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Research Note

A bleaching earth from egyptian local deposits

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RESUMEN

Tierras decolorantes de yacimientos egipcios.

La presente investigación trata de la decoloración de aceites vegetales usando tierras activadas obtenidas de yacimientos egipcios, comparándola con el Tonsil FF usado normalmente en la industria oleícola local. La comparación se realizó, no sólo sobre la base del poder decolorante de la tierra, sino también sobre la base de sus efectos en la acidez del aceite, la formación de peróxidos y la velocidad de descomposición de los peróxidos formados en aldehidos y cetonas durante el proceso de decoloración. La activación de las muestras de tierras recogidas se hizo utilizando ClH 4N, ClH 6N y H_2SO_4 30%. Los tests de decoloración de las muestras activadas se llevaron a cabo usando los cuatro tipos mayoritarios de aceites procesados en Egipto: aceite de semilla de algodón, de girasol, de soja y de palma. Además de los tests a escala de laboratorio, la evaluación de las muestras activadas, se realizó a escala industrial. La aplicación industrial ha demostrado que las tierras locales activadas pueden ser utilizadas con éxito como tierras decolorantes de aceites locales. De este modo pueden usarse como sustitutos de las variedades mas frecuentemente importadas y usadas por el sector aceitero.

PALABRAS-CLAVE: Aceite vegetal – Adsorbente – Tierra decolorante.

SUMMARY

A bleaching earth from egyptian local deposits.

The present investigation deals with the bleaching of vegetable oils using activated clays collected from some deposits in Egypt as compared to Tonsil FF currently used by local oil industry. The comparison was made; not only on the basis of the decolourising power of the earth, but also on the basis of its effects on the oil acidity, formation of the oil peroxides and the decomposition rate of the formed peroxides to aldehydes and ketones during the bleaching process. The activation of the collected earth samples was made using 4N HCl, 6N HCl and 30% H_2SO_4. The bleaching tests of the activated samples were performed using the major four oil types processed in Egypt being cottonseed, sunflower, soybean and palm oils. In addition to the laboratory-evaluation tests, the performance of the activated samples, which showed promise on the lab-scale have been also tested on an industrial scale. The industrial application has proved that the activated local earth's can be successfully used as bleaching earth of local oils. Thus it can be used as a substitute of the varieties currently imported and used by the local oil sector.

KEY-WORDS: Adsorbent - Bleaching - Vegetable oil.

1. INTRODUCTION

Vegetable oil bleaching has been generally practised for the purpose of removing the objectionable colour bodies from the refined oil (1). Adsorbents used in bleaching are usually materials with high surface activity such as Fuller's earth (2-4). The efficiency of the bleaching process will be thus determined by the type of adsorbent used and the nature of the colouring matters in the refined oil, in addition to some other factors such as the bleaching temperature and the mode of bleaching (5). Since different vegetable oils vary widely in their content of the natural pigments, a bleaching earth which is for instance excellent for a certain oil, may not be necessarily suitable for another type of oil.

In fact, bleaching earth does more than just bleach. It may have catalytic activity that affects the oil composition, acid properties that influence the level of free acids in the bleaching oil and an adsorption capacity to remove the metallic cations in the refined oil or the natural antioxidants such as tocopherols. The final quality of the oil is thus controlled not only by the adsorption capacity of the adsorbent to colouring matters but also its catalytic and acid properties (6). In addition, the stability of the bleached oil to rancidity is greatly determined by the adsorbent capacity to remove the metallic cations in the refined oil which act as prooxidants or to remove the tocopherols which act as antioxidants. Thus, the selection of the most suitable adsorbent to bleach certain oil should be made very carefully, in order to achieve the best results of a bleaching process (7).

In Egypt, 1,200,000 ton of oil is processed annually. The earth used in bleaching is totally imported from Germany, England and some other places. The average dose of earth used in bleaching is about 1% of oil (8).

This work assesses the feasibility of using activated earth samples from some local deposits in Egypt as a substitute of the imported earth currently used in local oil industry.

2. EXPERIMENTAL

The experimental work has been planned to evaluate some activated samples from some local deposits in Egypt as bleaching agents of vegetable oils. The parameters which were be considered include the oil colour, the peroxides of the oil that might develop in the oil or decompose during the bleaching process, the oil acidity and the stability of the bleached oil to oxidation after the bleaching process.

2.1. Materials

Three different clay samples were collected from the clay deposits in Egypt being the North Coast (south of Alamien), sample I, Abou Tartour plateau at western desert, sample II and Nile valley; sample III. Each of the three samples was then acid activated as will be explained later. In addition, Tonsil Clay FF, a product of Sud Chemie Co., Germany was also used in this investigation as the standard type currently used in local oil industry. These clays were used for bleaching of some alkali neutralized vegetable oils. These oils included cottonseed, palm, soybean and sunflower oils which are the most common oils processed in Egypt.

Analytical grade sulphuric and hydrochloric acids were used for earth activation.

2.2. Methods

Activation of the collected clay samples

The acid activation of the collected samples was made according to the procedure of I.A Ibrahim (9). Eight activated samples were prepared using 4N and 6N HCl and using 30% H_2SO_4 as described in the following table

Clay Sample	Sample Locality	Activating Acid	Activated Sample	Acidity % after Activation
I	North Coast	4N HCl	1	0.159
I	North Coast	30% H_2SO_4	2	0.138
II	Abou Tartour	4N HCl	3	0.125
II	Abou Tartour	6N HCl	4	0.130
II	Abou Tartour	30% H_2SO_4	5	0.129
III	Nile Valley	4N HCl	6	0.146
III	Nile Valley	6N HCl	7	0.152
III	Nile Valley	30% H_2SO_4	8	0.149

Activated clays are sub-bentonites, which mostly consist of low swelling types of montmorillonite. Interstratified structure of illite and montmorillonite with appreciable base exchange capacity are also activable. Acid treatment, by sulfuric or hydrochloric acid, replaces exchangeable k, Na and Ca by H in the interlamellar space and also leaches out a part of Al, Fe and Mg from the lattice structure to create micro- and macropores.

Bleaching procedure

About 20g oil were weighed in a conical flask (100 ml capacity) and heated to 373°k on a thermostatically temperature-controlled hot plate unit combined with a magnetic stirrer for about 600 sec. The bleaching earth was then added at a level of 1.5% of the oil weight at the same temperature followed by filtration. The oil colour, peroxide value and acid content of the oil before and after bleaching were determined. The oil colour was measured in terms of Lovibond colour units (using 1" cell) and in terms of colour index as will be explained later.

In addition to the lab-scale experimental work, it was also planned to assess the suitability of the activated samples on a full-scale industrial process. However, not all samples used on the lab-scale were applied on the industrial scale. The industrial application was performed using three activated samples only, which gave the best results on lab scale.

The industrial bleaching process was performed at Alexandria oil and Soap Company; Egypt using 0.4% of the earth based on the oil weight. The oil batch consisted of 4 ton cottonseed oil and 13 ton sunflower oil. The bleached oils were then measured for their Lovibond red colour units on 5 ¼ " cell, as usually done at the plant. The time of oil filtration from the earth was also measured in each case.

2.3. Analytical methods

The colour indices of refined and bleached oil samples were measured according to the recommendations of Pons *et al* (10). The colour index was estimated as the sum of the sixteen absorbancies of the oil over a wavelength range from 400 to 550 nm (10nm interval) multiplied by ten. Spectrophotometeric readings were made on Shimadzu Recording Spectrophotometer UV-240 using CCl_4 as a blank.

In addition to the colour index, peroxide value and acid value of the oils before and after bleaching have been determined according to the Official and Tentative Methods of Analysis (11).

3. RESULTS AND DISCUSSION

The results of this study were used to evaluate the efficiency of the activated samples from local deposits in Egypt as bleaching earth of vegetable oils compared to Tonsil FF. The parameters considered were; oil colour, peroxide content and oil acidity.

3.1. Effect on oil colour

It can be observed from Table I through (4) that a clay sample that gives good results with certain oil will not necessarily give similar results with other oils. For example, the best clay for bleaching of sunflower oil was that sample taken from the North Coast and activated using 4N HCl (sample 1). However this clay was the least efficient for bleaching both soybean and cottonseed oils. The best clays for bleaching of cottonseed oil were those taken from the North Coast and activated using 30% H_2SO_4 and that taken from the Nile Valley and activated using 6N HCl. The colour indices of the bleached oils using these clay samples were 93.71 and 94.02 compared to 99.46 using the standard earth (Tonsil clay). On the other hand, both clay samples taken from Abou Tartour and Nile Valley and activated using 6N HCl gave the best decolourising efficiency in case of soybean oil. The colour indices of the bleached oil using these two samples were 53.14 and 63.03 compared to 67.1 using Tonsil clay. Regarding palm oil, it can be observed that all activated local clay samples gave similar results as Tonsil FF.

In general it can be stated that the activated clay samples number 1, 4 and 7 were almost as efficient as Tonsil FF regarding its decolourising power. As previously described in the experimental work sample (1) is the sample taken from the North Coast and activated using 4N HCl. Samples (4) and (7) refer to those samples taken from Abou Tartour and the Nile Valley and activated using 6N HCl. These three samples were used in the full industrial scale application.

Effect of the bleaching clay on the peroxide and acid contents of the oils

It can be observed from Tables I-IV that the bleaching process using the activated clay samples as well as the imported earth (Tonsil) has insignificant effect on the oil acidity.

On the other hand, the bleaching effects a decrease in the peroxide content of the oil. For example, the peroxide content decreased from 28.7, 32.15, 26 and 30 meq/kg oil in case of palm, soybean, cottonseed and sunflower refined oils to 16, 16, 6.6 and 18 meq/kg oil respectively after the bleaching process. The effect of the clay which is taken from the Nile Valley and activated using 6N HCl (sample 7) was comparable to that of Tonsil FF.

Results of full -industrial scale application of the activated earth

The results of full-scale application of the most efficient activated samples numbers 1, 4 and 7 as previously described are listed in Table V. This Table lists the red Lovibond color of the bleached oil, the filtration time of the oil from the earth and the change in oil acidity due to bleaching. The Lovibond red color units of the oils bleached with the activated samples numbers 1, 4 and 7 were 7, 6 and 6.1, respectively. These values were within the acceptable color limits according to the Egyptian standard specification which states that the Lovibond red units should not exceed 7.0 using 5 ¼ ″. Sample 7 was advantageous over sample 4 since the filtration time was lower i.e. the filtration rate was higher.

Table I

Results of Sunflower Oil Bleaching using Local Clays as Compared to Tonsil FF

Oil Sample	Type of Clay Used	Activated Acid	Colour Index	Lovibond			Peroxide Value meq/kg	Acid Value mg KOH/g Oil
				Yellow Y	Red R	Y + 10R		
Refined R	None	—	157.38	6	0.8	14	31.00	1.950
T	Tonsil FF	—	83.6	3	0.1	4	25.737	1.750
1	North Coast	HCl(4N)	85.38	3.1	0.2	5.1	24.640	1.896
2	North Coast	H_2SO_4(30%)	93.63	3.6	0.2	5.6	25.230	1.817
3	Abou Tartour	HCl(4N)	89.15	3	0.2	5	23.492	1.711
4	Abou Tartour	HCl(6N)	97.13	3.2	0.5	8.2	19.189	1.782
5	Abou Tartour	H_2SO_4(30%)	90.20	3	0.2	5	18.289	1.922
6	Nile Valley	HCl(4N)	98.02	3.3	0.5	8.3	20.770	1.802
7	Nile Valley	HCl(6N)	101.08	3.3	0.6	9.3	22.976	1.869
8	Nile Valley	H_2SO_4(30%)	96.10	3.2	0.5	8.2	23.390	1.739

Table II

Results of Cottonseed Oil Bleaching using Local Clays as Compared to Tonsil FF

Oil Sample	Type of Clay Used	Activated Acid	Colour Index	Lovibond			Peroxide Value meq/kg	Acid Value mg KOH/g Oil
				Yellow Y	Red R	Y + 10R		
Refined R	None	—	182.13	6	1.3	19	26.00	0.691
T	Tonsil FF	—	99.46	5.9	1.0	15.9	7.936	0.347
1	North Coast	HCl(4N)	115.87	5.8	0.8	13.8	6.627	0.693
2	North Coast	H_2SO_4(30%)	93.71	5.8	0.9	14.8	6.621	0.468
3	Abou Tartour	HCl(4N)	101.00	5.9	0.8	13.9	19.740	0.400
4	Abou Tartour	HCl(6N)	119.89	6.0	0.8	14.0	8.630	0.467
5	Abou Tartour	H_2SO_4(30%)	112.06	5.8	1.0	15.8	22.270	0.892
6	Nile Valley	HCl(4N)	115.14	5.8	1.1	16.8	19.809	0.523
7	Nile Valley	HCl(6N)	94.02	5.0	0.8	13.0	10.305	0.396
8	Nile Valley	H_2SO_4(30%)	108.62	5.9	0.9	14.9	19.629	0.339

Table III

Results of Soybean Oil Bleaching using Local Clays as Compared to Tonsil FF

Oil Sample	Type of Clay Used	Activated Acid	Colour Index	Lovibond			Peroxide Value meq/kg	Acid Value mg KOH/g Oil
				Yellow Y	Red R	Y + 10R		
Refined R	None	—	291.92	11	0.9	20	32.15	0.44
T	Tonsil FF	—	67.10	10	0	10	21.96	0.29
1	North Coast	HCl(4N)	171.10	8	0.4	12	19.43	0.36
2	North Coast	H_2SO_4(30%)	149.08	7	0.4	11	16.97	0.40
3	Abou Tartour	HCl(4N)	89.31	8	0.3	11	16.31	0.30
4	Abou Tartour	HCl(6N)	53.14	3	0.3	6	18.17	0.35
5	Abou Tartour	H_2SO_4(30%)	108.24	9	0.3	12	18.90	0.31
6	Nile Valley	HCl(4N)	109.80	6	0.4	10	17.10	0.34
7	Nile Valley	HCl(6N)	63.03	3	0.4	7	19.70	0.32
8	Nile Valley	H_2SO_4(30%)	120.50	8	0.4	12	25.69	0.37

Table IV

Results of Palm Oil Bleaching using Local Clays as Compared to Tonsil FF

Oil Sample	Type of Clay Used	Activated Acid	Colour Index	Lovibond			Peroxide Value meq/kg	Acid Value mg KOH/g Oil
				Yellow Y	Red R	Y + 10R		
Refined R	None	—	57.26	1.0	0.3	3.0	28.71	0.39
T	Tonsil FF	—	38.53	0.9	0.0	0.9	16.15	0.36
1	North Coast	HCl(4N)	35.92	0.8	0.0	0.8	20.56	0.36
2	North Coast	H_2SO_4(30%)	36.45	0.9	0.0	0.9	19.63	0.35
3	Abou Tartour	HCl(4N)	31.13	0.7	0.0	0.7	22.33	0.39
4	Abou Tartour	HCl(6N)	29.67	0.6	0.0	0.6	19.69	0.34
5	Abou Tartour	H_2SO_4(30%)	31.18	0.7	0.0	0.7	25.55	0.35
6	Nile Valley	HCl(4N)	44.63	0.9	0.0	0.9	18.23	0.36
7	Nile Valley	HCl(6N)	37.03	0.9	0.0	0.9	16.00	0.38
8	Nile Valley	H_2SO_4(30%)	42.63	0.9	0.0	0.9	23.15	0.37

Table V
Results of industrial application of the activated clay

Bleaching Earth Used	Red Lovibond Color on 5"¼	Change in Oil Acidity	Filtration Time Sec. x 10^3
None (refined oil)	9.6	—	—
(1) North Coast	7	Nil	2.1
(4) Abou Tartour	6	Nil	2.7
(7) Nile Valley	6.1	Nil	2.1

4. CONCLUSION

I can concluded that the local clay deposits at the Nile Valley in Egypt can be successfully used as a substitute of the bleaching earth currently imported by the local oil sector, when the former is activated using 6N HCl.

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