

ACID ACTIVATION AND BLEACHING CAPACITY OF A LOW GRADE BENTONITE FROM MILOS ISLAND, GREECE.

G.E. CHRISTIDIS¹

ABSTRACT

Acid activation of a low grade bentonite from Milos with HCl, resulted to a 5-fold increase of the surface area of the bentonite and decrease of its CEC. The activated materials are suitable for decolourization (bleaching) of rapeseed oil through removal of β -carotene. Optimum bleaching takes place after long treatments with strong acid and is not associated with maximum surface area. The difficulty of activation is attributed to the bulk mineralogy and the crystal chemistry of smectite. The combination of acid strength and residence time which will be preferred on an industrial scale, is the least energy consuming. Thus the Rema bentonite is unlikely to be used as a bleaching earth.

KEY WORDS: Bentonite, smectite, acid activation, bleaching capacity, bleaching earth, surface area, adsorption, β -carotene, decolourization.

1. INTRODUCTION

Acid activation is a process which increases the sorptive properties of bentonites (Odom, 1984, Rupert et al., 1987), increasing their surface area and modifying the structure of smectites (Srasra et al., 1989, Rhodes and Brown 1992, Tkac et al. 1994, Kaviratna and Pinnavaia, 1994, Christidis et al. 1997a). Acid activated bentonites are used in numerous chemical and food industries and in environmental protection (Clarke, 1985, O'Driscoll, 1988); their most important use is the purification, decolourization, and stabilization of vegetable oils. They remove phospholipides, soaps, trace metals organic compounds and their degradation products, which impart undesirable colours to edible oils (Siddiqui, 1968, Kheok and Lim, 1982, Griffiths, 1990).

Activation proceeds with partial dissolution of smectite and involves a) initial replacement of interlayer cations by H^+ , b) dissolution of the tetrahedral and octahedral sheets and c) release of the structural cations (Osthaus, 1956, Granquist and Samner, 1959, Brückman et al., 1976, Novak and Cicel, 1978, Tkac et al., 1994, Kaviratna and Pinnavaia, 1994). It increases the specific surface area and average pore volume of bentonites (Morgan et al., 1985, Srasra et al., 1989, Rhodes and Brown, 1992). The extent of these changes depend on the acid strength, the time of treatment and temperature (Novak and Gregor, 1969, Kolta et al., 1975, Kheok and Lim, 1982, Zaki et al., 1986, Srasra et al., 1989, Rhodes and Brown, 1992). The bleaching process is not associated with maximum surface area (Morgan et al., 1985, Zaki et al., 1986).

Although Greece is a major bentonite producer it covers its needs for acid activated clays entirely by imports. Recently Christidis et al. (1997a) showed that acid activation of bentonites from Milos and Chios, Greece with HCl yield products with high surface area, which can remove β -carotene from edible oils. In this contribution a low grade bentonite from Milos was activated with HCl, in order to examine the physicochemical properties of the end products and evaluate their capacity to decolourize crude rapeseed oil.

2. MATERIALS AND METHODS

The low grade bentonite comes from the deposit of Rema, Milos. It consists principally of Tatatilla-type montmorillonite and beidellite opal-CT, quartz and subordinate pyrite (Christidis and Dunham, 1997), while its surface area and CEC is low (Table 1). The material was dried at 65°C overnight, ground in Tema mill and passed through a 125µm sieve.

Table 1: Mineralogy, CEC and specific surface area of the untreated bentonites.

| Mineralogical composition | CEC (meq/100g) | Specific surface area (m ² /g) |
|--|----------------|---|
| Beidellite and Tatatilla- type montmorillonite (M). opal-CT (M) quartz (Min), pyrite (T) | 52.8 | 24.11 |

M = major mineral phase, Min = minor mineral phase. T = trace mineral phase.

Activation was carried out using 0.5N-8N HCl, at the temperature of 70±2°C and solid to liquid ratio of 1:15. Residence time varied between 1 and 8 hours. At the end of each run the acid was discarded and the clay was washed until pH 6. The collected material was dried at 100°C for 3 hours and subsequently ground gently with pestle and mortar so as to pass through a 125µm sieve. Single point surface area measurements of the activated materials were obtained with a Stroblein Area Meter II using N₂, while the cation exchange capacity (CEC) of the acid treated samples was determined with a Kjeldahl microsteam apparatus after saturation with 1N ammonium acetate.

The bleaching capacity of the run products was tested using crude rapeseed oil (Seatons Ltd of Hull, UK), at a solid:liquid ratio 1:40. Experiments were performed in atmospheric conditions at 90±2°C, under stirring (atmospheric-type bleaching, Richardson, 1978) and residence time 20 minutes. The treated oils were filtered and the bleaching capacity of the acid activated bentonite was evaluated by means of removal of β-carotene from the crude oil. The colour changes in the treated oil were determined spectrophotometrically at 450nm and 430nm (CECIL CE303 series 2 absorption spectrophotometer) by dissolving the bleached oil in acetone. The adsorbed amount of the colouring agent was calculated by converting the absorbance units to β-carotene concentration. The bleaching capacity (W) of activated clays was determined from the following equation:

$$W = (C_0 - C / C_0) * 100 \quad (1)$$

where C₀=concentration (µg/ml) of β-carotene in the crude oil and

C=concentration of β-carotene in the bleached oil.

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

3. RESULTS

Evolution of surface area and the CEC of the activated materials.

The specific surface area (SA) of the Rema bentonite increased both with residence time and acid strength (Fig. 1,2). These two factors are equally important for activation (Fig. 1). The diagram in Fig. 2 is an STS diagram (Surface area-Time-acid Strength). Maximum increase of the SA was five times the raw bentonite. At first SA increases steadily up to a maximum remaining virtually constant thereafter (Fig. 1). A different trend, dominated by a decrease of SA after reaching a maximum value, was observed in the Ankeria (Milos), and the Chios bentonite (Christidis et al. 1997a).

Two are the most important features observed in Fig. 2: a) with increasing acid strength, the time at which maximum SA is attained decreases and b) with increasing time of treatment, the acid strength at which maximum SA is observed also decreases. Therefore the maximum values of SA are attained with

Ψηφιακή Βιβλιοθήκη "Θεόφραστος" - Τμήμα Γεωλογίας, Α.Π.Θ.

treatments characterized by many combinations between acid strength and time, as illustrated in the STS diagrams. Contrary to the bentonites from Ankeria deposit and Chios, significant SA has not developed after short treatments or after treatments with dilute acid.

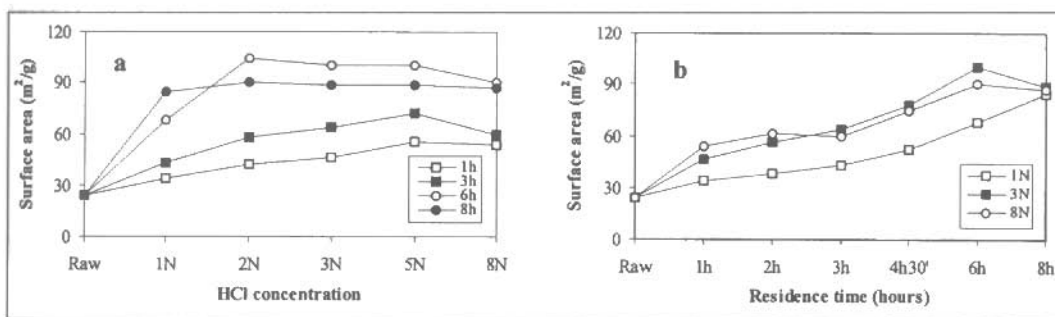


Fig. 1: Influence (a) of acid strength and (b) of residence time on the evolution of the surface area of the Rema bentonite.

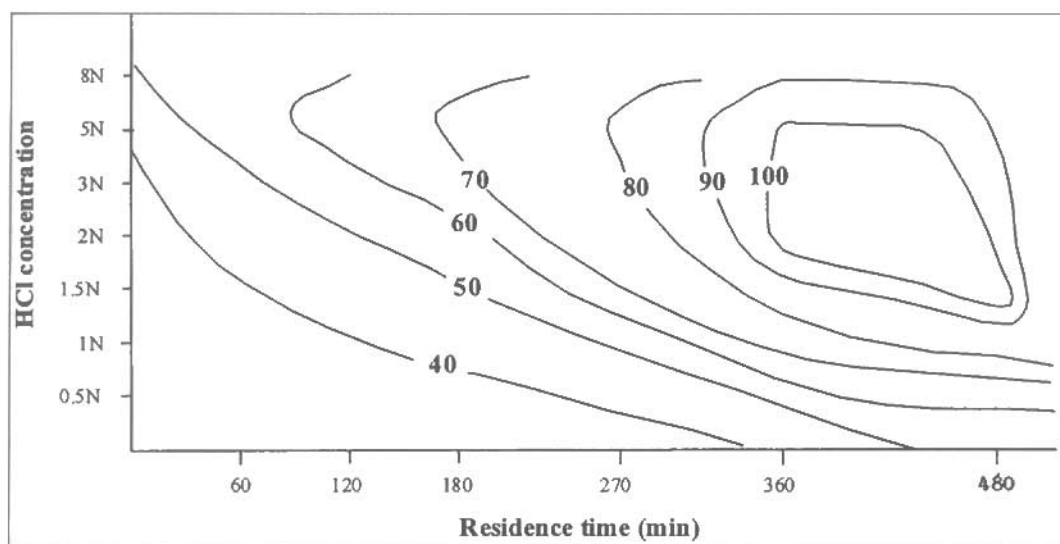


Fig. 2: STS (Surface area-Time-acid Strength) diagram for the Rema bentonite. The contours refer to the surface area (m^2/g) of the activated materials.

The CEC of the end products decreases continuously with increasing degree of activation (Table 2). Similar trends were observed for the Ankeria bentonite, while the Chios bentonite display an initial increase, followed by a decrease in more advanced treatments (Christidis et al., 1997a).

Table 2: Evolution of the CEC during acid activation of the Rema bentonite.

| Treatment | CEC (meq/100g) | Treatment | CEC (meq/100g) |
|-----------|----------------|-----------|----------------|
| Untreated | 52.8 | 5N/1h | 48.0 |
| 1N/1h | 47.0 | 2N/3h | 48.2 |
| 2N/1h | 49.0 | 2N/4h30' | 46.0 |
| 3N/1h | 48.0 | 2N/6h | 48.0 |

Bleaching capacity of the activated materials

The evolution of the bleaching capacity of the acid activated Rema bentonite is listed in Table 3 and is shown in Fig. 3.4. Although the smectite content is low, certain treatments yielded material with bleaching capacity exceeding 98% (shaded area in Fig. 4). Similar results were reported by Christidis et al., (1997a)

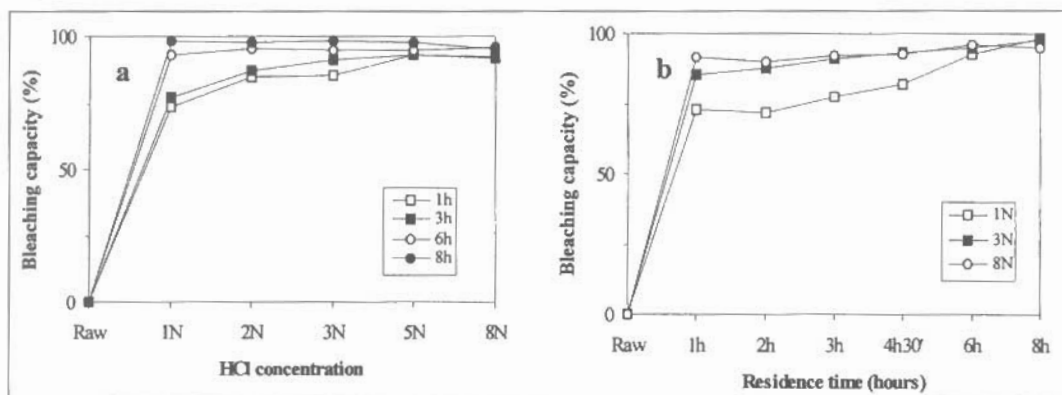


Fig. 3: Evolution of the bleaching capacity of the acid activated materials as a function of (a) acid strength and (b) of residence time

for the high grade Ankeria bentonite. However the material has to be treated with strong acid for considerable time in order to develop adsorptive properties. The bleaching capacity does not follow the variations of surface area with acid treatment (compare Fig. 2 and 4) in accordance with the findings of Morgan et al., (1985), and Zaki et al., (1986). Note that in Fig. 4 the combinations of acid strength and treating time which yielded optimum end products can be easily determined.

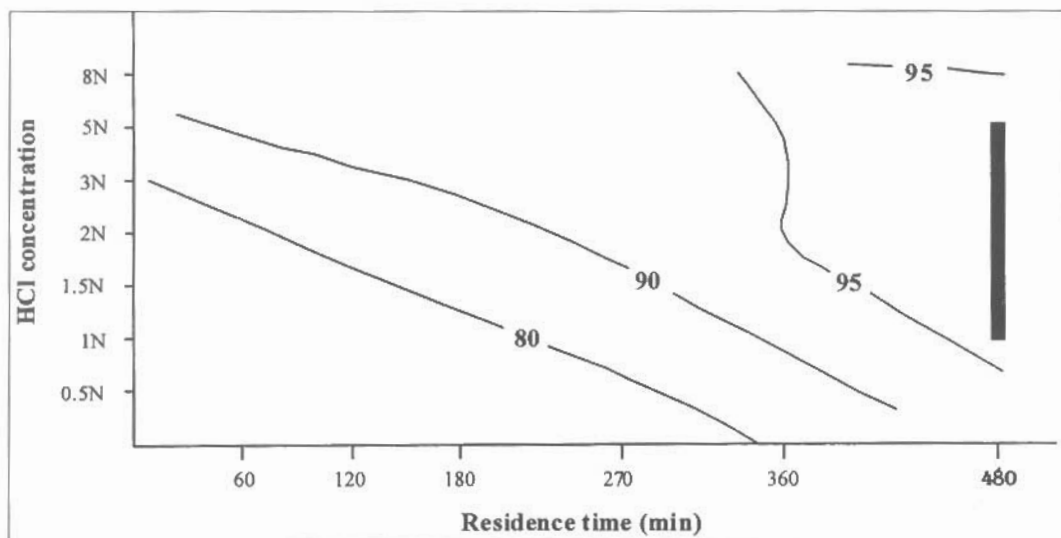


Fig. 4: Bleaching capacity of the Rema bentonite, in terms of % of β -carotene removed during bleaching of rapeseed oil. The shaded area corresponds to bleaching capacity greater than 98%

Table 3: Bleaching capacity and amount of β -carotene adsorbed from the acid activated Rema bentonite.

| Treatment | Bleaching capacity (%) | β -carotene adsorbed (10^{-4} moles/100g clay) | Treatment | Treatment Bleaching capacity (%) | β -carotene adsorbed (10^{-4} moles/100g clay) |
|-----------|------------------------|---|-----------|----------------------------------|---|
| 1h/1N | 73.3 | 8.0 | 4h30'/1N | 81.9 | 8.9 |
| 1h/2N | 84.9 | 9.3 | 4h30'/2N | 92.7 | 10.1 |
| 1h/3N | 85.3 | 9.3 | 4h30'/3N | 93.2 | 10.2 |
| 1h/5N | 92.8 | 10.1 | 4h30'/5N | 92.3 | 10.1 |
| 1h/8N | 91.5 | 10.0 | 4h30'/8N | 92.7 | 10.1 |
| 2h/1N | 72.0 | 7.9 | 6h/1N | 92.8 | 10.1 |
| 2h/2N | 84.9 | 9.3 | 6h/2N | 95.1 | 10.4 |
| 2h/3N | 87.5 | 9.5 | 6h/3N | 94.7 | 10.3 |
| 2h/5N | 93.1 | 10.2 | 6h/5N | 92.3 | 10.4 |
| 2h/8N | 89.7 | 9.8 | 6h/8N | 96.1 | 10.5 |
| 3h/1N | 77.3 | 8.4 | 8h/1N | 98.2 | 10.7 |
| 3h/2N | 87.0 | 9.5 | 8h/2N | 97.7 | 10.7 |
| 3h/3N | 91.1 | 9.9 | 8h/3N | 98.0 | 10.7 |
| 3h/5N | 92.7 | 10.1 | 8h/5N | 97.6 | 10.7 |
| 3h/8N | 92.3 | 10.1 | 8h/8N | 95.2 | |

The results for adsorption of β -carotene are illustrated in Table 3 and Fig. 5. The activated materials display a progressive increase in the adsorption of β -carotene with increasing both time and acid strength. It is obvious that adsorption of β -carotene i.e bleaching capacity, reaches a plateau and not a single

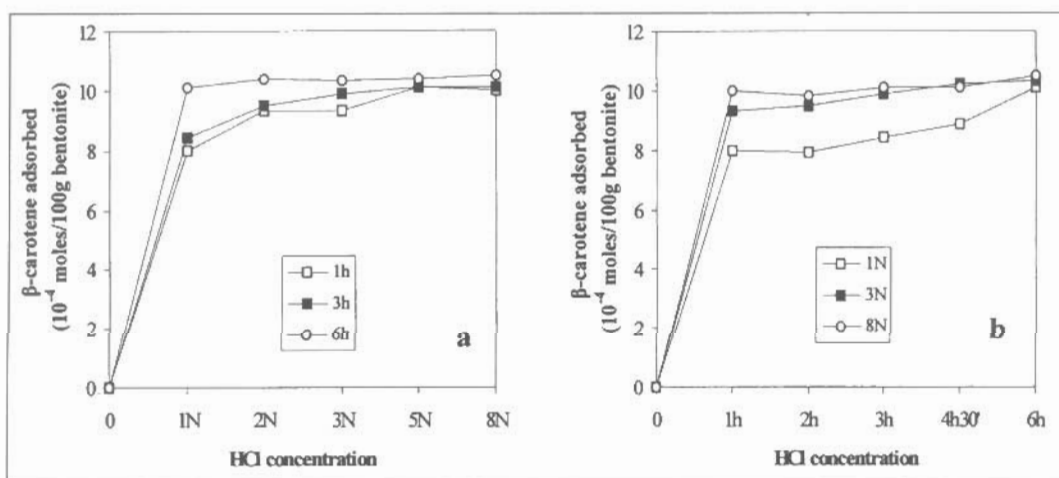


Fig. 5: Adsorption of β -carotene by the acid activated materials as a function (a) of acid strength and (b) of residence time.

maximum value. This plateau can be reached by using several combinations of acid strength and time during treatments. Although similar observations can be made for surface area, it is obvious that the latter is not associated with maximum adsorption of β -carotene therefore bleaching capacity (Fig. 2,4) in accordance with Morgan et al., (1985) and Zaki et al., (1986).

The degree of adsorption of β -carotene can also be observed in Fig. 6, in which the β -carotene absorption spectrum between 400 and 500nm is illustrated. The spectrum includes a maximum at 450nm between two shoulders. It can be observed that: a) absorption due to β -carotene is essentially minimized and b) the absorption maximum at 450nm is eliminated in the most prolonged treatments. This maximum appears only in the 4h30'/1N treatment, indicating that the bentonite is *under-activated* i.e. it has not acquired its maximum bleaching properties. Over-activated end products (c.f Christidis et al., 1997a), were not observed in this study.

4. DISCUSSION

This study showed that the Rema bentonite is activated only with prolonged treatments. In order to evaluate the activation process the material must be compared with the Chios bentonite which has a similar grade (Christidis et al., 1997a). Although the latter is activated with dilute acid and short treatments, the Rema bentonite is activated only at prolonged treatments with strong acids. Also, the performance of the Chios bentonite declines at prolonged treatments with strong acids. The observed differences depend on:

- i) the mineralogical composition of the bentonites
- ii) the mineral chemistry of the smectites present.

Both the Rema and the Chios bentonites contain abundant opal-CT while the latter contains also abundant carbonates, mainly dolomite. Dolomite dissolves in the initial stages of acid treatment causing effective enrichment of the smectite content, and thus an initial increase of the CEC (Christidis et al., 1997a). On the contrary, the Rema bentonite, which does not contain carbonates, displays a continuous decrease of the CEC, resulting from continuous dissolution of the smectite flakes and deposition of amorphous silica.

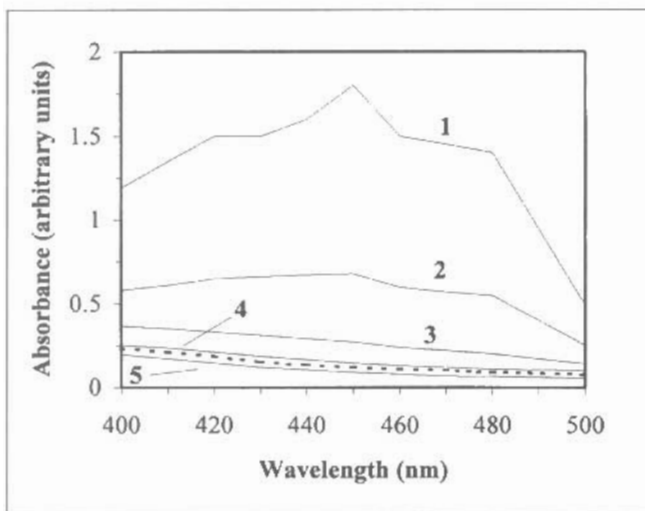


Fig. 6: Absorption spectra of β -carotene obtained from the crude rapeseed oil (1) and oil treated with acid of different acid strength for variable time. 2= 4h30'/1N, 3=6h/1N, 4=6h/8N, 5=8h/5N. The dashed line corresponds to FULLMONT AA.

The early dissolution of dolomite in the Chios bentonite increases the smectite-acid reaction area, enhancing activation. On the other hand, the presence of abundant opal-CT, which might impede acid attack by blocking part of the exposed octahedral sheet and the lack of carbonates, might be additional factors for the inferior

performance and the slow activation rate of the carbonate free-Rema bentonite.

The Rema bentonite consists of beidellite and Tatatilla-type montmorillonite (i.e Al-rich Mg-Fe-poor smectites), while Chios bentonite consists of Mg-rich Otay-type montmorillonite (Christidis & Dunham, 1997, Christidis et al., 1997). Χημική Βιβλιοθήκη Θεόφραστος Τμήμα Γεωλογίας, Α.Π.Θ.

1997a), suggesting that Mg-smectites might undergo structural changes faster than Al-rich ones. This is because substitution of Al by Mg and/or Fe lowers the stability of octahedral layer, rendering smectite prone to changes imposed by acid attack (Novak & Cícel 1978). Hence active sites might develop faster and the clay might be activated easier. It follows that the slow activation of the Rema bentonite which contains Al-rich smectites is not unexpected. On the other hand the possible role of tetrahedral Al on activation cannot be evaluated with the existing data. Christidis & Marcopoulos (1995) based on stoichiometric reactions have shown that beidellite is more prone to alteration than montmorillonite when attacked by acidic solutions. The behaviour of beidellite in acid activation is currently under thorough investigation.

The Rema bentonite might perform successfully as bleaching earth only after prolonged activation with strong acid. At these conditions it is possible that other reactions, like oxidation of β -carotene, might produce undesirable by-products. It is not believed that this bentonite will be an effective bleaching earth at least for crude rapeseed oil, because of the chemistry of smectites, its low grade, the presence of abundant opal-CT and the lack of carbonates.

5. CONCLUSIONS

1) Acid activation increased the surface area of the Rema bentonite up to a maximum after which it remained virtually constant. The increase of surface area is associated with changes in the smectite structure.

2) Acid activated materials produced from certain treatments can remove β -carotene from rapeseed oil.

3) Although surface area is an important feature of the activated materials, maximum bleaching capacity is not associated with maximum surface area.

4) Optimum decolourization properties are obtained with various combinations of acid strength and treating time.

5) The Rema bentonite display good bleaching properties only after prolonged treatment with strong acid due to its mineralogy and the chemistry of smectites. Therefore it is unlikely to be used successfully as a bleaching earth.

REFERENCES

- BRÜCKMAN, K., FIJAL, J., KLAPYTA, Z., WILTOWSKI, T. & ZABINSKI, W. (1976). Influence of different activation methods on the catalytic properties of montmorillonite. *Mineral. Polon.* 7, 5-14.
- CHRISTIDIS, G. & MARCOPOULOS, T. (1995) Mechanism of formation of kaolinite and halloysite in the bentonite deposits of Milos Island, Greece. *Chemie der Erde*, 55, 315-329.
- CHRISTIDIS, G., & DUNHAM, A.C. (1997) Compositional variations in smectites: Part II: alteration of acidic precursors, a case study from Milos Island, Greece. *Clay Miner.* 32, 253-270.
- CHRISTIDIS, G., SCOTT, P.W. & DUNHAM, A.C. (1997a) Acid activation and bleaching capacity of bentonites from the islands of Milos and Chios, Greece. *Appl. Clay Sci.* (in press)
- CHRISTIDIS, G., MARCOPOULOS, T., & FOSCOLOS, A. (1997b) Origin, physical and chemical properties of a bentonite deposit of Chios Island, Eastern Aegean, Greece. *Proc. 11th Int. Clay Conf. Ottawa Canada, Abstracts A16.*
- CLARKE, G.M. (1985). Special Clays. *Ind. Miner.* 216, 25-51.
- GRANQUIST, W.T. & SAMNER, G.G. (1959). Acid dissolution of a Texas bentonite. *Clays Clay Miner.* 6, 292-308.
- GRIFFITHS, J. (1990). Acid activated bleaching clays. What's cooking in the oil industry? *Ind. Miner.* 276, 55-67.
- KAVIRATNA, H., & PINNAVAIA, T. (1994) Acid hydrolysis of octahedral Mg²⁺ sites in 2:1 layered silicates: An assessment of leach attack and gallery access mechanisms. *Clays Clay Miner.* 42, 717-723.

- KHEOK, S.C. & LIM, E.E. (1982). Mechanism of palm oil bleaching by montmorillonite clay activated at various acid concentrations. *J. Am. Oil Chem. Soc.* **59**, 129-131.
- KHOO, L.E., MORSINGH, F. & LIEW, K.Y. (1979). The adsorption of β -carotene I. by bleaching earths. *J. Am. Oil Chem. Soc.* **56**, 672-675.
- KOLTA, G.A., NOVAK, I., SAMIR, Z. EL-T. & KAMILIA, A. EL-B. (1975). Evaluation of bleaching capacity of acid-leached Egyptian bentonites. *J. Appl. Chem. Biotechnol.* **26**, 355-360.
- MORGAN, D.A., SHAW, D.B., SIDEBOTTOM, T.C., SOON, T.C. & TAYLOR, R.S. (1985). The function of bleaching earths in the processing of palm, palm kernel and coconut oils. *J. Am. Oil Chem. Soc.* **62**, 292-299.
- NOVAK, I. & GREGOR, M. (1969). Surface area and decolourizing ability of some acid-treated montmorillonites. *Proc. Int. Clay Conf. Tokyo*, 851-857.
- NOVAK, I. & CICEL, B. (1978). Dissolution of smectites in hydrochloric acid: II. Dissolution rate as a function of crystallochemical composition. *Clays Clay Miner.* **26**, 341-344.
- ODOM, I.E. (1984). Smectite clay minerals: properties and uses. *Phil. Trans. R. Soc. Lond.* **A311**, 391-409.
- O'DRISCOLL, M. (1988). Bentonite: overcapacity in need of markets. *Ind. Miner.* **250**, 43-67.
- OSTHAUS, B. (1956). Kinetic studies on montmorillonites and nontronite by the acid-dissolution technique. *Clays Clay Miner.* **4**, 301-321.
- RHODES, C.N., & BROWN, D.R. (1992) Structural characterization and optimization of acid-treated montmorillonite and high-porosity silica supports for $ZnCl_2$ alkylation catalysts. *J. Chem. Faraday Trans.* **88**(15), 2269-2274.
- RICHARDSON, L.L. (1978). Use of bleaching clays in processing edible oils. *J. Am. Oil Chem. Soc.* **55**, 777-780.
- RUPERT, J.P., GRANQUIST, W.T., & PINNAVAIA, T.J (1987). Catalytic Properties of Clay Minerals. Pp 275-318 in: *Chemistry of Clays and Clay Minerals* (A.C.D. Newman editor), Mineralogical Society, London.
- SIDDIQI, M.K.H. (1968). *Bleaching earths*. Pergamon Press, Oxford, Pp 32-55.
- SRASRA, E., BERGAYA, F., VAN DAMME, H. & ARGUIB, N.K. (1989). Surface properties of an activated bentonite-Decolourization of rape-seed oil. *Appl. Clay Sci.* **4**, 411-421.
- STOCH, L., BAHRANOWSKI, K., BUDEK, L. & FIJAL, J. (1977). Bleaching properties of non-bentonitic clay materials and their modification. *Mineral. Polon.* **8**, 31-49.
- TKAC, I., KOMADEL, P., & MÜLLER, D. (1994). Acid treated montmorillonites-a study by ^{29}Si and ^{27}Al MAS-NMR. *Clay Miner.* **29**, 11-19.
- ZAKI, I., ABDEL-KHALIK, M. & HABASHI, G.M. (1986). Acid leaching and consequent pore structure and bleaching capacity modifications of Egyptian clays. *Colloids & Surfaces* **17**, 241-249.