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Acid activation and bleaching capacity of bentonites from the islands of Milos and Chios, Aegean, Greece

G.E. Christidis ^{a,*}, P.W. Scott ^b, A.C. Dunham ^c

^a *Department of Mineral Resources Engineering, Technical University of Crete, 73133 Chania, Greece*

^b *Camborne School of Mines, University of Exeter, Redruth, Cornwall TR15 3SE, UK*

^c *Department of Geology, University of Leicester, University Road, Leicester, LE1 7RH, UK*

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Abstract

Acid activation with HCl of two bentonites from the Aegean Islands of Milos and Chios, Greece, consisting of Chambers and Tatatilla-type and Otay-type montmorillonite, respectively, resulted in a 4 to 5-fold increase of the surface area of the raw materials. The activated materials have been rendered suitable for decolorization (bleaching) of rapeseed oil through removal of β -carotene. The optimum bleaching capacity is not associated with maximum surface area. Activation is characterized by destruction of the original smectite structure, removal of octahedral cations, uptake of OH^- and formation of an amorphous Si-rich phase. Mg is the most readily removed element affecting the tendency for activation. The Otay-type montmorillonites are activated more easily. Optimum conditions for activation are obtained using a variety of combinations of acid strength and residence time. The combination which is likely to be preferred on an industrial scale, is the least energy consuming. Therefore shorter treatments with more dilute acid are preferable. © 1997 Elsevier Science B.V.

Keywords: bentonite; montmorillonite; acid activation; bleaching capacity; adsorption; β -carotene

1. Introduction

Bentonites are highly valued for their sorptive properties, which stem from their high surface area and their tendency to absorb water in the interlayer sites.

* Corresponding author.

These properties are enhanced with acid activation and treatment with organics, (Odom, 1984; Rupert et al., 1987; Boyd and Jaynes, 1994). Acid activation increases the surface area (Grim, 1962; Rupert et al., 1987; Srasra et al., 1989; Kaviratna and Pinnavaia, 1994; among many authors) and modifies the structure of smectites (Rupert et al., 1987; Rhodes and Brown, 1992; Tkac et al., 1994). Acid activated bentonites are widely applied in the foodstuffs industry, sulphur production, forest and water conservation, the mineral oil industry, the beverages and sugar industry, the chemical industry, environmental protection, the paper industry as well as for cleaning and as detergents (Clarke, 1985; O'Driscoll, 1988).

In terms of consumption, the most important use of the acid activated bentonites is the purification, decolorization and stabilization of vegetable oils. They are used to remove phospholipides, soap, trace metals, organic compounds (carotenoids, especially β -carotene, and their derivatives, xanthophylls, chlorophyll, pheophytin, tocopherols, and gossypol) and their degradation products which impart undesirable colors to the edible oils (Siddiqui, 1968; Kheok and Lim, 1982; Griffiths, 1990). Moreover oxidation might convert the unsaturated fatty acids and glycerides to hydroperoxides which are also undesirable and are removed during bleaching.

Activation proceeds with partial dissolution of smectite, described by pseudo first order kinetics (Osthaus, 1956; Granquist and Samner, 1959) and is characterized by an initial replacement of the interlayer cations by H^+ (Thomas et al., 1950; Grim, 1962), followed by dissolution of the tetrahedral and octahedral sheets and subsequent release of the structural cations (Thomas et al., 1950; Mills et al., 1950; Brindley and Youell, 1951; Milliken et al., 1955; Osthaus, 1956; Granquist and Samner, 1959; Grim, 1962; Brückman et al., 1976; Novak and Cícel, 1978; Tkac et al., 1994; Kaviratna and Pinnavaia, 1994). The rates of depletion of the octahedral cations follow the order $Mg^{2+} > Fe^{2+} > Fe^{3+} > Al^{3+}$ (Corma et al., 1987; Luce et al., 1972). Also the release rates of tetrahedral and octahedral aluminium and iron are comparable in both smectites and sepiolite (Luca and MacLachlan, 1992; Tkac et al., 1994). Detailed structural composition of the acid treated smectites has not been published so far (Rupert et al., 1987).

The most important physical changes in activated smectites is the increase of their specific surface area and the average pore volume (Mills et al., 1950; Grim, 1962; Fijal et al., 1975; Morgan et al., 1985; Srasra et al., 1989; Rhodes and Brown, 1992). The extent of these changes depend on the acid strength and time of treatment (Novak and Gregor, 1969; Kolta et al., 1975; Kheok and Lim, 1982; Zaki et al., 1986; Srasra et al., 1989; Rhodes and Brown, 1992) as well as on temperature (Kolta et al., 1975). The increased surface area of the activated smectites and the surface acidity control the bleaching properties of the clay. The bleaching process is not associated with maximum surface area (Morgan et al., 1985; Zaki et al., 1986) because it is not merely a physical adsorption

process (Siddiqui, 1968; Khoo et al., 1979; Morgan et al., 1985). Moreover the interlayer space of montmorillonite does not contribute to the sorption of coloring matter from crude oils (Stoch et al., 1979b). Interaction with organic compounds (chiefly amines) might also increase the decolorizing efficiency of a smectite clay (Stoch et al., 1979b).

Although Greece is the third largest bentonite producer in the world it covers its needs for acid activated clays entirely by imports. Preliminary work (Christidis, 1989) showed that acid activation of bentonites from Milos, Greece with sulphuric acid increased surface area to about 300 m²/g depending on the acid strength and the time of treatment, and modified the texture of the clay. In this contribution (a) bentonites from Milos and Chios have been activated with HCl, (b) the mineralogical and physicochemical properties of the activation products are examined and (c) their capacity to decolorize crude rapeseed oil is evaluated.

2. Materials and methods

The bentonites come from the deposits of Ankeria, Milos, and the island of Chios. The Ankeria bentonite contains Tatatilla and Chambers type montmorillonite, while the Chios bentonite consists of Otay-type montmorillonite (Christidis, 1992; Christidis and Dunham, 1993). The latter contains abundant opal-CT and dolomite while the Ankeria bentonite consists principally of montmorillonite and is free of opal-CT and carbonates (Table 1). The materials were dried at 65°C overnight, ground in a Tema mill and passed through a 125 μm sieve.

Activation was carried out using HCl of analytical grade, with strength varying between 0.5 N and 8 N at the temperature of 70° ± 2°C and solid to

Table 1
Mineralogy, CEC and specific surface area of the activated bentonites

Material	Mineralogical composition	CEC (meq/100 g)	Specific surface area m ² /g
Ankeria bentonite	Tatatilla–Chambers type montmorillonite	104.4	61.76
Chios bentonite	Otay-type montmorillonite (M), opal-CT (M), dolomite (M), quartz (Min), plagioclase (Min).	60.25	53.47

M is the major mineral phase, Min the minor mineral phase and T is the trace mineral phase.

liquid ratio of 1:15. Residence time varied between 30 min and 6 h. At the end of each run the acid was discarded and the clay was washed until pH 6. The clay slurry was filtered and the collected material was dried at 100°C for 3 h and subsequently ground gently with pestle and mortar so as to pass through a 125 μm sieve.

Single point surface area measurements of the activated materials were obtained with a Strohlein Area Meter II using N_2 . The structural and morphological changes of the Ankeria bentonite during activation were examined by means of XRD, DTA, TG, FTIR and SEM. The LOI at 1000°C was also determined. The Ankeria bentonite was selected because it consists entirely of smectite. Therefore the changes observed reflect the structural changes of smectite. CEC measurements were performed in the acid treated samples of both materials.

XRD was performed on unorientated samples with a Philips diffractometer equipped with a PW1710 computerized control unit, operating at 40 kV and 30 mA, using Ni-filtered $\text{CuK}\alpha$ radiation, at a scanning speed of $1^\circ 2\theta/\text{min}$. FTIR spectra were obtained using a BIORAD FTS40 FTIR Spectrometer. 3 mg of each sample previously dried at 150°C were mixed with 160 mg of KBr and pressed on disks (Russell, 1987). DTA and TG was carried out with a Stanton Redcroft STA 1000/1500 Thermal Analyser using air atmosphere, in the temperature range 20–1000°C. SEM observation of the activated materials was carried out with a Hitachi S520 SEM operating at 20 kV and equipped with a Link AN10000 EDS for qualitative analysis. The CEC of the acid activated materials was determined with a Kjeldahl microsteam apparatus after saturation with 1 N ammonium acetate (Christidis, 1989).

The bleaching capacity of the run products was tested using crude rapeseed oil provided by Seatons Ltd of Hull, UK. 1 g of acid activated clay was added to 40 ml of crude oil. The experiments were performed at the constant temperature of $90^\circ \pm 2^\circ\text{C}$ in atmospheric conditions under stirring (atmospheric-type bleaching, Richardson, 1978). The residence time at the maximum temperature was 20 min. The treated oils were filtered under vacuum. The bleaching capacity of the activated clays was evaluated by means of removal of β -carotene from the crude oil.

The color changes in the treated oils were determined spectrophotometrically at 450 nm and 430 nm (CECIL CE303 series 2 absorption spectrophotometer) by diluting 5 ml of bleached oil in 15 ml acetone. For selected runs the full absorption spectrum between 400 and 500 nm was obtained. The adsorbed amount of the coloring agent was calculated by converting the absorbance units to β -carotene concentration. The bleaching capacity of the activated clays was determined from the following equation:

$$\text{Bleaching capacity} = (C_o - C/C_o) * 100, \quad (1)$$

where C_o is the concentration ($\mu\text{g}/\text{ml}$) of β -carotene in the crude oil and C the concentration of β -carotene in the bleached oil.

For terms of comparison the same bleaching experiment was performed using an industrial product available in the market (Fullmont AA), provided by Laporte Absorbents Ltd.

3. Results

3.1. Structural modification

The XRD results (Fig. 1) show that acid activation has caused structural changes in the treated smectites. This has also been observed by other workers (Brückman et al., 1976; Stoch et al., 1979a,b; Srasra et al., 1989; Rhodes and Brown, 1992). The effect of both time under constant acid strength and acid strength under constant time on the smectite structure is similar, although it seems that the variation of time for the acid strength chosen (i.e 2 N) caused more drastic changes. Activation has affected mainly the 001-order (basal) reflections; the 003 reflection has completely disappeared, while the intensity of the 001 and 005 reflections has been reduced significantly. On the other hand the prismatic reflections (110, 020 band and 060 reflection) do not seem to have been affected by the treatment. Acid activated samples display an increase of the background in the interval between 20 and 30°2 θ (a in Fig. 1) due to the deposition of amorphous silica gel caused after the attack on the octahedral layer and the exposure of the tetrahedral layer.

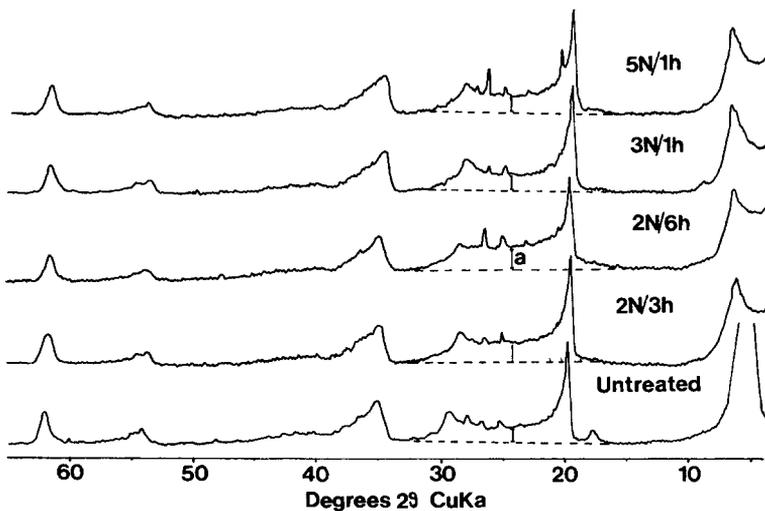


Fig. 1. XRD diagrams of the Ankeria bentonite and the products of acid activation using various combinations of acid strength and residence time. a represents the increase of the background in the interval 20–30° 2 θ , due to the dissolution of smectite and deposition of amorphous material.

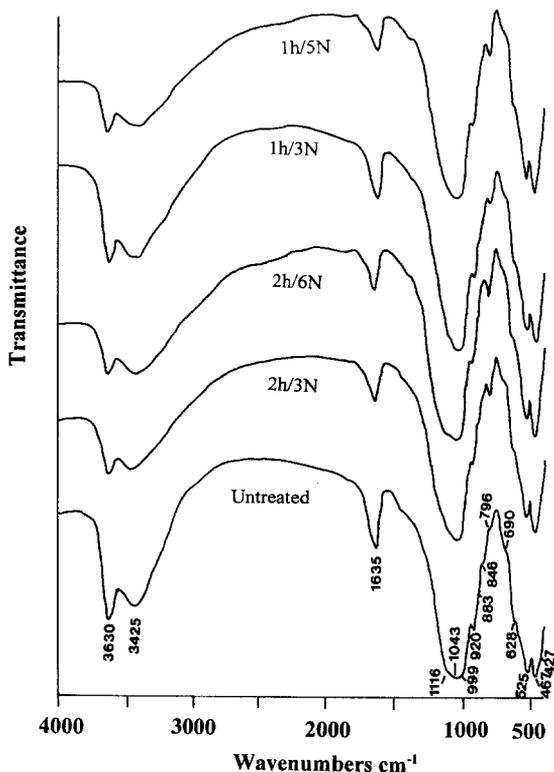


Fig. 2. FTIR spectra of the Ankeria bentonite and the products of acid activation, using various combinations of acid strength and residence time.

The effects of the acid activation process on the FTIR Spectra of the treated bentonites (Fig. 2) are summarized as follows: The intensity of the absorption band at 3630 cm^{-1} (AlAlOH coupled by AlMgOH stretching vibrations) decreases with increasing severity of treatment. The bands at 3425 cm^{-1} and 3200 cm^{-1} (absorption by the interlayer water) become more diffuse with increasing severity of treatment. The intensity of the Si–O out of plane and Si–O–Si (2 bands) in plane stretching bands at 1116 , 1043 and 999 cm^{-1} have not been affected by acid treatment. The AlAlOH (920 cm^{-1}), AlFe³⁺OH (883 cm^{-1}) and AlMgOH (846 cm^{-1}) deformation bands decrease with increasing intensity of treatment. The latter band is almost eliminated in the most severe treatments. The intensity of the band at 796 cm^{-1} (disordered opal-CT) increases significantly with increasing intensity of treatment in accordance to the findings of other workers (Brückman et al., 1976; Srasra et al., 1989; Komadel et al., 1990 among many others). The intensity of the band at 628 cm^{-1} (either Al–OH or Si–O bending and/or Al–O stretching vibration) gradually decreases with increasing severity of treatment in good agreement with the findings of Komadel et al. (1990). The intensity of the band at 467 cm^{-1} (Si–O–Al and

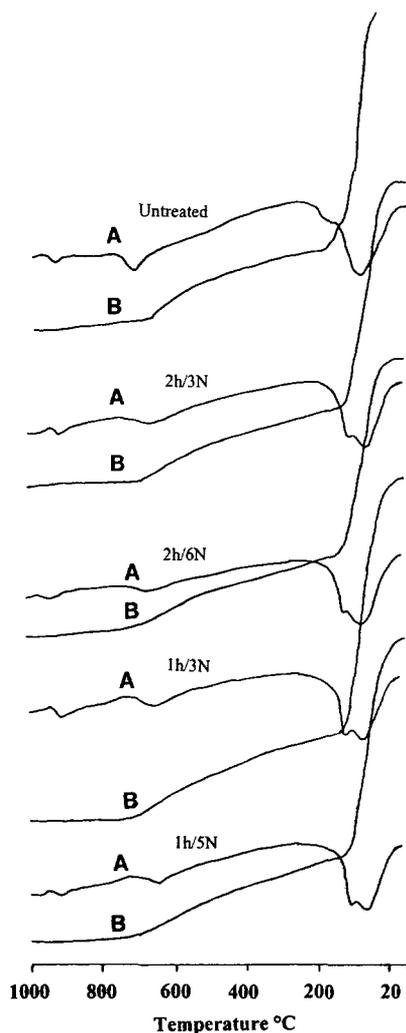


Fig. 3. DTA-TG thermodiagrams of the Ankeria bentonite and the products of acid activation, using various combinations of acid strength and residence time. (A) DTA curves, (B) TG curves.

Si–O–Mg coupled by OH vibrations or Si–O bending vibrations) is essentially unchanged. On the other hand, the absorption band at 525 cm^{-1} , assigned to the same vibrations, decreases with increasing severity of treatment.

The effects of the acid activation process on the thermal properties of the treated bentonites (Fig. 3) are summarized as follows: The two steps of the loss of interlayer water have been preserved in the acid treated samples, but occur at lower temperatures compared with the untreated sample (105°C instead of 140° and $150\text{--}155^\circ\text{C}$ instead of 210°C). The area of the interlayer water peak remains essentially unchanged with increasing severity of treatment. The main dehydroxylation peak becomes more diffuse with increasing both the acid strength and

Table 2
Cation exchange capacity and LOI of the acid activated bentonites

Sample SM16	CEC (meq/100 g)	LOI (%)	Sample SM 324	CEC (meq/100 g)
untreated	104.4	7.09	untreated	60.25
1 N/1 h	88.0	7.28	1 N/1 h	69.0
2 N/1 h	87.1	6.77	2 N/1 h	63.8
3 N/1 h	80.1	7.36	3 N/1 h	62.9
5 N/1 h	73.4	6.98	5 N/1 h	57.1
2 N/3 h	79.2	6.93	2 N/3 h	61.0
2 N/4 h 30 min	80.1	7.31	2 N/4 h 30 min	45.0
2 N/6 h	72.9	7.16	2 N/6 h	45.1

time of treatment and shifts to a lower temperature (from 720°C to 675°C). The intensity of the third endothermic peak increases during treatment with dilute acids and decreases when more concentrated acids are used. It also shifts to a higher temperature (925–930°C). An exothermic peak occurs immediately after the third endothermic peak at about 950°C. This is not observed in the untreated sample. The rate loss of hydroxyls during the main part of the reaction is much slower in the activated samples compared to the untreated sample, since the



Fig. 4. SEM micrographs of the Ankeria bentonite and products of acid activation using various combinations of acid strength and residence time. The amorphous material formed during the treatments is shown by arrows. The smectite flakes have been flattened and vermicular textures have formed. (a) Untreated material, (b) 1 N/3 h, (c) 1 N/5 h, (d) 2 N/3 h.

slope of the TG curve between the first two endothermic peaks is greater in the activated samples. Therefore the rate of the hydroxyl loss before all the interlayer water has been removed is much greater in the activated samples.

The CEC of the activated materials (Table 2), displays different trends in the two materials. It decreases continuously with increasing degree of activation in the Ankeria bentonite, while increases initially, decreasing later in the Chios bentonite. Examination under the SEM showed that the original wavy smectite flakes have been replaced by flat flakes (Fig. 4). Spherical Si-rich textures which probably belong to amorphous Si-rich material produced during activation are also observed (Fig. 4). At more advanced stages of alteration vermicular textures also appear. Similar textures were observed for the activated bentonites from the Aspro Horio deposit, Milos (Christidis, 1989).

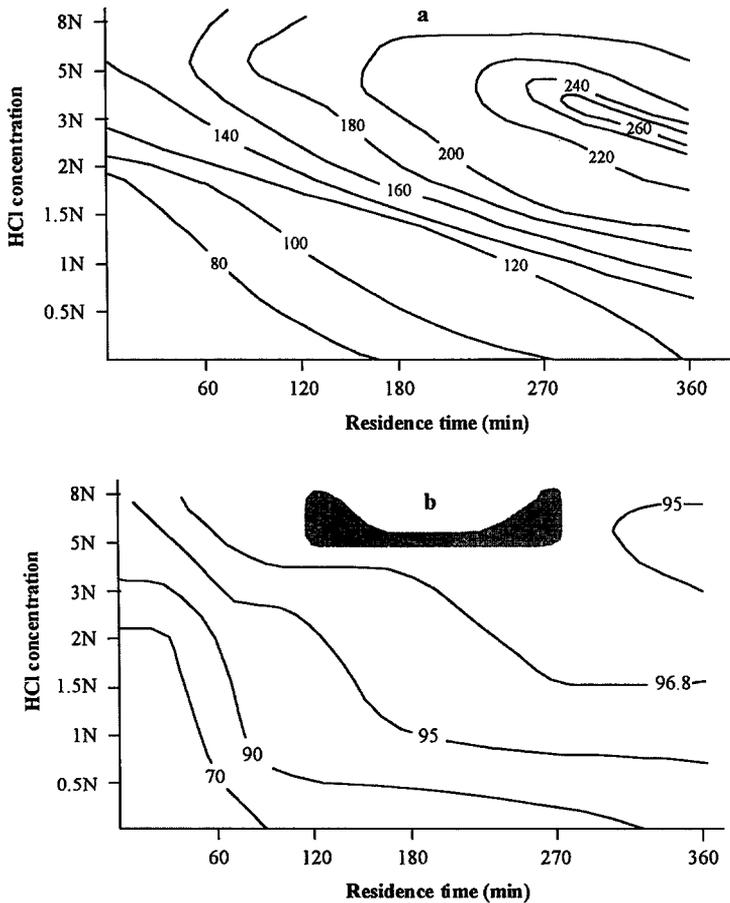


Fig. 5. (a) STS (surface area-time-acid strength) diagram for the bentonite from Ankeria deposit, Milos. (b) Evolution of the bleaching capacity of the Ankeria bentonite with time and acid strength. The shaded area corresponds to the highest bleaching capacity. See text for discussion.

3.2. Surface area

The surface area displays a maximum four fold increase with both the time of treatment and acid strength in both samples as seen in the surface area-time-acid strength (STS diagram) of Fig. 5a and Fig. 6a. As in the studies of other workers (Novak and Gregor, 1969; Kolta et al., 1975; Kheok and Lim, 1982; Zaki et al., 1986) it increases continuously up to a maximum value and then it decreases in both samples (Fig. 5a, Fig. 6a and Fig. 7). The surface area evolution paths depend on both the acid strength and time, but the dependance on these factors

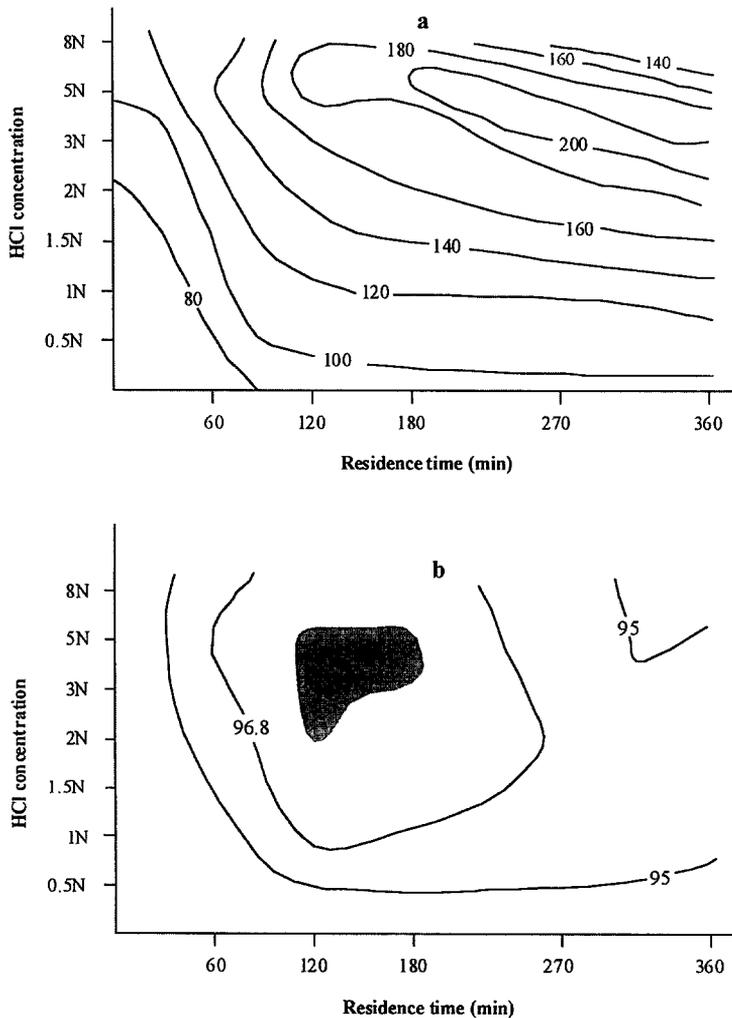


Fig. 6. (a) STS (surface area-time-acid strength) diagram for the bentonite from Chios. (b) Evolution of the bleaching capacity of the Chios bentonite with time and acid strength. The shaded area corresponds to the highest bleaching capacity. See text for discussion.

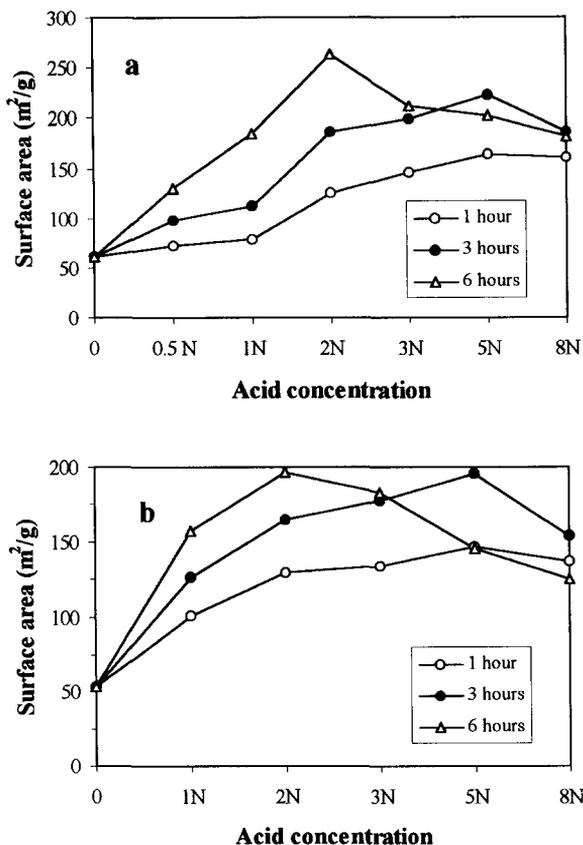


Fig. 7. Evolution of surface area as a result of acid activation with HCl of variable strength at various residence times. (a) Ankeria bentonite, (b) Chios bentonite. The curves essentially are sections of the composite diagrams in Fig. 5a and Fig. 6a.

is different in the different bentonites. The Chios bentonite develops its maximum surface area faster than the Ankeria bentonite. Moreover it can be observed that: (a) with increasing acid strength, the time at which maximum surface area is attained decreases and (b) with increasing residence time, the acid strength at which surface area maximum is obtained also decreases. Therefore the maximum values of surface area are attained with treatments characterized by many combinations between acid strength and time. Also, in both samples the surface area declines in treatments performed with acid more concentrated than 5 N, unless the treatment is short.

3.3. Bleaching capacity

The results of the bleaching experiments are given in Table 3 and the evolution of the bleaching capacity of the bentonites is shown in Fig. 5b and

Table 3

Bleaching capacity and amount of β -carotene adsorbed from the products of acid activation of the Ankeria and Chios bentonites

Treatment	Bleaching capacity (%)	β -carotene adsorbed (10^{-4} mol/100 g clay)	Treatment	Bleaching capacity (%)	β -carotene adsorbed (10^{-4} mol/100 g clay)
Sample SM16					
30 min/2 N	65.9	7.2	3 h/1 N	95.2	10.4
30 min/3 N	69.1	7.5	3 h/2 N	96.3	10.5
30 min/5 N	89.3	9.7	3 h/3 N	96.1	10.5
30 min/8 N	94.3	10.3	3 h/5 N	98.1	10.7
1 h/1 N	86.9	9.5	4 h 30 min/1 N	96.3	10.5
1 h/2 N	95.1	10.4	4 h 30 min/2 N	98.2	10.7
1 h/3 N	95.6	10.4	4 h 30 min/3 N	97.3	10.6
1 h/5 N	96.8	10.6	4 h 30 min/5 N	98.4	10.7
1 h/8 N	94.1	10.3	4 h 30 min/8 N	98.1	10.7
2 h/1 N	93.9	10.2	6 h/1 N	96.0	10.5
2 h/2 N	90.4	9.9	6 h/2 N	97.6	10.7
2 h/3 N	96.0	10.5	6 h/3 N	96.0	10.5
2 h/5 N	98.4	10.7	6 h/5 N	96.3	10.5
2 h/8 N	98.1	10.7	6 h/8 N	95.9	10.5
Sample SM324					
30 min/1 N	—	—	3 h/1 N	96.8	10.6
30 min/2 N	93.8	10.2	3 h/2 N	96.9	10.6
30 min/5 N	94.5	10.3	3 h/5 N	98.3	10.7
30 min/8 N	95.4	10.4	3 h/8 N	97.2	10.6
1 h/1 N	94.8	10.3	4 h 30 min/1 N	96.8	10.6
1 h/2 N	95.7	10.4	4 h 30 min/2 N	96.1	10.5
1 h/3 N	96.5	10.5	4 h 30 min/3 N	96.1	10.5
1 h/5 N	97.1	10.6	4 h 30 min/5 N	96.1	10.5
1 h/8 N	96.1	10.5	4 h 30 min/8 N	95.5	10.4
2 h/1 N	97.2	10.6	6 h/1 N	96.9	10.6
2 h/2 N	98.1	10.7	6 h/2 N	96.4	10.5
2 h/3 N	98.6	10.8	6 h/3 N	96.0	10.5
2 h/5 N	98.7	10.8	6 h/5 N	80.8	8.8
2 h/8 N	97.6	10.7	6 h/8 N	76.0	8.3

Fig. 6b. Although the mineralogy, the smectite content and the smectite crystal chemistry is different in the two materials, they display high bleaching capacities in excess of 95%. The bleaching capacity of Fullmont AA was found 96.8%. Thus the 96.8% curve in Fig. 5b and Fig. 6b indicates the combinations of acid strength-residence time which imparted to the treated materials higher bleaching capacity than the industrial product. Finally the shaded areas in Fig. 5b and Fig. 6b, correspond to the combinations of acid strength and residence

time which imparted bleaching capacity greater than 98% to each material. Therefore the outcome of these diagrams is the determination of the combinations of acid strength and treating time which produce optimum products.

Activation is fast in the Chios bentonite, since 1 N acid for 1 h treatment imparts more than 95% of the final bleaching capacity. The Ankeria bentonite is activated at a somewhat slower rate. Also the Chios bentonite loses its decolorizing properties after prolonged activation, when treated with acids more concentrated than 5 N. A decrease of a much smaller scale is observed in the Ankeria material as well. Thus, the differences between the two materials concerning their bleaching capacity are (a) the rate at which the latter is acquired (b) the ease with which their decolorizing properties deteriorate after prolonged treatment with concentrated HCl acid. Obviously the different smectite content of the two bentonites, expressed by the CEC, is not related to both the bleaching capacity and the amount of the β -carotene adsorbed.

The bleaching capacity does not follow the variations of the surface area with acid treatment (Figs. 5 and 6). Only in the Chios bentonite for prolonged treatments with concentrated acid (6 h/8 N) the bleaching properties deteriorate following the decrease of the surface area. Furthermore, in accordance with other workers (Morgan et al., 1985; Zaki et al., 1986) short treatments with dilute acid (e.g. 1 N/3 h treatment for SM16 and 1 N/1 h treatment for SM324) are sufficient for development of most of the bleaching capacity of the clay, although its surface area is less than 50% of the maximum observed at more severe treatments.

The results for adsorption of β -carotene are illustrated in Fig. 8. The Chios bentonite is rendered suitable to adsorb β -carotene if treated with dilute acids for short periods. On the other hand, the Ankeria bentonite displays a more

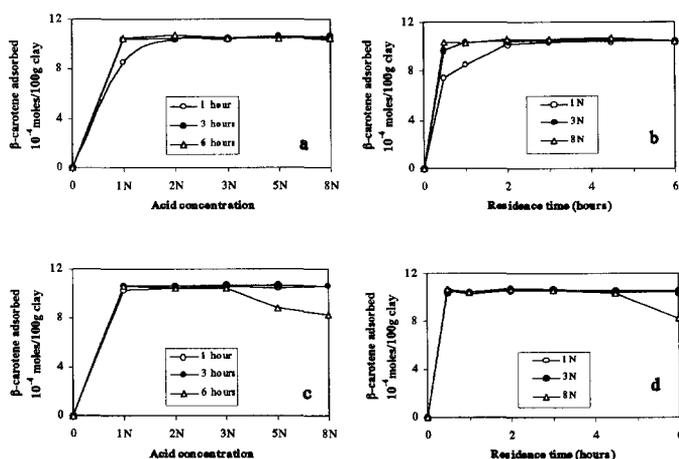


Fig. 8. Adsorption of β -carotene from the Ankeria bentonite (a and b) and the Chios bentonite (c and d) as a function of acid strength and residence time.

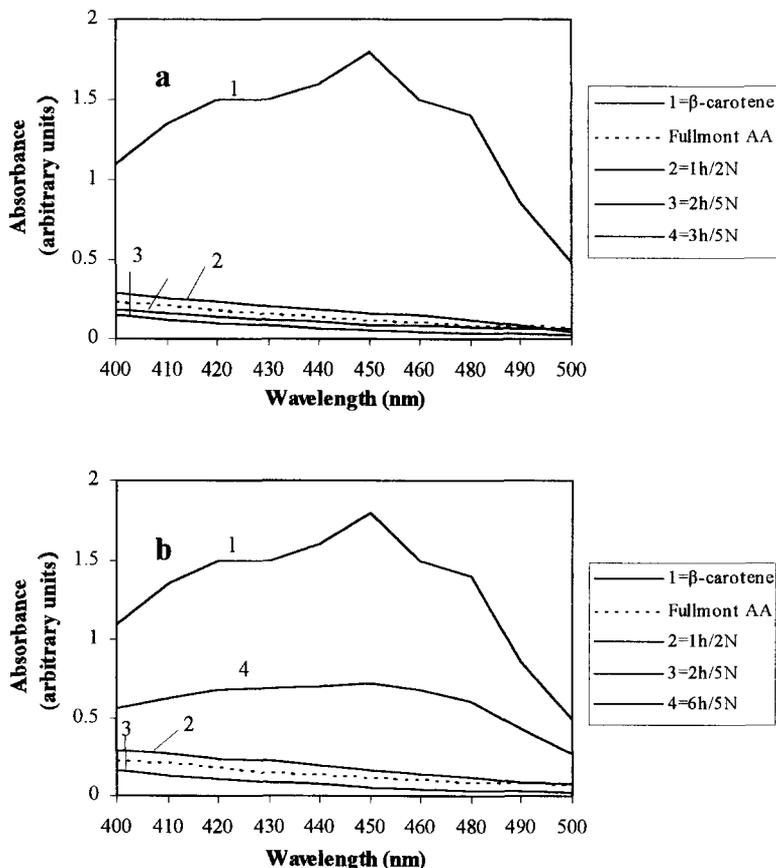


Fig. 9. Absorption spectra of β -carotene obtained from the crude rapeseed oil and oil treated with acid of variable strength for variable time. (a) Ankeria bentonite, (b) Chios bentonite.

progressive increase in the adsorption of β -carotene with increasing both residence time and acid strength. Also, the amount of β -carotene adsorbed by Chios bentonite decreases significantly after prolonged treatments (6 h) with acids more concentrated than 5 N. The adsorption of β -carotene reaches a maximum value, which is obtained using several combinations of acid strength and time during treatments. It is obvious that surface area is not associated with the maximum adsorption of β -carotene.

The efficiency of the materials to adsorb β -carotene is also observed in Fig. 9. The β -carotene spectrum is characterized by the existence of an absorption maximum at about 450 nm, sandwiched between two shoulders (spectrum 1 in Fig. 9a and b). As well as the decrease of the overall intensity of the absorption spectrum due to the removal of the β -carotene, the maximum at 450 nm is also eliminated. This maximum at 450 nm persists only in the 6 h/5 N treatment of the Chios bentonite (spectrum 4 in Fig. 9b) which is considered over-activated,

because less severe treatments cause an almost complete elimination in the absorption spectra of β -carotene, producing better products.

4. Discussion

The results in Figs. 5 and 6 demonstrate that, although the Chios bentonite has a lower CEC than its Ankeria counterpart, optimum activation can be achieved with a more dilute acid. Moreover the evolution of the CEC is different in the two materials. Also the performance of the Chios bentonite deteriorates significantly at prolonged treatments with concentrated acids. This behavior of the Chios bentonite depends on: (a) the mineralogical composition of this particular bentonite and (b) the mineral chemistry of the smectites.

The Chios bentonite contains abundant carbonates, mainly dolomite. In the initial stages of the acid treatment carbonates dissolve causing effective enrichment of the smectite content. Simultaneously, the acid attacks the smectite flakes, releasing octahedral cations in the solution and causing deposition of amorphous silica in the edges of the flakes. The dissolution of the carbonates by the hot acid is vigorous and overcomes the effect of the dissolution of smectite, which is a slower process, leading to an increase of the CEC.

In more advanced stages of the acid treatment the dissolution of the smectite continues, causing a continuously decreasing proportion of smectite, which yields (a) a continuous decrease in the CEC capacity of the activated bentonite and (b) increasingly imbalanced smectite crystallites with continuous release of the octahedral cations, leading to an actual increase of the CEC of the smectite flakes (Granquist and Samner, 1959). In the Ankeria bentonite which contains minimal carbonates, the CEC of the treated bentonites continuously decreases as a result of the continuous dissolution of the smectite flakes and deposition of amorphous silica (Figs. 1 and 2).

Both bentonites contain Cheto smectites. Ankeria bentonite contains Tatatilla and Chambers-type montmorillonite richer in Mg than Fe (Christidis and Dunham, 1993), while Chios bentonite contains Mg-rich Otay-type montmorillonite. Similar to other workers (Luce et al., 1972; Stoch et al., 1977; Corma et al., 1987), Mg is released more readily than other octahedral cations during activation. Thus the IR band at 846 cm^{-1} (AlMgOH deformation band) is almost eliminated, while that at 883 cm^{-1} (AlFe³⁺OH deformation band) is observed even at the most advanced stages of alteration (Fig. 2). Mg-rich smectites are expected to be more susceptible to structural changes than Al-rich ones, since substitution of Al by Mg and/or Fe lowers the stability of the octahedral layer and renders the smectite crystals prone to changes imposed by acid attack (Novak and Cicel, 1978). Hence the active sites might develop faster and the clay might be activated easier. Mg-release might proceed either through

edge attack or through a gallery access mechanism, in the more advanced stages of alteration (Kaviratna and Pinnavaia, 1994).

The presence of abundant accessory minerals like opal-CT and carbonates in the Chios bentonite might affect the behavior of the clay during treatment. If opal-CT is intimately associated with smectite it might impede acid attack by blocking part of the exposed octahedral sheet (Christidis, 1992). On the other hand carbonates are believed to enhance activation, since their vigorous dissolution at the incipient stages of the treatment is expected to increase the smectite-acid reaction area significantly. Therefore the possible limiting role of the opal-CT is balanced.

It is possible that any existing octahedral Fe^{2+} is oxidized during activation. In natural samples oxidation of iron is associated by OH-uptake; therefore the CEC does not decrease (Lear and Stucki, 1985). The loss of ignition of the activated bentonites is not lower than that of the untreated sample (Table 3), although early reports (Thomas et al., 1950; Granquist and Samner, 1959) mention that in activated materials hydroxyls are removed during treatment. Since the loss of ignition was determined on materials previously dried at 105°C, significant amounts of the interlayer water had been removed from the activated samples, because the first step of interlayer water loss of the acid activated materials occurred at 105°C (Fig. 3). Thus in order to display similar or even higher loss on ignition, the activated bentonites must have a higher hydroxyl-content than their untreated counterparts. Therefore during activation, although a number of hydroxyls have probably been removed during the partial dissolution of the octahedral sheet, the migration of H^+ protons from Brönsted acid centres caused disruption of Si–O–Si, Si–O–Al, Si–O or Al–O bonds, which in turn led to the formation of new SiOH AlOH or $(\text{SiO}_3)\text{SiOH}$ groups (Brückman et al., 1976; Stoch et al., 1979a; Tkac et al., 1994; Kaviratna and Pinnavaia, 1994). The structure of the activated bentonite is expected to be different than the untreated material and the new hydroxyls are probably bound in a less cohesive manner. Similar groups exist also in the Si-rich amorphous phase (Figs. 1 and 2) resulting from the dissolution of the smectite flakes (Tkac et al., 1994), which cause increase of the surface area of the activated material (Rhodes and Brown, 1992). Therefore hydroxyls are removed easier and at a larger temperature range, yielding to the inclined TG curves and the less well defined second endothermic peak.

Rupert et al. (1987) proposed that the adsorptive properties of the bentonite clays are due to the presence of tetrahedrally coordinated Al, formed from exposure of Al which substitutes for Si in the tetrahedral sheet. The results of this work clearly demonstrate that the bentonites from Chios, which contain Otay-type montmorillonite with very low or without tetrahedral substitution, can be activated very successfully. Hence, the active acid centres do not exist 'waiting to be exposed' (Rupert et al., 1987), but are formed during activation. Whether these centres will be formed or not might depend on the degree the

octahedral cations are removed and thus on the degree of the octahedral substitution (Novak and Cícel, 1978). Active centres probably exist, both in the activated smectite and the amorphous Si-rich phase. However, the contribution of the latter is rather minor, since the bleaching capacity deteriorates in prolonged treatments, in which smectite structure collapses.

The observed increase of the intensity of the third endothermic peak at relatively mild treatments and the appearance of the exothermic peak immediately after is well known (e.g. Granquist and Samner, 1959). Green-Kelly (1957) suggested that after the main dehydroxylation peak loss of the structural hydroxyls is not complete. A gradual loss might lead to a decrease of the intensity or even complete elimination of the third endothermic peak. In the acid activated samples the partial loss of the hydroxyls during the acid treatment, and the formation of new weaker Si–OH and Al–OH bonds might cause complete dehydroxylation during the second endothermic peak, leading to a more pronounced third endothermic peak which is associated with the total collapse of the smectite structure. In prolonged treatments or treatments with concentrated acids the structure has already been affected significantly by dissolution. Thus the entropy difference before and after the reaction (Mackenzie, 1970) is not expected to be great; therefore the intensity of the third endothermic peak decreases.

5. Conclusions

Acid activation increased the surface area of the bentonites examined up to a maximum value after which it decreases. The modification of the surface area is associated with changes in the smectite structure which occurred during activation. The acid activated bentonites can efficiently decolorize rape seed oil through removal of coloring agents like β -carotene. This is possibly due to the formation of active acid centres on the smectite flakes from structural modifications caused during activation. Although the acid activated bentonites have increased surface area, the maximum bleaching capacity of all the materials tested is not associated with maximum surface area.

The optimum decolorization properties for both bentonites can be obtained with a variety of combinations between acid strength and treating time. The combination which is most likely to be preferred in an industrial scale, is the least energy consuming. Therefore shorter treatments with more dilute acid are preferable. The bentonite from Chios was activated faster than the Ankeria bentonite. This is due to the higher Mg-content of the smectites present (Otay-type montmorillonites) as well as to the presence of carbonates which dissolve, thus increasing the effective smectite content. However, the presence of abundant carbonates suggests that some acid will be consumed for the dissolution of the carbonates, thus increasing the cost of the activation. Both the

Chios bentonite and the Ankeria bentonite might be used successfully for decolorization of rapeseed oil. However before use, a series of other tests like the determination of the free fatty acid of the bleached oil as well as its acidity might be necessary.

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