosages of virgin activated and reactivated bleaching earths on color of the bleached oils

		Color of the neutralized oil (Before the bleaching)	Virgin activated bleaching earth pH= 3			Reactivated bleaching earth					
						pH=2.5-3			pH=6-7		
Dosages of bleaching earth (% from the oil weight)		zero	1.0	1.5	2.0	1.0	1.5	2.0	1.0	1.5	2.0
Color of sunflower oil	Yellow	20.0	8.1	7.0	7.0	8.1	7.0	6.9	6.5	6.4	6.0
	Red	5.1	1.0	0.5	0.4	1.0	0.4	0.4	0.6	0.3	0.2
	Blue	zero	zero	zero	zero	zero	zero	zero	zero	zero	zero
Total color		71.0	18.1	12.0	11.0	18.1	11.0	10.9	12.5	9.4	8.0
Color of soybean oil	Yellow	35.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0
	Red	6.5	5.1	4.8	4.1	5.2	4.9	4.0	5.4	5.1	4.4
	Blue	1.0	0.5	0.4	0.1	0.6	0.5	Zero	0.7	0.5	0.2
Total color		110.0	76.0	72.0	62.0	78.0	74.0	60.0	81.0	76.0	66.0
Color of corn oil	Yellow	35.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0
	Red	6.0	5.6	5.2	4.9	6.0	5.8	5.2	5.0	4.7	4.3
	Blue	zero	zero	zero	zero	zero	zero	zero	zero	zero	zero
Total color		95.0	76.0	72.0	69.0	80.0	78.0	72.0	70.0	67.0	63.0

using 1% of the same earth (Total color = 78.0). These reductions were somewhat similar to those obtained by the same dose levels of virgin activated bleaching earth (pH = 3). These results are better than those obtained by using neutral reactivated bleaching earth (pH 6 – 7) at the same dosages. The color of corn oil recorded a high reduction after bleaching it with 2 % neutral reactivated bleaching earth (pH = 6 – 7) compared with the same earth but at the lowest dosage (1%). These results are in agreement with those found by Kheok and Lim (1982) and Nnadozie et al. (1989) who reported that an increase in clay dosage would be expected to lead to an increase in color reduction.

It can be concluded that for sunflower oil, about 1% neutral reactivated bleaching earth (pH = 6 – 7) was generally the best dose, giving the high reduction in color. While for soybean oil, 2 % acid reactivated bleaching earth (pH = 2.5 – 3) was the best dose used to achieve a light color. As for corn oil, 2 % neutral reactivated bleaching earth (pH 6 – 7) was the best dosage used to provide a high reduction in color.

3.4. Effect of the bleaching with reactivated bleaching earth on some properties of the oils used

Efficient bleaching requires measurements such as red color, peroxide value, free fatty acid content, iron concentration, and conjugation values (Mag, 1990).

The changes in levels of acidity, peroxide value, iron, phosphorus, conjugated dienes and trienes, and soap of sunflower, soybean and corn oils before and after their bleaching (with either virgin activated bleaching earth or reactivated bleaching earth) are shown in Table IV. From these results, it can be concluded that the acidity values of sunflower, soybean and corn oils treated with virgin activated bleaching earth (pH = 3) undergo a slight increase. This increase also occurs in soybean oil after bleaching it with acid reactivated bleaching earth (pH = 2.5 – 3). These results agreey with those reported by Morgan et al. (1985) and Hoffmann (1989) who reported that free fatty acids increase in the bleached oil with acid bleaching earth. On the other hand, no changes in the acidity values of sunflower and corn oils before and after their bleaching with neutralized reactivated bleaching earth (pH = 6 – 7) were observed. This datum is in agreement with that found by Hong et al. (2000) who revealed that acid treated soy hull carbon reduced free fatty acids adsorption relative to non activated soy hull carbon. On the contrary, high reductions were found in peroxide values of the above oil after their bleaching with all kinds of bleaching earths. These data agree with those presented by Young (1987), Boki et al. (1989) and Mag (1990) who showed that oxidation levels are reduced by the breakdown of hydroperoxide primary oxidation product on the adsorbent surfaces such as bleaching earth. Boki et al. (1989) suggested that a decrease in peroxide value is due to the decomposition of peroxides by the strongest acid on the surface of bleaching earth.

Table IV again shows that the differences in pH values of reactivated bleached earth had a minor effect on soap content in the bleached oils in which the highly acidic-reactivated bleaching earth produced decreases in the soap content of the bleached oils. These findings are in agreement with those stated by Hoffmann (1989) and Anderson (1996) who indicated that high acidity activated bleaching earth causes splitting of the adsorbed soap.

As to the iron in the above oils after their bleaching, it is clear that bleaching by using either virgin activated or reactivated bleaching earths produced decrements in the levels of iron in all the bleached oils. These values are in line with those stated by The Egyptian Standard Specifications (1993), which recommended that the level of iron in refined, bleached and deodorized oil must be less than 1.5 ppm. Iron is the major pro-oxidant metal to be removed from oils in the course of the refining process (Kheok and Lim 1982; Mag, 1990). Results obtained by Tan et al. (1985) showed that traces of iron and some other metallic contaminants greatly favor color development in some fats, and certain pigments are very refractory to ordinary refining and bleaching treatments. A similar effect was observed for the aforementioned oils after their bleaching (with virgin activated or reactivated bleaching earths) in which the phosphorus contents were declined. These data agree with those expressed by Ostric et al. (1980) and Kheok and Lim (1982) who reported that oil treated with bleaching clay tends to give a lower phosphorus content.

With regards to the $E^{1\%}_{1\,cm}$ values of the bleached oil samples, it is clear that the bleaching produced decrements in the values of conjugated dienes and at the same time slight increments in conjugated trienes contents occurred in the bleached oils. These data are the same as those reported by Morrison (1975), Hoffmann (1989) and Topallar (1998) who cited that bleaching increases the level of conjugated trienes and reduces the content of conjugated dienes. Overall, all the results tabulated in Table IV agree with those established by Topallar (1998) who stated that bleaching clay performs not only color removal but also removes trace metals, adsorbs phospholipids and soaps, and decomposes oxidation products such as peroxides.

From the above findings, it can be concluded that properties of the bleached oil samples with reactivated bleaching earth are somewhat similar to

Table IV

Influence of the bleaching with either virgin activated or reactivated bleaching earths on some properties of the bleached oils

Oils / Items	Neutralized oils (Before the bleaching)			Oils after their bleaching with virgin activated bleaching earth (pH =3.0)			Oils after their bleaching with reactivated bleaching earth		
	Sunflower	Soybean	corn	Sunflower (1%virgin earth)	Soybean (2% virgin earth)	Corn (2% virgin earth)	Sunflower oil bleached with 1% reactivated bleaching earth of pH 6 – 7	Soybean oil bleached with 2%reactivated bleaching earth of pH 2.5 - 3	Corn oil bleached with 2% reactivated bleaching earth of pH 6 - 7
Acidity % (as oleic acid)	0.04	0.02	0.05	0.07	0.08	0.09	0.04	0.07	0.06
Peroxide value (meq. O_2 /Kg oil)	2.5	0.9	2.3	1.1	0.3	0.9	1.3	0.3	1.1
Iron (ppm)	0.25	0.3	0.21	0.06	0.08	0.05	0.07	0.07	0.06
Phosphorus (ppm)	12	20	17	8	9	11	8	10	9
Conjugated dienes ($K^{1\%}_{232}$)	0.11	0.09	0.14	0.07	0.06	0.10	0.06	0.05	0.09
Conjugated trienes ($K^{1\%}_{270}$)	0.03	0.03	0.04	0.08	0.07	0.09	0.07	0.06	0.09
Soap (ppm)	40	33	31	8	9	7	13	8	15

Table V

Effect of the bleaching with virgin activated and reactivated bleaching earths on the Rancimat induction period of the bleached oils at 100 °C

Oils	Induction period of the neutralized oils (Before the bleaching)	Induction period (h) of some bleached oils with		
		Virgin activated bleaching earth (pH=3)	Reactivated bleaching earths	
			(pH = 6 – 7)	(pH = 2.5 – 3)
Sunflower[(a)]	10.1	8.0	8.2	8.1
Soybean[(b)]	13.2	12.3	12.0	12.45
Corn[(b)]	11.1	10.2	10.4	10.3

(a) Bleached using 1 % either virgin activated or reactivated bleaching earths.
(b) Bleached using 2 % either virgin activated or reactivated bleaching earths.

Table VI

Impact of reusable discarded deactivated bleaching earth after reactivation on the bleaching efficiency of some oils

Number of using reactivated bleaching earth	Bleached sunflower oil *					Bleached soybean oil*					Bleached corn oil*				
	Color			Total color Y+10 (R+B)	Bleaching efficiency (%)	color			Total color Y+ 10 (R+B)	Bleaching efficiency (%)	color			Total color Y+10 (R+B)	Bleaching efficiency (%)
	Yellow	Red	Blue			Yellow	Red	Blue			Yellow	Red	Blue		
1	6.5	0.6	zero	12.5	100	20	4.0	zero	60.0	100	20	4.3	zero	63.0	100
2	6.7	0.6	zero	12.7	98.4	20.3	4.1	zero	61.3	97.8	20.8	4.5	zero	65.8	95.5
3	7.0	0.6	zero	13.0	96.0	20.9	4.2	zero	62.9	95.2	21.1	4.7	zero	68.1	91.9
4	7.1	0.7	zero	14.1	87.2	22.7	4.7	zero	69.7	83.8	21.9	5.1	zero	72.9	84.3
5	7.2	0.7	zero	14.9	80.8	22.8	5.5	zero	78.8	70.3	22.3	5.8	zero	80.3	67.8
6	8.0	1.0	zero	18.0	56.0	23.6	7.2	0.2	97.6	37.3	25.0	7.1	zero	96.0	47.6

* Bleaching conditions as in Table V.

those obtained using virgin activated bleaching earth.

3.5. Impact of the bleaching with virgin activated and reactivated bleaching earths on the Rancimat induction period of the bleached oils at 100°C

Table V show the effect of bleaching by either virgin activated or reactivated bleaching earths on the Rancimat induction period of sunflower, soybean and corn oils at 100 °C. It is clear that the induction period of neutralized sunflower, soybean and corn oils dropped after their bleaching. These reductions may be due to the fact that some antioxidants were adsorbed (removed) onto the surface of the bleaching earth. These results are agreement with those found by Ostric et al. (1980), Nnadozie et al. (1989), Micheal and Ibrahim (1991), and Hui (1996), who reported that the bleaching process decreases the oxidative stability of oil.

It is clear that no big differences were observed in the induction periods of either sunflower or corn oils treated with either neutralized reactivated bleaching earth (pH 6 – 7) or acid reactivated bleaching earth (pH 2.5 – 3) compared with virgin activated bleaching earth (pH = 3) (as a reference).

As to the stability of soybean oil treated with acid reactivated bleaching earth (pH = 2.5 – 3) it was somewhat higher than that found in the same oil when bleached with neutralized reactivated bleaching earth (pH = 6 – 7). These differences are closely attributed to acid reactivated bleaching earth, which produced a higher adsorption of chlorophyllic compounds than neutralized reactivated bleaching earth. These results are similar to those shown by Hoffmann (1989) who cited that oil treated with acid activated bleaching earth has a much lower residual color (chlorophyllic and caratonoid) than the same amount with an earth of natural activity. On the other hand, Coultate (1989) recommended that chlorophyllic compounds must be removed from the oil to avoid rapid oxidation of the oil in the presence of light.

3.6. Effect of reusable discarded deactivated bleaching earth after its reactivation on bleaching efficiency of the used oils

Table VI shows the effect of reactivation of discarded deactivated bleaching earth on the bleaching efficiency of sunflower, soybean and corn oils. The results point out that the reactivated bleaching earth, which used the same dosages found in Table III, can be used for the bleaching of sunflower oil in more than six cycles and only five cycles for the bleaching of both soybean and corn oils. This limitation is due to the red color for each bleached soybean and corn oil (7.2 and 7.1, respectively) which became over the limit recommended by The Egyptian Standards Specifications (1993), which stipulated that red color Lovibond of bleached oil must be less than 7.0 in a 5.25 inch cell. These results are the same as those reported by Abul Kalam and Joshi (1988) who found that the degree of regeneration of spent earth reduced according to the number of cycles.

Hence, from the aforementioned data, it could be concluded that reactivated bleaching earth can be used for the bleaching of oils till red color (Lovibond) of the bleached oil reaches 7 red. Hence, it can be recommended that the reactivated bleaching earth can be used for 5 cycles of bleaching for both soybean and corn oils and for more than 6 cycles for the bleaching of sunflower oil (note that the recycled bleaching earth must be reactivate after each use). This produced a high reduction in the colors.

4. CONCLUSIONS

It could be concluded that reactivated bleaching earth was suitable for the bleaching of sunflower, soybean and corn oils which gave similar results when compared to those obtained from virgin activated bleaching earth, which produced great color reduction with high stability in the bleached oils. Therefore, it could be recommended that discarded deactivated bleaching earth were reused after its reactivation for the bleaching of oils.

REFERENCES

Kalam A, Joshi J. 1988. Regeneration of spent earth in aqueous medium. *J. Amer. Oil Chem. Soc.* **65,** 1917-1921.

Anderson D. 1996. A primer on oils processing technology en Hui Y. (Ed) *Bailey's industrial oil and fat products* 4, 27-31. John Wiley and Sons Inc., New York.

Anthony O, Ogugua C. 1988. Laboratory trials on bleaching palm oil with selected acid-activated Nigerian clays. *Food Chemistry* **27,** 311-317.

A. O. C. S. (1993). Official and Tentative Methods for the American Oil Chemists' Society. 6th ed. American Oil Chemists' Society, Champaign, U.S.A.

A. O. C. S. (1997). Official and Tentative Methods for the American Oil Chemists' Society. 7th ed. American Oil Chemists' Society, Champaign, U.S.A.

Boki K., Shinoda S, Ohno S. 1989. Effects of filtering through bleaching media decrease of peroxide value of autoxidized soybean oil. *J. Food Science* **54,** 1601-1603.

Boki K, Wada T, Ohno S. (1991). Effects of filtration through activated carbons on peroxide, thiobarbituric acid and carbonyl values of autoxidized soybean oil. *J. Amer. Oil Chem. Soc.* **68**, 561-565.

Brimberg U. 1982. Kinetics of bleaching of vegetable oils. *J. Amer. Oil Chem.Soc.*, **59,** 74-78.

Coultate T. 1989. Food en *The chemistry of its components* 2nd ed., 64. Royal Society of Chemistry Paperbacks, London, England.

FAO / WHO (Food and Agriculture Organization / World Health Organization) 1970. Recommend international

and standard for olive oil. Codex Alimenterius Commission (CAC) / RS 33, Roma, Italy.
Hoffmann G. 1989. *The chemistry and technology of edible oils and fats and their high fat products*. 164-167. Academic Press Inc., London.
Hong Y, Proctor A, Shultz J. 2000. Acid-treated soy hull carbon structure and adsorption performance. *J. Amer. Oil Chem. Soc.* **77**, 785-790.
Hui Y. 1996. *Bailey's industrial oil and fat products* 4, 281-282. John Wiley and Sons Inc., New York.
Jackson M. L. 1967. *Soil chemical analysis*, 144-177. Printca-Hall of India, India.
Kaufmann H. 1986. *Modern Technology of fats and fats products* 5, 733. Aschendorffche Verlagsbuch handlung, Münstere.
Kheok S, Lim E. 1982. Mechanism of palm oil bleaching by montmorillonite clay activated at various acid concentrations. *J. Amer. Oil Chem. Soc*. **59**, 129-131.
Krishnan S. 1975. Bernam bleachability test method for palm oil. *J. Amer. Oil Chem. Soc*. **52**, 23-27. Loncin M. 1970. Palm oil. A major tropical product, p. 113. Congopalm, Brussels.
Loranz L, Weadon O, Wolb A. 1980. Natural levels of nutrient commercially milled wheat flour mineral analysis. *Cereal Chem.* **57**, 111-115.
Mag T. 1990 Bleaching- theory and practice en David R. (Ed) *Edible fats and oils processing,* 107. American Oil Chemists' Society, Champaign, U.S.A.
Micheal H, Ibrahim A. 1991. Effect of processing on the composition and oxidation stability of coconut oil. *J. Amer. Oil Chem. Soc*. **68,** 574-576.
Micheal H, Philip J, Mike H. 1992. Adsorptive bleaching of soybean oil with non-montmorillonite Zambian clays. *J. Amer. Oil Chem. Soc.* **69,** 379-383.
Morgan D, Shaw D, Sidebottom M, Soon T, Taylor R. 1985. The function of bleaching earths in the processing of palm, palm kernel and coconut oils. *J. Amer. Oil Chem. Soc*. **62,** 292-299.
Morrison W.1975. Effects of refining and bleaching on oxidative stability of sunflower seed oil. *J. Amer. Oil Chem. Soc.* **52,** 522-525.
Nnadozie N, Arowolo T, Akpan H. 1989. Quality of Nigerian palm oil after bleaching with local treated clays. *J. Amer. Oil Chem. Soc.* **66,** 218-222.
Ostric B, Turkulor J, Karlovic D. 1980. Quality of sunflower oil bleached during deodorization. *J. Amer. Oil Chem. Soc*. **57,** 232 – 235.
Patent (2002). Trade secret patent Egyptian I P R Law 82/2002.
Rolando C. 1991. Practical considerations in refining soybean oil. *INFORM* **2,** 208-213.
Segers J. 1992. Pretreatment of edible oils for physical refining. *J. Amer. Oil Chem. Soc.* **69,** 262-264.
Tan Y, Ong K, Berger H, Oon H, Poh B. 1985. A study of the cause of rapid color development of heated refined palm oil. *J. Amer. Oil Chem. Soc.* **62**, 999-1006.
The Egyptian Industry Ministry. 2002a. The annual report of the Egyptian Industrials Federation, Cairo, Egypt.
The Egyptian Industry Ministry. 2002b. The annual report of the Holding Company for Industrials Food, Cairo, Egypt.
The Egyptian Standard Specifications.1993. The Standard Specifications for Vegetable Edible Oil (N^0. 44/1993). Egyptian Organization for Standardization and Quality Control, The Egyptian Industry Ministry, Cairo, Egypt.
Topallar H. 1998. Bleaching kinetics of sunflower oil. *J. Amer. Oil Chem. Soc.* **75,** 531-533.
Tsaknis J, Lalas S, Gergis V, Dourtoglou V, Spiliotis V. 1999. Characterization of moringa oleifera variety mbololo seed oil of Kenya. *J. Agric. Food Chem.* **47,** 4495-4499.
Waldmann C, Eggers R. 1991. De-oiling contaminated bleaching clay by high - pressure extraction. *J. Amer. Oil Chem. Soc*. **68**, 922- 930.
Young F. 1987. Refining and fractionation of palm oil en: Gunston F. (Ed) *Palm oil*, 47, 51. The Society of Chemical Industry Publication, John Wiley and Sons Inc., New York.

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