Mineral. Deposita 31, 584–588 (1996)

MINERALIUM DEPOSITA

Oil decolorization properties of the Emirler clinoptilolite (Bigadiç, Turkey)

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Received: 6 May 1995/Accepted: 10 April 1996

Abstract. Oil decolorization properties of the Emirler clinoptilolite and its acid-activated forms were studied using neutralized cottonseed oil. Although the oil decolorization capacity of natural clinoptilolite is low, it can be improved by a factor of 1.8 after HCl activation under the optimized conditions (1M HCl, solid/liquid ratio = 1/20, T = 25 °C, t = 1 hour). Acid activation increases the total specific surface area from 40 to 70 m^2/g which is mostly realized with a pore diameter range smaller than 15 nm. The bleaching capacity of acid-activated clinoptilolite is comparable to that of natural bentonitic clays but it is 1.6 times lower than the capacity of activated bleaching earths such as Tonsil and others. However, the amount of oil absorbed by clinoptilolite during the bleaching process is almost half that compared with the commonly used natural and acid-activated clays.

The coloring matter in vegetable oils is removed by using bleaching earths that can be grouped into two as bentonites and fuller's earths. The main constituent of bentonite is montmorillonite, but in some cases it may be attapulgite or sepiolite or a mixture of attapulgite-sepiolite-montmorillonite for fuller's earth. Both types of bleaching earth are used as adsorbents in the decolorization of edible oils after acid activation treatments (Clarke 1985; Murray 1991; Gürgev and Tanin 1993). In Turkey both imported and domestic bleaching earths are used by the edible oil industry. The imported products with the brand names such as Tonsil Optimum FF, Filtrol Grade 105 and Optima-D are all activated bentonitic clays of common use, and a product with the brand name of Trisyl is a synthetic silica which is usually used together with other products in the refining of oils. Domestic products in the market with the brand names of Bent Ey-08 and TT-N are also acid-activated and natural bentonitic bleaching earths respectively.

Although the ion-exchange, adsorption, dehydration and rehydration properties of natural zeolites are utilized for many purposes (Gradev et al. 1978; Mumpton 1978; Csicsery 1984; Dyer and Keir 1984; Abrudean et al. 1985; Burriesci et al. 1985; Loizidou and Townsend 1987), no published work was found in the literature on their use as adsorbents in oil decolorization. This study was aimed at determining the vegetable oil decolorization properties of clinoptilolite from Emirler, Bigadiç.

Material and methods

Sample characteristics

The Emirler zeolite deposit, which was studied in detail by Gündoğdu (1982), consists of rhyolitic coarse and fine-grained tuffs almost completely transformed into clinoptilolite with an average content of 85%. The impurities were determined as opal-CT, K-feldspar and quartz with no or a trace amount of smectite. No other zeolite minerals such as erionite and mordenite commonly associated with clinoptilolite were detected in XRD and SEM analyses of more than 400 samples (see Gündoğdu et al. in this issue). The outcropping part of this deposit has a reserve of about 1.4 billion tons (Baysal et al. 1986).

Representative Emirler fine-grained tuff samples containing 90% clinoptilolite were crushed using jaw and roll crushers and then pulverized to −0.104 mm to obtain a particle size distribution similar to bleaching earths. The chemical composition of the samples were determined by XRF technique. Specific surface area (BET), pore volumes and pore size distributions were determined from the adsorption isotherms (Gregg and Sing 1967) obtained using a Micromeritics ASAP 2000 Model instrument. Samples were dried at 300 °C for three hours and outgassed at the same temperature for one hour. Physical and chemical properties of the clinoptilolite samples used in the experimental work, as well as those of imported and domestic bleaching earths, are given in Tables 1 and 2 respectively.

Acid activation

For the prevention of $CaSO_4$ precipitation, Merck grade hydrochloric acid was used in the activation tests rather than sulphuric acid.

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Table 1. Physical and chemical properties of natural and acid activated Emirler clinoptilolite

	Natural	Activated
Bulk density (g/cm^3)		
Loose	0.75	0.75
Compact	0.88	0.88
Specific surface area (BET), m^2/g	40.05	69.70
External surface area, m^2/g	34.08	46.38
Micropore area, m^2/g	5.97	23.34
Screen analysis (%)		
– 0.104 mm	98.82	98.82
– 0.074 mm	94.64	94.64
– 0.043 mm	91.36	91.36
Absorbed oil (%)		Maximum 20
pH of 10% suspension		4.0
Chemical composition on anhydrous basis (%)		
SiO_2	77.97	80.78
Al_2O_3	13.17	12.31
Fe_2O_3	1.06	1.23
MnO	0.01	0.01
MgO	1.53	1.26
TiO_2	0.08	0.07
CaO	3.80	2.32
Na_2O	0.16	0.12
K_2O	2.20	1.87

In these tests, clinoptilolite samples were mixed with 100 ml of hydrochloric acid solutions of 0.01 to 12 M for obtaining different solid/liquid ratios and agitated by a magnetic stirrer for a specified time, filtered through Whatman 42 filter paper, and the residues were washed with distilled water until the filtrates become neutral. Then they were dried at 105 °C for 2 h and used in the bleaching experiments.

Bleaching experiments

Neutralized cotton seed oil from the Çukobirlik Central Oil Factory (Adana) containing β-carotene complexes as coloring matter (Sarikaya et al. 1985) was used in the bleaching experiments. To determine the optimum activation conditions (acid concentration, activation time and temperature, solid/liquid ratio) a series of bleaching experiments were done with mixtures of natural and acid activated clinoptilolite samples and neutralized cotton seed oil (color index = 10.16). These bleaching tests were carried out on mixtures containing 1% clinoptilolite at standard conditions (90 °C for 20 min) under magnetic stirring so as to keep all the solid particles in suspension. Then, oil was separated by filtration through Whatman-42 filter paper and the absorbance values for the samples were determined at 415 nm using a spectrophotometer. The color index of the oil samples were calculated by using the following equation: $N = k\ln[1/(1 - A)]$, where A = absorbance, N = color index oil, k = constant ($k = 5$ for cottonseed oil, Kaufman and Mukherjee 1968).

To find out the effect of bleaching time the same bleaching tests were repeated between 10 to 90 min with 1% Tonsil and

Table 2. Typical properties of imported and domestic bleaching earths

	Tonsil Optimum FF	Filtrol Grade 105	Optima D	Trysil	Bent Ey-08	TT-N
Moisture at 110°C (%)	Maximum 10	16	⩽10		Maximum 10	
Acidity						
mg KOH/g		3				
H_2SO_4, %	Maximum 0.3		⩽1.5			
pH						
5% Suspension				4.5		
10% Suspension	2.5–3.0				3.0	5.5
25% Suspension		3.5				
Bulk density						
Loose, g/cm^3	0.50	0.64	<0.50		0.50	
Compact, g/cm^3	0.70	0.70		0.50	0.70	
Specific surface area (BET), m^2/g	320–350	280	200		220	
Absorbed oil (%)	42–47	30			40	(35)[a]
Screen analysis (%)						
0.019 mm				100		
– 0.147 mm	(97.5)	98	97		98	94.3
– 0.074 mm	(88.5)	90	80		90	83.8
– 0.043 mm	(78.2)	75			80	78.3
Chemical composition (%)						
SiO_2	75.4	(67.39)	69.1	99.00	70.00	61.16
Al_2O_3	11.3	(8.84)	12.9		14.00	19.44
Fe_2O_3	3.0	(2.32)	2.6		1.80	4.60
MgO	1.8	(1.44)	2.7		1.70	2.26
TiO_2		(0.61)	0.2			
CaO	0.6	(3.94)	2.0		0.70	0.38
Na_2O	0.1	(0.18)	0.5	0.20	0.40	0.22
K_2O	0.8	(0.53)	0.2		1.85	2.05
SO_3			2.5	0.17		
L.O.I (1000 °C)	Max. 8		7.3		10.00	8.40

[a] Values in parentheses are determined by the authors

clinoptilolite activated under optimum conditions. The effect of the amount of bleaching material was determined from the results of tests conducted on mixtures containing 0.5 to 2.5% of activated clinoptilolite and other bleaching earths.

The percentage of absorbed oil for equal amounts of activated clinoptilolite and other bleaching earths were determined as percent increases in the weights after the separation of bleaching materials from the oil by filtration.

Results

According to the result of the bleaching tests, it was not possible to bleach neutralized cotton seed oil with even 8% natural clinoptilolite to the point that could be reached with 1% Tonsil (Fig. 1). Taking into consideration all the data obtained from the bleaching experiments on acid activated clinoptilolite samples (Table 3), it was concluded that reasonable results could be achieved at the following optimum conditions: HCl concentration of 1 mole/l, solid/liquid ratio of 1/20, temperature of 25 °C and agitation time of 1 h. Some physical and chemical characteristics of clinoptilolite activated at these conditions are given in Table 1.

The relation between color index of oil and bleaching time for Tonsil and clinoptilolite activated under optimum conditions is shown in Fig. 2. The maximum bleaching time for Tonsil is between 10 and 20 min, whereas acid activated clinoptilolite shows a different behavior and the best result is obtained after 20 min. Therefore, bleaching time seems to be longer for clinoptilolite than Tonsil.

The bleaching characteristics of natural and activated clinoptilolites are compared with those of other bleaching earths for different solid/oil ratios (Table 4). It was possible to reduce the color index of neutral cotton seed oil from 10.16 to 3.94 using 2% activated clinoptilolite. This value is 1.6 times higher than that of activated bleaching earths such as Tonsil (2.46), but is comparable to natural bentonitic clays (TT-N).

On the other hand, the amount of oil absorbed by activated clinoptilolite during bleaching is almost half that compared with those of other bleaching earths (Table 5). This property, probably due to molecular sieving, which is one of the major differences between clinoptilolite and clays, should be considered as an important advantage since it may minimize oil losses during bleaching process.

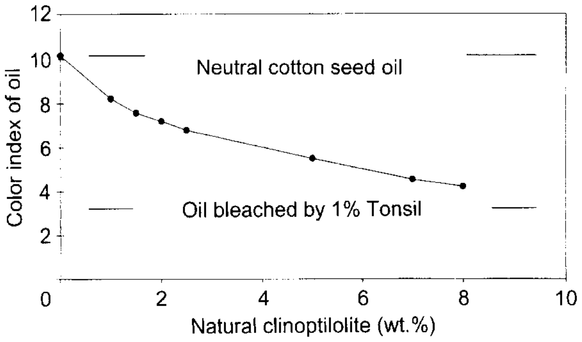

Fig. 1. Bleaching properties of natural clinoptilolite

Table 3. The effects of acid activation, temperature, solid/liquid ratio and time on oil bleaching properties of clinoptilolite

HCl Solution (moles/l)	Temperature °C	Solid/liquid ratio	Activation time hours	Color index of bleached oil
0.00	25	1/20	1	8.21
0.01	25	1/20	1	5.39
0.01	50	1/20	1	6.55
0.01	75	1/20	1	6.64
0.10	25	1/20	1	5.23
1.00	25	1/20	1	5.04
3.00	25	1/20	1	5.03
6.00	25	1/20	1	4.96
12.00	25	1/20	1	5.14
1.00	25	1/2	1	5.23
1.00	25	1/5	1	5.23
1.00	25	1/10	1	5.20
1.00	25	1/20	1	5.04
1.00	25	1/30	1	5.03
1.00	25	1/20	1/2	5.51
1.00	25	1/20	2	5.01
1.00	25	1/20	4	4.96
1.00	25	1/20	7	4.86
1.00	25	1/20	15	4.84

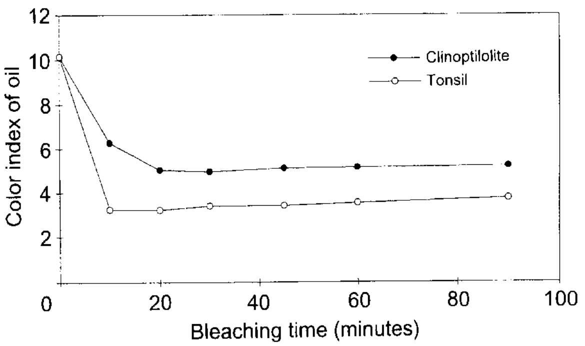

Fig. 2. Effect of time on bleaching

Table 4. Bleaching properties of Emirler clinoptilolite and other bleaching earths at different solid/oil ratios

	Filtrol Grade 105	Tonsil	Bent Ey-0.8	TT-N	Natural clinoptilolite	Acid-activated clinoptilolite
Wt. %	Color index of bleached oil					
0.5	3.82	3.81	5.00	6.19	8.40	7.11
1.0	3.01	3.22	3.44	4.79	8.21	5.23
1.5	2.42	2.94	3.27	3.82	7.57	4.33
2.0	2.04	2.46	3.01	3.57	7.19	3.94
2.5	1.83	2.12	2.81	3.43	6.78	3.53

Table 5. Oil absorbed by acid activated Emirler clinoptilolite and other bleaching earths

Bleaching earth	Absorbed oil %
Tonsil Optimum FF	46.86
Filtrol grade 105	47.94
TT-N	34.79
Natural clinoptilolite	21.51
Activated clinoptilolite	18.94

Discussions and conclusions

The mechanism of bleaching of vegetable oils with acid activated clays is explained by the adsorption of coloring matter and by the oxidative decrease in color (Siddiqui 1968). In addition to physical adsorption, processes involving chemisorption are believed to be effective and metallic ions such as Fe^{+3} are suggested to be the active sites for chemisorption (Khoo et al. 1979). The optimum bleaching capacity in acid activated clays is observed in the surface area range of 200–300 m^2/g where the mesopores predominate, beyond which the surface area and the bleaching performance fall progressively with increasing acid strength (Sarikaya et al. 1985; Adams 1987; Jovanovic and Janackovic 1991). Acid treatment dissolves some Al^{+3}, Fe^{+3} and Mg^{+2} from the lattice structure and causes the exchange of K^+, Na^+, Ca^{+2} by H^+ in the interlamellar spaces (Girgis and Ishak 1978; Clarke 1985). Removal of cations creates additional micropores ($d < 2$ nm) that are converted into mesopores ($2 \text{ nm} < d < 0$ nm) with increasing severity of acid treatment (Sarikaya and Ceylan 1981; Sarikaya et al. 1985; Jovanovic and Janackovic 1991). Also, edges of clay platelets open up and separate, and active surfaces are set free which in their natural condition were sealed with cations (Clarke 1985). Thus, important physical changes are observed after acid activation in relation to specific surface area, specific pore volume and pore size distribution of the clay minerals that effect the sorption and ion-exchange capacities.

Acid activation produces also a considerable increase in the adsorption property of clinoptilolite by opening and enlarging the intracrystalline micropores (Barrer and Makki 1964; Tsitsishvili 1978). According to the experimental work of Barrer and Makki (1964), the exchangeable cations were completely replaced by H_3O^+ and 5% of Al was removed from the tetrahedral structures after refluxing Hector clinoptilolite rich in Na even with 0.25 N HCl around 100 °C for 4 h. With increasing acid strength up to 1 and 2 N HCl, H_3O^+ and Al were progressively removed in equal amounts (up to 90%) and high area molecular sieve sorbents were obtained. The monolayer equivalent areas obtained by the BET method were also increased from 30 m^2/g to 380 m^2/g. With further increase in acid concentration a steady decline was observed similar to clays.

Considering the chemical analyses of the natural and acid-activated forms of the Emirler clinoptilolite (Table 1), their approximate structural formulas are determined as $(Na_{0.12}K_{1.07}Mg_{0.87}Ca_{1.56})\ (Fe_{0.30}Al_{5.93}Si_{29.79})\ O_{72} \cdot nH_2O$ and $(Na_{0.09}K_{0.9}Mg_{0.71}Ca_{0.94})\ (Fe_{0.35}Al_{5.48}Si_{30.53})\ O_{72} \cdot nH_2O$ respectively. It is obvious that the exchangeable cations, especially Ca^{+2}, are partly removed and the framework Al^{+3} ions are made slightly soluble (7.5%). This result, in contrast to that of Barrer and Makki (1964), can be attributed to the differences in the activation methods and in the chemical compositions of the clinoptilolites, especially in terms of Na contents. It is most likely that the removal of the exchangeable cations and Al are compensated by the replacement of hydronium and hydroxyl ions (Barrer and Makki 1964) giving rise to increase of active acid sites probably by forming $(Na_{0.09}K_{0.9}Mg_{0.71}Ca_{0.94}H_3O_{1.76})\ (Fe_{0.35}Al_{5.48}Si_{29.79}(OH)_{1.2})\ O_{70.8} \cdot nH_2O$.

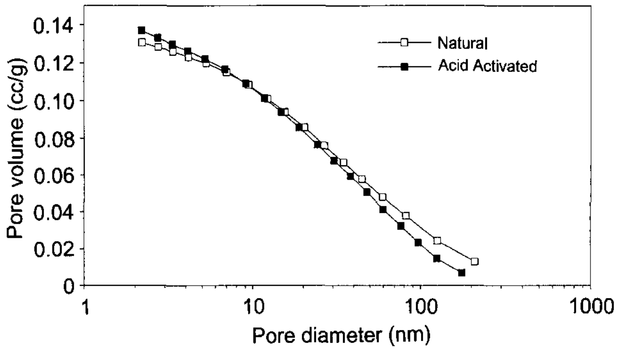

Fig. 3. Cumulative adsorption pore volume plots of natural and acid-activated clinoptilolites

The BET measurements show that the acid activation affects the pore size distribution and specific surface area of clinoptilolite. Natural clinoptilolite has an average pore diameter of 12 nm and a total specific surface area of 40 m^2/g (Table 1). Due to the replacement of exchangeable cations by H_3O^+ and partial dissolution of Al from the framework, the acid activated sample shows a greater total specific surface area (70 m^2/g) but low average pore diameter of 8 nm (Table 1). The increase in the total specific surface area of the acid activated clinoptilolite mostly takes place in the pore diameter range of approximately 15 nm as indicated by the cumulative adsorption pore volume plot (Fig. 3). In addition, the ratio of the total specific surface area of acid activated and natural clinoptilolites is 1.75 which is comparable with the ratio (1.8) of the color index of oil bleached by 2% of natural and activated clinoptilolites. Therefore, the pore diameter range lower than 15 nm seems to be more effective in the adsorption process of the coloring material in cotton seed oil.

From these discussions, it can be concluded that the oil decolorization capacity of the Emirler clinoptilolite can be improved by acid activation, which increases the total specific surface area and gives rise to smaller pore radius in the mesopore range by opening up and enlarging intracrystalline micropores. The bleaching capacity of acid activated Emirler clinoptilolite is not as great as that of other activated bleaching earths, but its low oil absorption property permits the use of two times more material and thus nearly the same results as in Tonsil can be obtained.

Acknowledgements. This study was carried out with the financial support of the Etibank company that mines the borates in the Bigadiç area. We are also grateful to two anonymous referees for their excellent reviews and very constructive criticisms.

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Editorial handling: A. Hall