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ScienceDirect
Food Chemistry 105 (2007) 156–163
Food Chemistry
www.elsevier.com/locate/foodchem

The effect of sulphuric acid activation on the crystallinity, surface area, porosity, surface acidity, and bleaching power of a bentonite

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Received 6 December 2006; received in revised form 22 March 2007; accepted 26 March 2007

Abstract

The Hançılı (Keskin, Ankara, Turkey) bentonite was activated with H_2SO_4 by dry method at 97 °C for 6 h to obtain optimum parameters for imparting a maximum bleaching power towards soybean oil. The H_2SO_4 content in dry bentonite-acid mixture was changed between 0% and 70%. The natural and activated samples were examined by X-ray diffraction (XRD), N_2 adsorption–desorption, and *n*-butylamine adsorption (from the solution in cyclohexane). The specific surface area (*S*), specific micro–mesopore volume (*V*), mesopore size distribution (PSD), and surface acidity (n_m) of the samples were determined. The bleaching power (BP) of each sample for alkali-refined soybean oil was determined. The *S*, *V*, n_m, and BP increase after activation at various acid contents up to 40% H_2SO_4 without any considerable change in crystal structure of the smectite. The BP is controlled more by the PSD rather than other adsorptive properties of the bleaching earth. The optimum parameters for activation to obtain maximum bleaching power, are $H_2SO_4\% = 50$–60, $S = 250$–$230\ m^2\ g^{-1}$, $V = 0.46$–$0.47\ cm^3\ g^{-1}$, $n_m = 9.0 \times 10^{-4}$–$8.4 \times 10^{-4}\ mol\ g^{-1}$ and PSD mainly distributed between 1.4 and 6.0 nm.

Keywords: Acid activation; Bentonite; Bleaching; Porosity; Surface acidity; Surface area

1. Introduction

Besides numerous industrial application areas, bentonites and their major clay mineral smectites have been used in food technology such as bleaching earth, clarification of beer and wine, animal feed bond, and food additives (Grim & Güven, 1978; Murray, 1991, 2000). Bentonites may also contain other clay- and non-clay minerals as impurities. Smectites generally are 2:1 layered, hydrated aluminum silicates. Bentonites are treated by the inorganic acids such as HNO_3, HCl and H_2SO_4 to remove some of the impurities and thereby to obtain more adsorptive materials (Heyding, Ironside, Norris, & Pryslazniuk, 1960; Komadel, 2003; Komadel et al., 1996; Komadel, Schmidt, Madejová, & Čičel, 1990; Mills, Holmes, & Cornelius, 1950; Van Rompaey, Van Ranst, De Coninck, & Vindevogel, 2002). Due to their widespread use in edible oil bleaching, the activated bentonites are called as bleaching earths (Beneke & Lagaly, 2002; Boukerroui & Ouali, 2000; Christidis, Scott, & Dunham, 1997; Griffiths, 1990; Siddiqui, 1968; Tsai, Chang, Lai, & Lo, 2005).

Crude edible oils obtained by solvent extraction or compression from plants such as soybean, safflower, sunflower, corn, cottonseed, rapeseed, mustard seed, sesame, palm, peanut, coconut and olive, can be processed by chemical or physical refining techniques (Mounts, 1981). The conventional chemical technique consists of water or acid degumming, caustic refining, deodorization, and winterization steps. Besides color pigments, other impurities such as soap, sulphur, phosphates, trace metals, and oxidation products are removed from the alkali-refined oils by bleaching (Falaras, Kovanis, Lezou,

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doi:10.1016/j.foodchem.2007.03.060

& Seiragakis, 1999; Kheok & Lim, 1982; Morgan, Shaw, Sidebottom, Soon, & Taylor, 1985; Oboh & Aworh, 1988; Rossi, Gianazza, Alamprese, & Stanga, 2003; Temuujin et al., 2006; Zschau, 2001). Bleaching is based on the physical adsorption, chemical adsorption, ion exchange, and chemical decomposition of coloring organic pigments and other impurities on the bleaching earth.

Like other adsorptive solids, the pores of a bleaching earth may be micropores (width <2 nm), mesopores (width 2–50 nm) and macropores (width >50 nm) (Gregg & Sing, 1982). The radius of a pore, assumed to be cylindrical, can be taken as half the pore width. The total volume of pores in 1 g of solid is defined as the specific pore volume (V). The area of the inner and outer walls of the pores located intra- and interparticles in 1 g solid is taken as the specific surface area (S). The adsorptive surface originates from the micro- and mesopores. The contribution of macropores on the surface area is negligible. Furthermore, bleaching earths behave as solid acids. Brönsted and Lewis acid sites on their surfaces are proton donors and electron pair acceptors, respectively (Brown & Rhodes, 1997a; Frenkel, 1974; Kumar, Jasra, & Bhat, 1995; Noyan, Önal, & Sarıkaya, 2006; Walling, 1950). The molar number of acid sites in 1 g solid is defined as surface acidity (n_m). The acid strength of a surface can be characterized by the equilibrium constant (K) of its neutralization reaction with a weak base such as ammonia, and amines (Benesi, 1956, 1957; Brown & Rhodes, 1997b; Loeppert, Zelazny, & Volk, 1986).

Bleaching power is dependent on the surface area, surface acidity, catalytic activity, porosity and pore size distribution of the bleaching earth (Boki, Kubo, Wada, & Tamura, 1992; Boki, Kubo, Kawasaki, & Mori, 1992; Breen, Zahoor, Madejová, & Komadel, 1997; González-Paradas, Villafranca-Sánchez, & Gallego-Campo, 1993; Önal, submitted for publication; Önal, Sarıkaya, Alemdaroğlu, & Bozdoğan, 2002; Srasra, Bergaya, Van Damme, & Ariguib, 1989; Vicente-Rodriquez, Suarez, Lopez-González, & Bánares-Munoz, 1996). These physicochemical properties of bleaching earths change depending on the mineralogical and chemical composition of the activated bentonite, type and concentration of the inorganic acid, used in the process and also temperature and time of activation.

The bleaching power of an acid-activated bentonite is generally examined on the basis of the β-carotene and chlorophyll adsorption capacities (González-Paradas, Villafranca-Sánchez, Socias-Viciana, & Gallego-Campo, 1994; Khoo, Morsingh, & Liew, 1979; Liew, Tan, Morsingh, & Khoo, 1982; Mokaya, Jones, Davies, & Whittle, 1993; Sarıer & Güler, 1988, 1989). The adsorption mechanism has been discussed by using both the Langmuir and Freundlich isotherms (Sabah, Çınar, & Çelik, 2007; Topallar, 1998; Tsai, Chang, Ing, & Chang, 2004; Teng & Lin, 2006). The kinetics of the bleaching process has been examined on the basis of a first order reaction model applied to chemical reactions (Brimberg, 1982; Christidis & Kosiari, 2003).

Although several workers mentioned above have made extensive studies on the numerous properties of bleaching earths and bleaching processes, no report specifically concentrated on the surface properties of bleaching earths has yet appeared. The aim of this study is to examine of the bleaching power of some H_2SO_4-treated bentonite samples by making use of surface area, surface acidity, porosity and mesopore size distribution parameters.

2. Materials and methods

2.1. Materials

A calcium-rich bentonite (CaB) sample from the Hançılı bed (Keskin, Ankara, Turkey) was used in the experiments. The effects of heating and acid activation on some physicochemical properties of this material were previously investigated (Noyan, Önal, & Sarıkaya, in press, submitted for publication). The bulk chemical analysis of the bentonite (mass %) is SiO_2, 60.85; TiO_2, 0.85; Al_2O_3, 16.50; Fe_2O_3, 5.74; MgO, 2.71; CaO, 2.37; Na_2O, 1.53; K_2O, 0.83 and loss on ignition (LOI), 8.40. The H_2SO_4 (98%, $d = 1.98$ g cm^{-3}) and other chemicals used are of analytical grade and were supplied from Merck Chemical Company. The bentonite was ground to pass through a 0.074 mm (200 mesh) sieve, dried at 105 °C for 24 h, and stored in tightly closed plastic bottles for use in the experiments. Alkali-refined soybean oil used in the bleaching experiments was supplied from a vegetable oil plant (Marsa, İstanbul, Turkey).

2.2. Acid activation

Eleven samples, each having a mass of 40 g, were weighed from the dried bentonite powder. The samples were activated with H_2SO_4 by dry method (Heyding et al., 1960). The content of H_2SO_4 in dry bentonite-acid mixture was changed between 0% and 70% by mass. Acid content was increased in smaller increments around 40% H_2SO_4, the likely optimum rate by experience. Eleven gel-like mixtures were prepared by adding the concentrated acid having calculated amounts of H_2SO_4. Acid activation was conducted by heating the mixtures in an oven at 97 °C for 6 h. Each activated sample was suspended in water, and centrifuged. Obtained precipitate was washed with distilled water until it was free from SO_4^{2-} against 5% $BaCl_2$ solution. After drying at 105 °C for 4 h, the activated samples were stored in tightly closed plastic bottles. In this way, eleven bleaching earths were obtained. Prior experience (Noyan et al., 2006; Önal et al., 2002; Önal & Sarıkaya, 2007) with same and other bentonites indicates that the physicochemical properties of acid treated bentonite samples do not differ appreciably from batch to batch. Therefore, acid treatment procedures were done once.

2.3. Instrumentation

The X-ray diffraction (XRD) patterns of natural and acid activated samples were recorded from random mounts prepared by glass slide method using a Rikagu D-Max 2200 Powder Diffractometer, operating at 40 kV and 30 mA, using Ni-filtered CuK_α radiation having 0.15418 nm wavelength, at a scanning speed of $2°2\theta\ min^{-1}$ (Moore & Reynolds, 1997).

The adsorption and desorption isotherms of N_2, at liquid N_2 temperature, on the natural and acid activated samples were determined by a volumetric adsorption instrument of pyrex glass connected to a high vacuum system (Sarıkaya & Aybar, 1978; Sarıkaya, Önal, Baran, & Alemdaroğlu, 2000; Sarıkaya, Sevinç, & Akınç, 2001). Before measurements, the samples were outgassed at 150 °C for 4 h under a vacuum of 10^{-3} mm Hg. The technique of gas adsorption manometry was used for the determination of the adsorbed amount (Rouquerol, Rouquerol, & Sing, 1999; Sing, 2001). This point-by-point procedure is based on the measurement of the gas pressure in a calibrated constant volume at a known temperature. Pre-calibrated dosing volume at dead space volume on the adsorbent bulb was kept constant by the pressure measurements with mercury manometers. Pressure of dosing chamber was measured at room temperature before and after nitrogen allowed to enter adsorbent bulb. Dead space pressure, which is also equilibrium pressure of adsorption, was measured for each point. The amount adsorbed was calculated for each point by evaluating the known parameters. For each point, the cumulative amount of the adsorbed nitrogen until equilibrium pressure was reached, has been taken as the attained adsorption capacity.

The adsorption of *n*-butylamine, from a cyclohexane-solution, on the natural and acid-activated samples was recorded by a UV–VIS spectrophotometer (Varian, Cary 50). In each experiment, a series of 10 mL test tubes was loaded with 0.1 g of bentonite sample. Then, to each tube, 10 mL of freshly prepared *n*-butylamine solutions (in cyclohexane) with a concentration ranging from 2.0×10^{-3} M to 1.8×10^{-2} M were pipetted. To reach adsorption equilibrium, the tubes were shaken mechanically at 25 °C for 75 h. The absorbance values of the solutions were then measured at the wavelength of maximum absorption, $\lambda = 227$ nm, and equilibrium concentrations were determined from a calibration plot.

Each bleaching experiment was carried out in an open 400 mL beaker containing a stirred suspension of a 1% by mass bleaching earth in alkali-refined soybean oil. The mixture was then heated to 95–105 °C, kept at this temperature interval for 15 min, similar to the standard AOCS procedures (Chamkasem & Johnson, 1988; Önal, submitted for publication). The oil was than filtered through Whatman No. 41 filter paper. The color index of the oil, in red-yellow units, was determined by using a Lovibond Automatic Tintometer (Type D) equipped with 2.54 cm cells according to the AOCS Official Method Cc 13b-45 (1973).

3. Result and discussion

3.1. XRD analysis

The XRD powder-patterns for some representative bentonites, natural and acid-activated, are given in Fig. 1. The bentonite investigated displays peaks belonging to the clay mineral smectite (with a d_{001} value of 1.49 nm), and non-clay minerals, quartz, opal, and feldspar. Characteristic XRD peaks were identified according to the literature (Moore & Reynolds, 1997). The XRD patterns show that the crystallinity of the smectite decreases when the mass-percentage of H_2SO_4 in the acid treatment exceeds 10%. However, the crystal structure of the smectite is still partly preserved even after activation with a H_2SO_4 content of 50% by mass. The crystallinity of the non-clay minerals are not affected by the acid activation process.

3.2. Nitrogen adsorption and desorption isotherms

The N_2 adsorption/desorption isotherms at the liquid N_2 temperature (~77 K) for natural and all acid-activated samples were examined, and representative ones, for natural and acid-activated samples are shown in Fig. 2. Here, p is the adsorption and desorption equilibrium pressure, p^0 is the vapor pressure of bulk liquid nitrogen at experimental temperature, $p/p^0 = x$ is the relative equilibrium pressure, and n is the adsorption capacity defined as the number of moles of nitrogen adsorbed on 1 g of sample at any x.

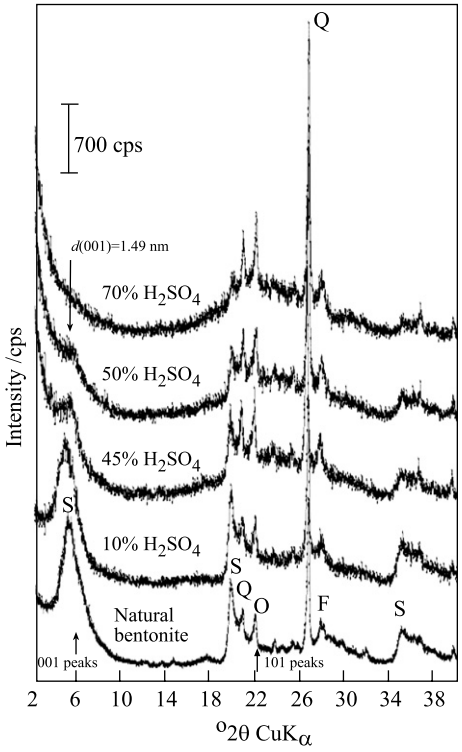

Fig. 1. XRD patterns of natural bentonite and some acid activated samples (S: smectite, Q: quartz, O: opal, F: feldspar).

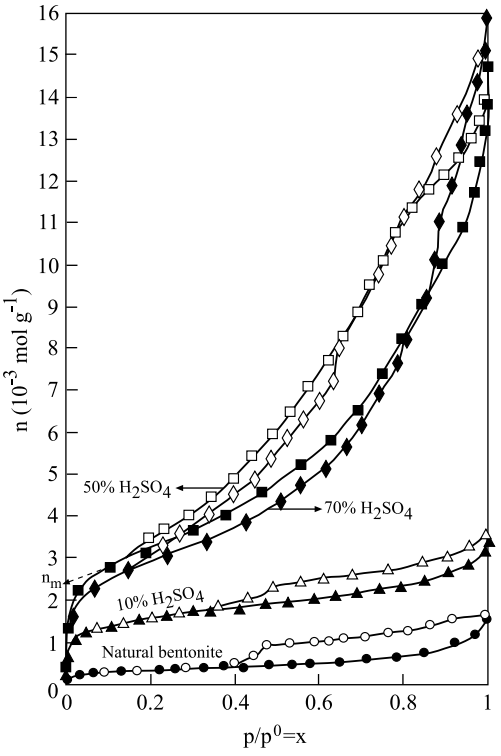

Fig. 2. Adsorption/desorption isotherms of N_2 at liquid N_2 temperature for natural bentonite and some acid activated samples.

The isotherms show that the adsorption capacity increases with increasing acid content up to 50% H_2SO_4 and than decreases slowly through 70% H_2SO_4.

According to Brunauer, the classification of these isotherms is similar to Type II (Brunauer, Deming, Deming, & Teller, 1940). The shapes of the adsorption/desorption isotherms indicate that the prepared bleaching earths are mainly mesoporous solids but also contain some micropores. The overlapping of the adsorption desorption isotherms over the interval $0.35 < x < 0$ shows that the multimolecular and monomolecular adsorptions are reversible. After multimolecular adsorption was complete at $x = 0.35$, capillary condensation begins, and all mesopores filled up to $x = 0.96$. Bulk liquid nitrogen forms at $x = 1$ (Linsen, 1970). At the interval of $1 < x < 0.96$, the liquid nitrogen outside the mesopores evaporates spontaneously so long as the relative equilibrium pressure due to desorption is low enough. The same is true for the liquid nitrogen within the mesopores at the interval, $0.96 < x < 0.35$. The shapes of mesopores in a solid may be of cylindrical-, parallel-sides-, slit-, and wedge-shaped or like an ink-bottle. Capillary condensation begins in the narrowest mesopores first, while capillary evaporation starts earlier in the largest mesopores. This difference is the major cause of the hysteresis between adsorption and desorption isotherms. The hysteresis phenomenon becomes more prominent with acid activation because the amount of mesopores increases by the structural deformation. Due to the same reason, capillary condensation on acid-treated (50–70% H_2SO_4) bentonite is discernible under a relative pressure of $x \cong 0.2$ while, with the natural material, capillary condensation can only occur at $x = 0.4$.

3.3. Surface area

The specific surface areas of the samples were obtained from the standard Brunauer, Emmett and Teller (BET) method by using the adsorption data of N_2 in the interval $0.05 < x < 0.35$ (Brunauer, Emmett, & Teller, 1938; Everett, Parfitt, Sing, & Wilson, 1974; McClellan & Hornsberger, 1967; Sarıkaya, Ada, Alemdaroğlu, & Bozdoğan, 2002). The representative BET plots were given in Fig. 3. These plots fit to the BET equation in the form

$$x/n(1-x) = 1/n_m x + [(c-1)/n_m c]x \quad (1)$$

where, n_m is the monomolecular adsorption capacity and c is a constant. The values n_m and c were determined by solving the simultaneous equations obtained from the slope and intercept of the BET straight line. The specific surface areas, $S/m^2\ g^{-1}$, were calculated from the equation

$$S = n_m N_A a_m \quad (2)$$

where, $N_A = 6.02 \times 10^{-23}\ mol^{-1}$ is the Avogadro constant and $a_m = 16.2 \times 10^{-20}\ m^2$ is the area occupied by a single nitrogen molecule.

As seen in Fig. 3, the slope of BET straight lines decreases up to 50% H_2SO_4 and then tends to increase slightly up to 70% H_2SO_4. A reverse behavior is also reflected in the surface area versus acid content plots (Fig. 4). As seen in Fig. 4, the S value increases rapidly from 25 $m^2\ g^{-1}$ to its maximum value of 285 $m^2\ g^{-1}$ as the acid content increases from zero to 40–45% H_2SO_4, and then decreases slowly.

3.4. Micro–mesopore volume

All micro- and mesopores are full with liquid nitrogen by desorption at $x = 0.96$, as mentioned above. Hence,

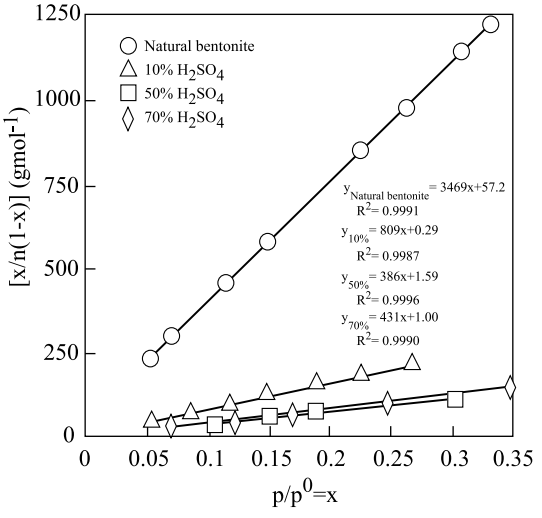

Fig. 3. BET plots for natural bentonite and some acid activated samples.

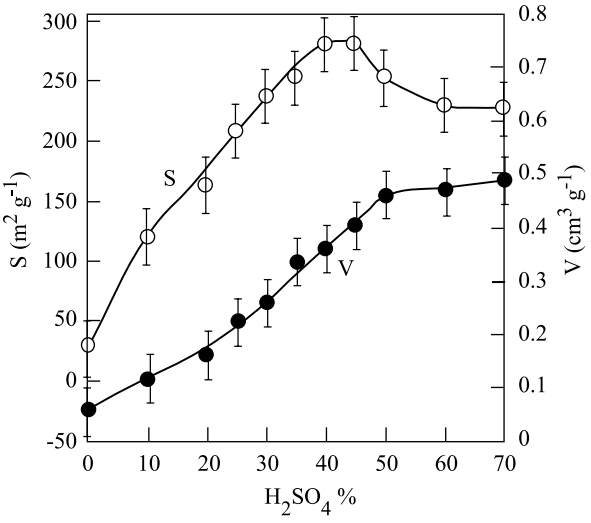

Fig. 4. Variation of the specific surface area (S) and the specific micro–mesopore volume (V) with the H_2SO_4 content in activation.

the adsorption capacities as liquid nitrogen volumes estimated from desorption isotherms at $x = 0.96$ are taken as the specific micro–mesopore volumes, V/cm^3 g^{-1}, of the samples.

The variation of the micro–mesopore volume with the H_2SO_4 content used in activation is shown in Fig. 4. The V value increases rapidly from 0.05 cm^3 g^{-1} to 0.45 cm^3 g^{-1} as the acid content changes from zero to 50% H_2SO_4, and then stays approximately constant. The S and V curves do not change parallel as seen in Fig. 4. The increase in porosity is due to the partial dissolution of the exchangeable cations such as Na^+ and Ca^{2+}, and also structural cations such as Al^{3+}, Fe^{3+}, and Mg^{2+} from 2:1 layers of the smectite mineral.

3.5. Pore size distribution

The pore size distributions (PSD) of the samples were obtained and representative curves are given in Fig. 5. Here, r is the radius of the mesopores (assumed to be cylindrical) and V is the specific micro–mesopore volume. The r values were calculated from desorption isotherms by using corrected Kelvin equation which is a relationship between r and x values (Gregg & Sing, 1982; Önal & Sarıkaya, 2007). The V values corresponding to r values were also calculated from the desorption isotherms as the liquid nitrogen volumes for each x. The area under the PSD curve and two known abscissa values is related to the relative amount of mesopores having sizes that fall into the range defined by the abscissa limits. The most abundant approximate pore size increases from 1.84 to 2 nm up to 50% H_2SO_4, probably due to the transformation of some micropores to mesopores during the development of the activation. Seventy percent of H_2SO_4 sample has two maxima at 1.84 and 2.68 nm. On the other hand, the area of the PSD curve increases with increasing acid content as seen in Fig. 5. After the 50% acid content, all samples have maximum r

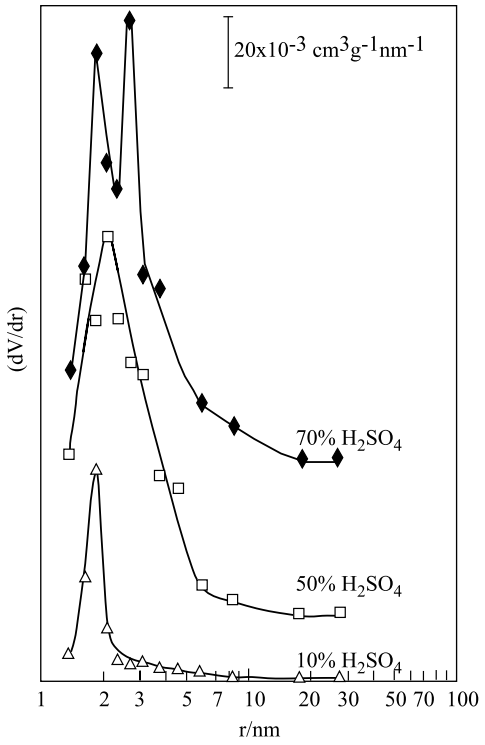

Fig. 5. Mesopore size distribution (PSD) curves of some acid activated samples.

values and the area of PSD curves display a slight increase. This indicates that the rate of transformation of micropores to mesopores decreases. So the rapid increases in the S and V values decreases by the activation above the 50% H_2SO_4 as seen in Fig. 4.

3.6. Surface acidity

The average surface acidity (n_m/mol g^{-1}) of each sample was determined from three Langmuir plots drawn by using the data obtained from n-butylamine adsorptions (Brown & Rhodes, 1997a; Noyan et al., 2006; Varma, 2002). The surface acidity versus the H_2SO_4 content is shown in Fig. 6. The n_m value increases rapidly from 4.2×10^{-4} to 9.4×10^{-4} mol g^{-1} with an increase of the acid content from zero to 45% H_2SO_4. The result shows that the surface acidity and surface area change parallel to each other by the activation.

3.7. Bleaching power

Bleaching or decolorizing power (BP) of the bleaching earths was calculated from the equation;

$$BP = 100(R_0 - R)/R_0 \quad (3)$$

where, R_0 and R are the red color units on Lovibond scale of the alkali-refined oil before and after bleaching. The variation of the BP with the H_2SO_4 content is seen in Fig. 6. The BP value increases rapidly from 3 to 70 with an increase of the acid content from zero to 50–60% H_2SO_4,

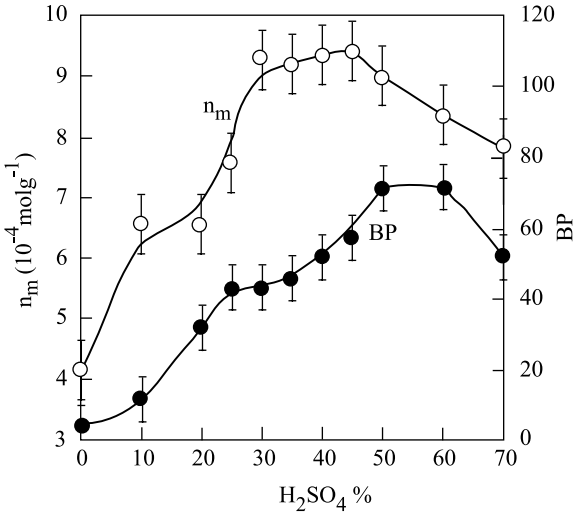

Fig. 6. Variation of the surface acidity (n_m) and the bleaching power (BP) by increasing H_2SO_4 content in activation.

and then decreases slowly. Although the changes in the S, V, n_m, and BP are similar until up to the 40% H_2SO_4, their maxima do not exactly overlap. However, the BP does not have a maximum when S, V, and n_m reach to their maxima. The BP reaches to a maximum at the optimum conditions, i.e., 50–60% H_2SO_4, $S = 250$–$230\ m^2\ g^{-1}$, $V = 0.46$–$0.47\ cm^3\ g^{-1}$, and $n_m = 9.0 \times 10^{-4}$–8.4×10^{-4} mol g^{-1}. The maximum BPs of this bleaching earth and commercial Tonsil 131 (Süd Chemie) are comparable as 0.71 and 0.69, respectively. This shows that bleaching earth prepared under optimum conditions is suitable for industrial uses. With an acid content of 50%, the area of the PSD curve reaches a maximum value and r is fit to the sizes of pigments as seen in Fig. 5. The large-size, colored organic pigments in the soybean oil can penetrate into the mesopores with a radius between 1.4 and 3.0 nm and strongly adsorbed on their surface. However, the BP is mainly controlled by the PSD, rather than the other adsorptive properties.

As to oil retention characteristics of the natural and acid-activated bentonites, the natural material is found to have trapped some mass of oil roughly 20% of its own weight after use, whereas, after acid-activation, the relative mass of oil increases up to 40%. In summary, oil retainment property increases as the acid content in activation increases, but never exceeds 40%.

4. Conclusion

The exchangeable, and to a lesser extent, structural cations of the smectite in a bentonite are removed by acid activation. The surface area, micro–mesopore volume, mesopore size distribution, surface acidity and bleaching power of a bentonite are greatly affected from acid activation at limited acid contents without any considerable change in crystal structure of the smectite. Although, the bleaching power increases with increasing surface area, porosity and surface acidity, it depends more on the mesopore size distribution of the bleaching earth. The bleaching earths obtained by acid activation are more porous materials than the natural bentonite for use as adsorbents, filtering medium, catalyst and precursors for pillared clays.

Acknowledgements

The authors thank the Scientific Research Council of Ankara University, Turkey for supporting this study under a Project No: 2003.07.05.082.

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