ELSEVIER

Applied Clay Science 12 (1998) 419–429

APPLIED CLAY SCIENCE

The use of sepiolite for decolorization of sugar juice

Halil İbrahim Ünal *, Baki Erdoğan

Chemistry Department, Science and Arts Faculty, Gazi University, Teknikokullar, 06500 Ankara, Turkey

Received 20 August 1996; revised 10 September 1997; accepted 15 September 1997

Abstract

Brown, beige and dolomitic (white) sepiolites from the area around Ankara–Polatlı–Türktaciri village were tested for the decolorization of sugar solutions at different pH and temperature. The decolorizing effect of various quaternary ammonium salts in combination with the sepiolites was also investigated. The sepiolites were characterized by its zeta potential, filtration capacity, particle size and specific surface area. Before and after the treatment of sepiolite with the sugar juice, the sepiolites were investigated by DTA/TG and SEM. The brown sepiolite had a more developed fiber structure, smaller particle size when dispersed in water, a larger surface area and a greater decolorizing activity than the other samples. Addition of small quantities of quaternary ammonium salts to the brown sepiolite improved the removal of sugar juice color by up to 80%. © 1998 Elsevier Science B.V.

Keywords: sepiolite; industrial applications; decolorization of sugar juice

1. Introduction

Sepiolite has attracted remarkable attention by its sorptive, rheological and catalytic properties, and the use of sepiolitic clays is expanding (Bennet, 1982; Sarıkaya et al., 1987; Inagahi et al., 1990; Sugiura et al., 1991; Daza et al., 1991). In Turkey, the exploration of deposits at the Sivrihisar, Polatlı and Eshişehir area has been initiated (Inukai et al., 1994). These products were used for a long time for meerschaum pipe manufacture and pet litter. The main purpose of this study is to establish new applications of sepiolite in industry.

---

[*] Corresponding author.

PII S0169-1317(97)00023-9

The quality and cost of the production of crystal sugars depend on the color and turbidity of the juices obtained from sugar beet. Sugar beet contains numerous organic and inorganic substances besides sucrose. During the sugar production in a factory these substances are transferred to the sugar juice and affect the sugar production. They especially increase the molasses formation and give rise to colored sugar. Color is a very important criterion in the sugar production. Bentonite type clays are widely used for decolorization of sugar juice (Akay, 1994). Sugar industry is forced to investigate other alternatives due to the expensive working conditions of ion-exchange resins (Novontony, 1985). Sepiolite can adsorbs positively charged and polarizable colloidal particles and molecules (Bennet, 1982).

In this study, an attempt has been made to establish the optimum conditions for the decolorization of sugar juice by three types of sepiolites (beige, white (dolomitic), brown) as well as in combination with quaternary ammonium salts.

2. Experimental methods

2.1. Materials

The sepiolites used were provided by the General Directorate of Mineral Research and Exploration Institute of Ankara. The samples were of 32, 60, 100 and 200 mesh particle size, and had previously been characterized (Fukushima and Shimosaka, 1987; Irkeç, 1988). Quaternary ammonium salts [methyltrioctaylamoniumchloride, (quartamine THL), tributylmethylamoniumchloride, alkyltrimethylamoniumchloride and dialkyldimethylamoniumchloride] were obtained from Kao Corporation S.A (Japan). The sepiolites and quaternary ammonium salts were used without any further purification. The dry sepiolites were directly added to the sugar juice.

2.2. Characterization of the sepiolites

2.2.1. Measurements of the zeta-potential

The Zetameter system 3.0 (Zetameter) was used to determine the zeta-potential of the 200 mesh sepiolites. The measurements were based on the microelectrophoresis. A total of 10 g of each sepiolite sample was mixed with 10 g of sodium chloride. Distilled water was added into the sample to give 1 l of the suspension. The suspension was shaken by a shaking machine for 1 h. For measuring the mobility 10 ml from the stock suspension were diluted with distilled water to 1 l. This suspension was allowed to stand for 1 h before being used at room temperature for the measurement. 10 ml of sample was taken from the above suspension and put into the electrophoresis cell. Electrodes (molybdenum cylinder anode and platinum rod cathode) were placed in each end of the cell and were connected to a power supply (20–300 V). 100 V was automatically chosen by the zetameter during the measurements. Zeta potentials were calculated from the mobility data by the Helmholtz–Smoluchowski equation via a computer software.

2.2.2. Filtration measurements

Filtration measurements were carried out under 6.89×10^5 N m^{-2} pressure for 30 min at the Turkish Standardization Institute according to TSE (1992).

2.2.3. Particle size measurements

The particle size of the samples was determined by Fraunhofer scattering (Malvern Mastersizer E, version 1.2b). The samples were dispersed in distilled water and stirred at a constant temperature of 20°C. The data collected was evaluated by the Malvern software computer according to Fraunhofer diffraction theory.

2.2.4. Surface area measurements

Specific surface areas were determined by N_2 adsorption, using the BET-method (Quantochrome Monosorb surface area analyzer). The gas mixture used was 30% nitrogen and 70% helium. Sepiolite samples were dried in a vacuum oven at 105°C before the surface area measurements were carried out. A cell containing the samples was dipped into a liquid nitrogen container (Dewar flask) to provide the adsorption of nitrogen gas onto the sepiolites. The Dewar flask was removed automatically when the adsorption was completed. Hot air was blown into the sample cell for the desorption of adsorbed nitrogen. The area of desorbed nitrogen was obtained from the amount of nitrogen desorbed.

2.2.5. Scanning electron microscopy

Scanning electron micrographs were obtained using a Topcon abt-60. Samples were coated with gold by a Polaron SC 502 sputter coater for examination.

2.2.6. Thermal analysis

A Rigaku thermal analyzer Tas-100 (version 2.22E2) was used for differential and thermogravimetric (DTA/TG) analysis. The working atmosphere was air and the heating rate was 10°/min.

2.3. Decolorization measurements

To investigate the effect of the quantity of sepiolite on the decolorization of the sugar juice, a series of experiments was carried out with different sepiolite samples. A stock sugar solution was freshly prepared for each run. The amount of brix (dry matter content of sugar juice) was determined by a Carl Zeiss Abbe refractometer. 100 ml samples were taken from the stock sugar solution and heated to 80°C. Various amounts of sepiolite were added. The dispersions were stirred for 20 min and filtered through a Millipore blue band filter paper. The filtrate was allowed to cool to 20°C and its absorbance was measured at 420 nm with a Spectronic 2000 spectrophotometer.

Decolorization of sugar juice, based on spectrophotometric absorbance measurements, are given as ICUMSA units (International Commission of Uniform Methods of Sugar Analysis, ICUMSA, 1978). For sugar technology the optimum wavelength of 420 nm is recommended by ICUMSA. Studies on this wavelength is called ICUMSA method 4, which is used in most countries for the measurement of color of molasses of raw sugar, white sugar, sugar juice and all other sugar solutions related to the sugar industry. The ICUMSA color was calculated using the following equation:

$$\text{ICUMSA 4} = 1000(A/bC) \text{ or } 1000(-\log T)/bC,$$

where A is the absorbance, T the transmittance, C the solid (or dry substance) content in g/ml, b is the path length of light in cm.

The degree of decolorization was calculated as follows:

$$\text{Decolorization (\%)} = 100 - 100(\text{ICUMSA}_{\text{filtrate}})/(\text{ICUMSA}_{\text{sugarjuice}})$$

An amount of 2.0 g of each quaternary ammonium salt was dissolved in 100 ml distilled water. The decolorization effect was measured after adding quaternary ammonium salts at certain concentrations (ppm) to the sugar juice.

3. Results and discussion

The chemical composition of the raw sepiolite samples were determined at the General Directorate of the Mineral Research and Exploration Centre of

Table 1
Chemical and mineral compositions of brown, beige and white sepiolites (in wt%)

	Brown	Beige	White
SiO_2	50.05	40.80	15.10
Al_2O_3	1.17	2.34	1.25
Fe_2O_3	0.49	0.79	0.31
TiO_2	0.12	0.12	0.12
CaO	6.00	10.00	22.70
MgO	25.50	25.00	23.00
Na_2O	0.05	< 0.01	0.08
K_2O	0.17	0.31	0.11
Loss on ignition	16.86	21.36	37.65
Dolomite	< 10.00	< 30.00	75.00
Sepiolite	90.00	70.00	25.00

Table 2
Zeta potential of sepiolites

Sepiolite	Number of measurements	Average zeta measurements potentials (mV)
Beige	20	-3.59 ± 0.34
White	20	-3.45 ± 0.25
Brown	20	-3.30 ± 0.21

Ankara (Table 1). White sepiolite is very rich in CaO, poor in SiO_2 and contains 75 wt% dolomite. Brown sepiolite contains less than 10 wt% dolomite. Beige sepiolite consists of 30 wt% dolomite and approximately 70 wt% sepiolite (determined from XRD patterns).

The zeta potential of the three sepiolites is very small and insufficient for the particles to remain suspended for a long time (Table 2). This is due to the considerable amount of calcium and magnesium ions provided by the admixed dolomite.

Particle sizes obtained from Fraunhofer scattering agree, within experimental error, with the corresponding mesh sizes. As seen from Table 3 the finer particles of beige and white sepiolite particles were larger than the corresponding mesh sizes, due to the agglomeration of particles when dispersed in water. On the other hand, the sizes of the larger particles of brown sepiolite were smaller than those expected. This may be attributed to disaggregation in water as a consequence of the lower dolomite content. SEM also showed the brown sepiolite to have a more developed fiber structure.

Table 3
Particle size distribution of sepiolites

Type of sepiolite	Particle size (mesh)	Particle size (μm)	Measured particle size (μm)* (diameter)
Brown	32	500	354
	60	250	241
	100	150	124
	200	74	74
Beige	32	500	508
	60	250	387
	100	150	207
	200	74	83
White	32	500	514
	60	250	347
	100	150	155
	200	74	61

* Diameters of the 90% of sepiolite particles dispersed in water.

Table 4
Surface area measurements of sepiolites

Type of sepiolite	Particle size (mesh)	Surface area (m^2/g)
Beige	32	163
	60	168
	100	174
	200	187
Brown	32	269
	60	271
	100	272
	200	275

The specific surface areas of brown sepiolite is larger than of beige sepiolite which is in good agreement with the decolorization and SEM results (Table 4).

For industrial application, sepiolites should present a very good filtration capacity. The filtration capacity of sepiolites varying in particle size is given in Table 5. In contrast, the bentonite type of clays form a gel and their filtration capacity is around 15–20 ml. White and brown sepiolite had the highest filtration capacity and, therefore, are suitable for industrial use.

Scanning electron microscopy (SEM) showed that brown sepiolite has a fiber structure (Fig. 1a). The structure is regular and massive and the length of fibers is approximately 6–7 μm. SEM micrograph of sugar juice treated brown sepiolite (Fig. 1b) showed that the fibrous structure was not distorted. The white masses appearing between the sepiolite fibers were glucose particles and impurities.

Table 5
Filtration values of sepiolites

Sepiolite	Particle size (mesh)	Filtration (ml)
Beige	32	75
	60	71
	100	68
	200	68
White	32	190
	60	187
	100	180
	200	150
Brown	32	175
	60	172
	100	170
	200	168

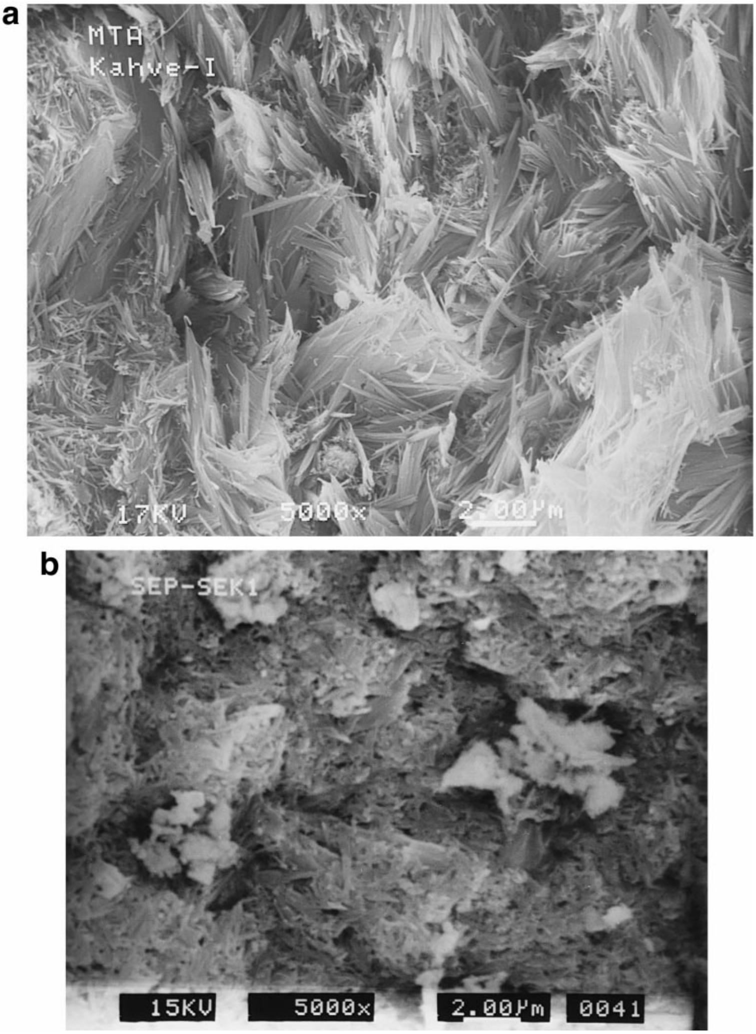

Fig. 1. Scanning electron micrographs of (a) brown sepiolite (200 mesh); (b) sugar juice treated brown sepiolite.

The decolorizing activity of brown and beige sepiolite increased with the amount used (Fig. 2). White sepiolite showed poor decolorizing effect due to the high dolomite content (Inukai et al., 1994).

Sepiolites are better decolorizing agents than bentonites. If sepiolites were used alone, without adding any quaternary ammonium salts, decolorization was 38% (Fig. 2), which is insufficient for industrial uses. Addition of quaternary ammonium salts, increases the decolorizing activity. Among the examined quaternary ammonium salts, quartamine THL was most effective (Fig. 3). With 800 ppm quartamine THL decolorization of 80% was obtained. This is a

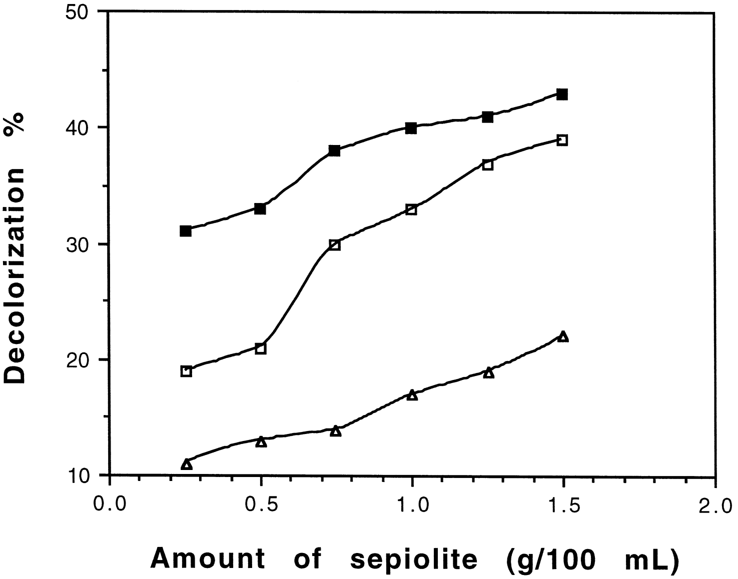

Fig. 2. Decolorization activity of sepiolite samples. Particle size: 200 mesh, temperature: 80°C, (■) brown, (□) beige and (△) white sepiolite.

reasonable result for practical use. The quaternary ammonium ions are adsorbed by the negative surface of the sepiolite, and flocks are formed which remove the pigment molecules of sugar juice. With increasing temperature the decoloriza-

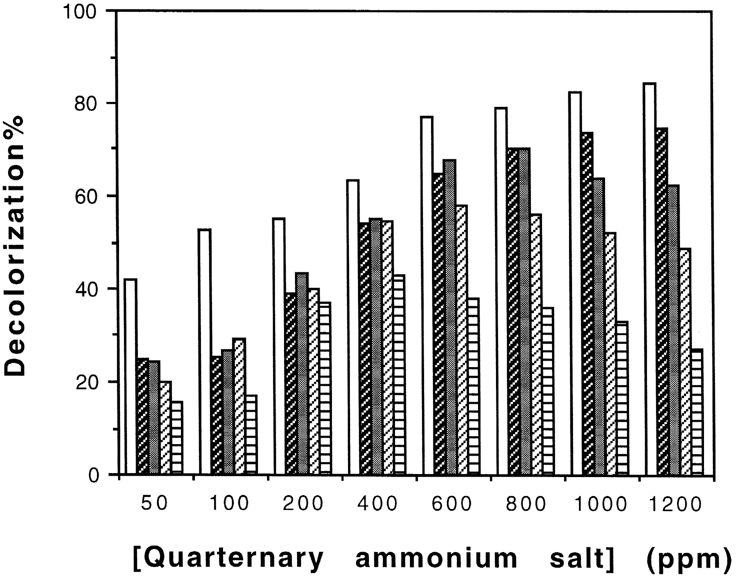

Fig. 3. Decolorization by sepiolite in the presence of quartamine THL. Amount of brown sepiolite (200 mesh) in 100 ml sugar juice: 0.75 g (□), 0.50 g (dark diagonal stripes), 0.30 g (hatched), 0.20 g (light diagonal stripes) and 0.10 g (light horizontal stripes).

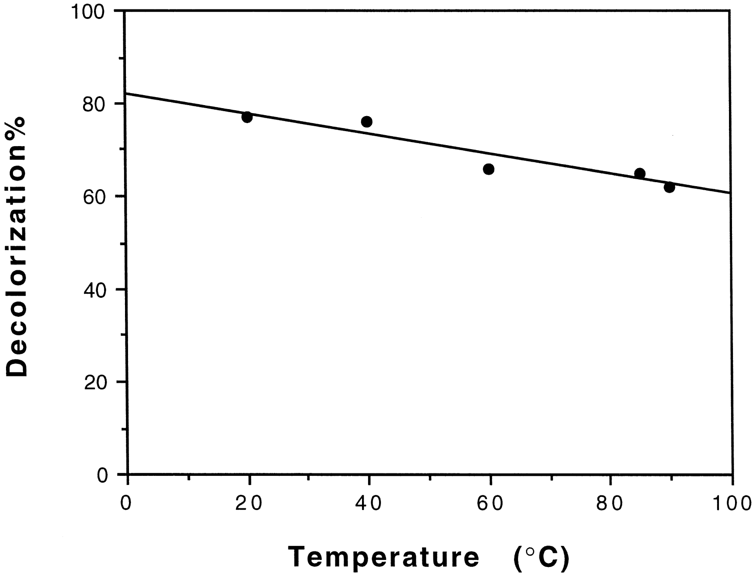

Fig. 4. The change of decolorization with temperature. Brown sepiolite, 200 mesh; 800 ppm quartamine THL; pH = 7.21.

tion of sugar juice is slightly reduced (Fig. 4). Decolorization is also influenced by the acidity of the medium (Fig. 5). With decreasing pH the decolorizing activity is enhanced.

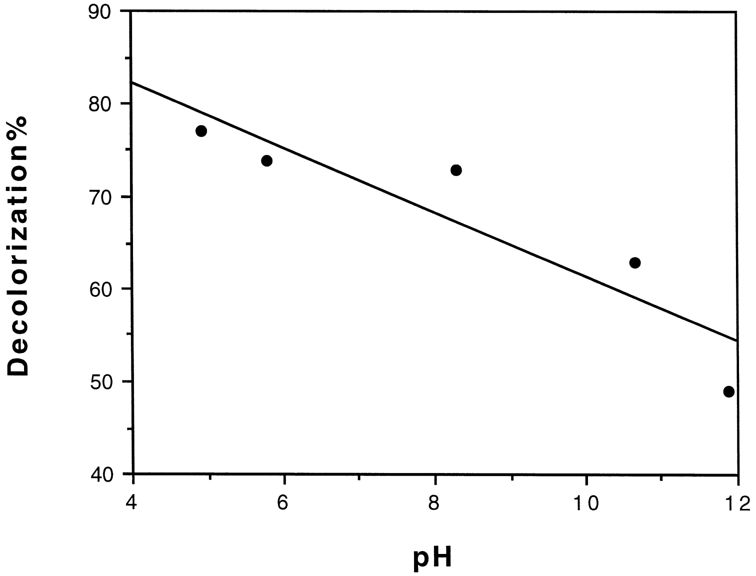

Fig. 5. Effect of pH on decolorization at 80°C; 800 ppm quartamine THL; brown sepiolite 200 mesh.

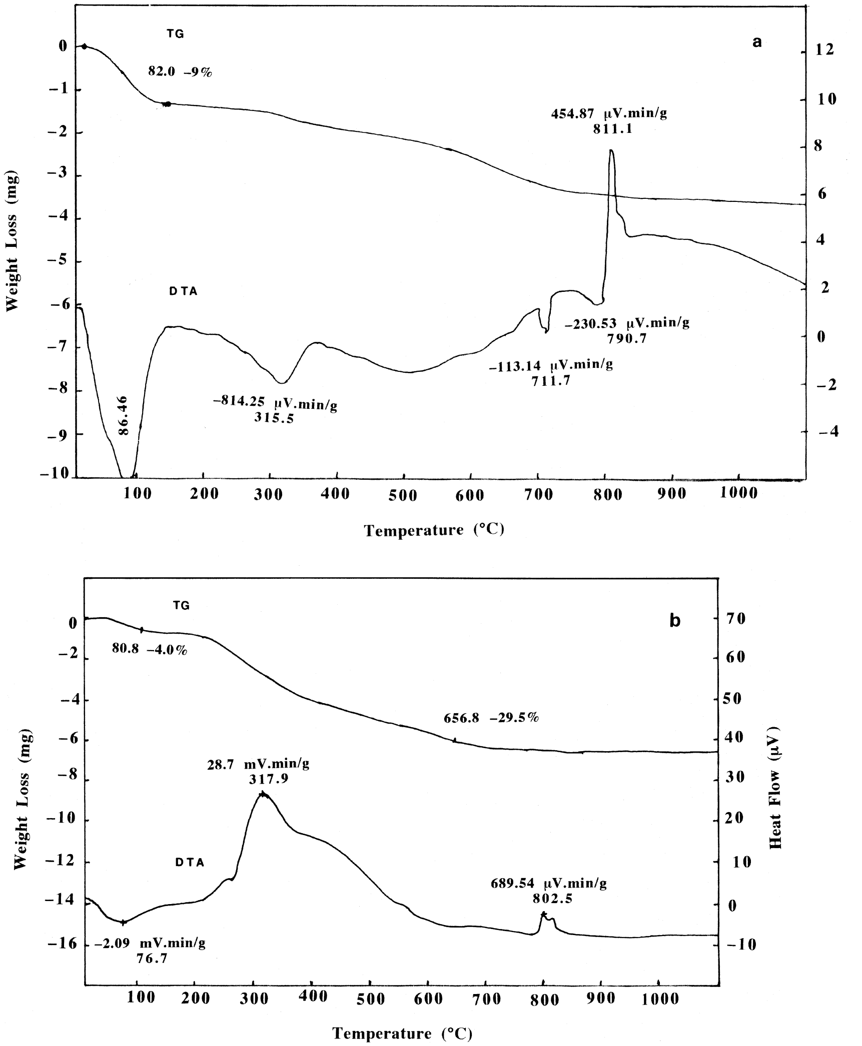

Fig. 6. DTA/TG thermograms of (a) brown sepolite (200 mesh); (b) brown sepiolite treated with sugar juice.

The DTA/TG thermograms for the brown sepiolite are given in Fig. 6. The endothermic peak at 30–140°C corresponds to 9% loss of weight; two endothermic peaks at 230–360°C are due to zeolitic loss of water; two other endothermic peaks at 700–800°C result from water desorption from OH groups. Exothermic recrystallization of sepiolite takes place at 811°C. The DTA curve for the brown sepiolite after treatment with the sugar juice showed an additional exothermic peak at 200–600°C (Fig. 5b), which is due to thermal degradation of glucose itself.

4. Conclusions

Sepiolite is an effective decolorizing and clarifying agent. Brown sepiolite showed the highest activity with 80% decolorization when used together with quaternary ammonium salts.

References

Akay, Y., 1994. Removal of turbidity and color of sugar containing liquids by flocculation and filtration. M.Sc. thesis, Gazi University, Ankara.

Bennet, M.C., 1982. The taloflock/taloflate process for simultaneous decolorization and clarification of refinery liquor. In: Baikow, Y.E. (Ed), Manufacture and Refining of Raw Cane Sugar. Elsevier Scientific Publishing Company, Amsterdam, pp. 339–342.

Daza, L., Mendioroz, S., Pajares, J.A., 1991. Mercury adsorption by sulfurized fibrous silicates. Clays Clay Miner. 39 (1), 14–21.

Fukushima, Y., Shimosaka, K., 1987. Sepiolite deposit in central Anatolia. Summaries Proc. 6th Meeting of the European Clay Groups, Sevilla, pp. 226–228.

ICUMSA, 1978. Method 4 (official) for the determination of color of sugar in solution. International Commission for Uniform Methods of Sugar Analysis, pp. 343–344.

Inagahi, S., Fukushima, Y., Doi, H., Kamigaito, O., 1990. Pore size distribution and adsorption selectivity of sepiolite. Clay Miner. 25, 99–105.

Inukai, K., Miyawaki, R., Tomura, S., Shimosaka, K., Irkeç, T., 1994. Purification of Turkish sepiolite through hydrochloric acid treatment. Appl. Clay Sci. 9, 11–29.

Irkeç, A.T., 1988. General geological setting and character of Turkish sepiolite deposits. Acta Miner. Petrogr. Szeged 29, 95–106.

Novontony, C.S., 1985. Ion exchange. In: Chen, J.C.P. (Ed), Cane Sugar Handbook. Wiley Interscience Publication, New York, pp. 591–598.

Sarıkaya, Y., Biçer, N., Biçer, C., Ceylan, H., Bozdoğan, İ., 1987. Effect of heat activation on the adsorptive properties of sepiolite having dolomite, 3rd National Clay Symp., 21–27 September, Ankara, pp. 221–227.

Sugiura, M., Hayashi, H., Suzuki, T., 1991. Adsorption of ammonia by sepiolite in ambient air. Clay Sci. 8, 87–100.

TSE, 1992. Bentonite as drilling fluid material (TS 977), Turkish Standardization Institute, Ankara.