Journal of Bangladesh Chemical Society, Vol. 24(2), 191-201, 2011.
DOI: 10.3329/jbcs.v24i2.9708

PERFORMANCE OF SUDANESE ACTIVATED BENTONITE IN BLEACHING COTTONSEED OIL

KAMAL K. TAHA,*. TAGELSIR M. SULEIMAN, and MUSA A. MUSA

College of Applied and Industrial Science University of Juba,Khartoum, Sudan

Abstract

Bentonite clay collected from Jabal Umm Ali area NE of Khartoum (Sudan) was characterized by X-ray diffraction (XRD). It was then purified by treatment with distilled water and activated with sulfuric acid at 90 ºC for 3.5 hrs. XRD indicated modification of activated bentonite with enhanced surface area. Several cations were removed from octahedral sheet (Mg, Al, and Fe). Increasing the acid concentration enhanced the degree of destruction of bentonite structure. On bleaching semi-refined cottonseed oil with activated bentonite, 30% acid concentration was found to be optimal for color removal and that the local activated bentonite is more efficient in bleaching vegetable oil than the standard one.

Introduction

Clay minerals are small fragments of hydrous layer silicates. The most important of these minerals are kaolinite, montmorillonite, illite, vermiculite and chlorite, each having specific characteristics. Bentonite structure is based on silica-oxygen tetrahedral sheet and aluminum-magnesium-oxygen-hydroxyl octahedral sheet. Clays have variety of industrial uses and applications e.g. removal of colorizing pigments like carotene and chlorophyll[1,2]. Sudan is rich in clay deposit that may be a potential input for local industry[3]. The total annual production of bleaching clays is approx 0.85×10^6 tons with price range of $250-$600 per ton[4], while the reserve at Jabal Umm Ali area is estimated to be 1.8×10^3 tons. Bentonite may be classified according to its chemical composition and its behavior, when it is in contact with water, into swelling (sodium bentonite) and non-swelling (calcium bentonite) type[5]. The local bentonite is in the form of the latter type which can be used as bleaching earth for removing coloring compounds from edible and mineral oils. Bentonite used as a bleaching agent, has to be activated using mineral acids. The acid treatment of bentonite produces different physicochemical properties from the non-activated clays e.g. surface area and cation exchange capacity (CEC)[6-8] thus increasing the adsorption capacity[9-11]. The objective of this study is to investigate the performance of local activated bentonite for bleaching off colors from vegetable edible oils.

Materials And Methods

10 kg bentonite sample representing 1.25 km^2 areas of ore was collected from different bore holes of an average depth of 11m. The clay is ground to powder and purified with distilled water (1:5 w/w)

Determination of chemical composition

0.2 g sample was digested in acid mixture (HF, $HClO_4$, HNO_3, and HCl 10 mL each). The digested material was heated to dryness. The final solution was diluted in aqua regia. The chemical composition of bentonite was determined using ACTIVA-M ICP-AES Simadzu inductively coupled plasma (ICP). Silica was determined gravimetrically according to standard method[12].

Activation of bentonite

The purified material was ground to pass 88 micrometer sieve followed by treatment with 10, 20, 30 and 40% sulphuric acid. The acid to bentonite ratio was 2:1. The activation of solid- acid mixture was carried in a round bottom flask with reflux. The temperature was adjusted to 90° C and the contact time was 3.5 hours. When activation was completed, the mixture was washed several time with distilled water and then dried overnight at 105°C to reduce the moisture content[13].

X-ray diffractograms

The X-ray diffractogram of the samples (ore and acidified) were obtained with Philip 3020 Analyzer equipped with a PW 3710 controller, using Cu-kα (λ=1.5405Å) radiation and Ni filter at 40 kV and 20 mA.

Infrared spectra

The FT-IR spectra were recorded with FT-IR Spectrophotometer Model 8400S (Shimadzu Corporation, Japan) with 4 cm^{-1} resolution and in the range 500-4000cm^{-1}. Solid clay was mixed with KBr in 1:10 ratio. The mixture was grinded to very fine powder. The fine powder was pressed under 10 ton pressure into pellet. The Infrared spectra were obtained from solid samples and KBr pellets[14].

Determination of surface area

The surface area was determined using ethylene glycol monoethylether (EGME)[15,16]. Clay samples were first air-dried and pulverized to pass a No. 40 sieve. A small amount of the sample was then placed in an oven at a temperature of 105°C overnight to remove water. After oven drying, it was dried using P_2O_5. Approximately one gram of the dried clay was spread into the bottom of the aluminum tare. The mass of the clay sample was determined using an analytical balance with an accuracy of 0.001 g. Approximately 3.0 mL of laboratory grade EGME was added to the clay with a pipette and mixed together with a gentle swirling motion to create a uniform slurry. All clay particles were covered with the EGME in order to obtain an accurate surface area measurement. The tare was then placed inside a standard laboratory glass sealed vacuum desiccator and allowed to equilibrate for

20 min. The desiccators were then evacuated using a vacuum pump of 635 mm Hg for 24 hours. The tares were removed from the desiccators and weighed after a period of 12,16 and 24 hours. When the mass of the sample varied by more than 0.001 grams between two measurements, the sample was placed back in the desiccators and evacuated again for an additional 2 hours. The process was continued until the sample mass did not vary by more than 0.001 g. The routine procedure of weighing the samples between 12,16 and again at 24 hours, was adopted and found adequate for samples with the highest SSA. The surface area was expressed follows:

$$A = \frac{W_a}{0.000286 W_s}$$

A = Surface area, W_a = weight of EGME retained by the sample, Ws = weight of P_2O_5-dried sample, 0.000286 is the weight of EGME required to form a unimolecular layer on a square meter of the surface[17].

Bleaching off colors of cotton seed oil using activated bentonite

100 g of semi-refined oil were bleached at 90°C using 0.5, 1.0, 1.5, and 2.0g of activated clay with continuous stirring for 30 minutes. The absorbances of bleached and unbleached oil were measured by using Perkin Elmer Lambda 4B UV/Vis Spectrophotometer at wavelength 408 nm [1] and bleaching efficiency (BE) of activated bentonite was determined according to the following expression[18]:

$$\text{Bleaching efficiency BE \%} = 100 \times \frac{A_{unbleached} - A_{bleached}}{0.000286 W_s}$$

Where: $A_{unbleached}$ and $A_{bleached}$ are absorbances of unbleached and bleached oil respectively, at 401nm.

Results and Discussion

The X-ray analysis of bentonite ore indicated that it contains montmorillonite and kaolinite as clay minerals while quartz and calcite as non-clay minerals (Figure1).

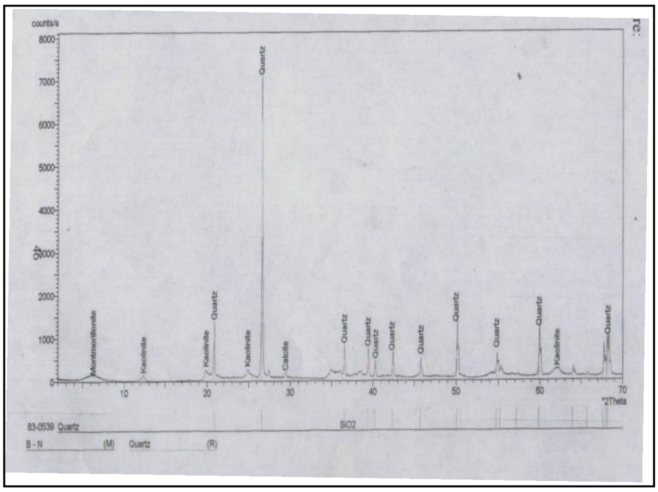

Fig. 1. X-ray diffraction (XRD) pattern of the original sample

The 2θ peak at 8.84 confirms the presence of montmorillonite, while the other peaks identified at 2θ are 12.35, 26.64 and 29.47 corresponding to kaolinite, quartz and calcite respectively[19].

The chemical composition and loss on ignition (L. O. I.) of untreated and treated bentonite with different concentration of H_2SO_4 is shown in Table 2.

Table 2. Chemical composition of untreated and treated bentonite

Component percent	Bentonite				
	untreated	treated with different concentration of H_2SO_4			
		10%	20%	30%	40%
SiO_2	61.68	70.69	72.64	74.30	76.42
Al_2O_3	13.91	11.98	11.07	10.34	10.09
Fe_2O_3	3.49	2.44	2.12	1.96	1.84
MgO	6.95	2.15	1.77	1.64	1.64
CaO	1.71	0.10	0.13	0.11	0.13
Na_2O	0.18	0.08	0.08	0.08	0.09
K_2O	1.78	0.83	0.84	0.83	0.84
TiO_2	0.014	0.014	0.014	0.014	0.013
P_2O_5	0.014	0.021	0.021	0.021	0.018
L.O.I	8.69	8.69	8.69	8.69	8.63
Total	97.42	96.99	97.37	97.96	97.46
Si/(Al+Fe+Mg)		4.3	4.9	5.3	5.6

Acid treatment has modified the structure of bentonite as indicated by the change in the chemical composition. As acid concentration increases, SiO_2 % increases, while Al, Fe and Mg decrease throughout at all acid concentrations. Almost similar results were reported by Kirali and Lacin[1]. The results thus indicate the replacement of these cations during the activation process[20].

It is expected that the exchangeable cations Ca^{+2}, K^+ and Na^+ were removed during the acid treatment of bentonite. However, considerable amounts of these elements remain in the activated samples. This may be due to the presence of insoluble quartz as impurities. It can be seen from Table 2 that CaO / $Na_2O > 1$ which indicates a calcium (non-swelling) bentonite[8]. It is observed that decrease in Al_2O_3, Fe_2O_3 and MgO in 2: 1 layers is accompanied by an increase in silica content (SiO_2).

It is also observed that as acid concentration increases, the amount of cations in octahedral sheet (Al, Fe, Mg) decrease, (Table 2). It is presumed that at low acid concentration the attack on the structure is weak and that the exchangeable cations replaced by H^+ ions are few. It may be concluded that at high acid concentration, the attack on the structure and the dissociation of the cations (Al, Fe, and Mg) may be favorable and hence their concentrations are decreased as a result of acid treatment.

Acid activation of bentonite results in an increase of silica SiO_2 content (Table 2). This increase in SiO_2 is accompanied by decrease in Al_2O_3, F_2O_3 and MgO[21]. The analyses of the results show decrease in relative amount of cations belonging to octahedral sheet and increase in the Si/Al + Fe+ Mg ratio (Table 2).

It is assumed that the chemical changes that take place in the structure during activation due to acid treatment leads to vacancies in the crystal lattice. As a consequence there will be an increase in adsorptive power of the activated bentonite. In order to provide charge equilibrium, due to activation of bentonite, the protons of sulphuric acid replaces the exchangeable cations such as Na^+ and Ca^{+2} which are present between the layers. However, the protons of H_2SO_4 cannot fill all the empty spaces left by ions such as Al^{+3} and Mg^{+2} that occupy the octahedrons center, hence vacancies will occur. It is also possible that the protons of the hydroxyl groups may become more labile as a result of the structural deformation due to acid activation. In order to confirm the presence of montmorillonite in the original sample, X-ray diffraction analysis was carried out for the purified sample and acid activated sample (Figure 2). It is clear that montmorillonite is the basic clay minerals in the sample. The sharp and intense peak corresponding to an interplanar distance d(001) with the value 15.0 $\overset{\circ}{A}$, has shifted to 16.4 $\overset{\circ}{A}$ after acid treatment [22].

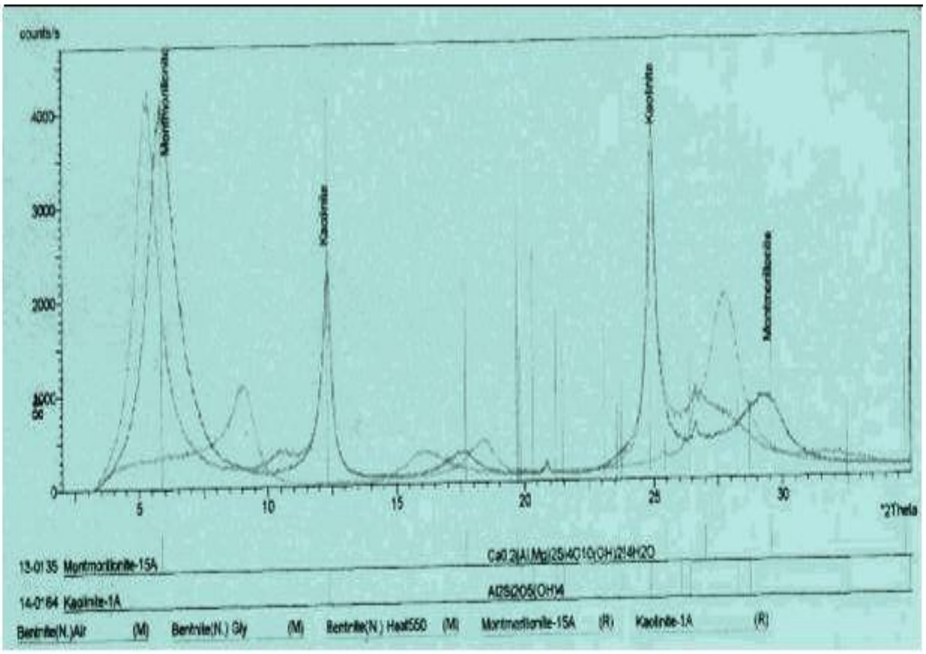

Fig. 2. X-ray diffraction patterns of bentonite sample showing montmorillonite peaks

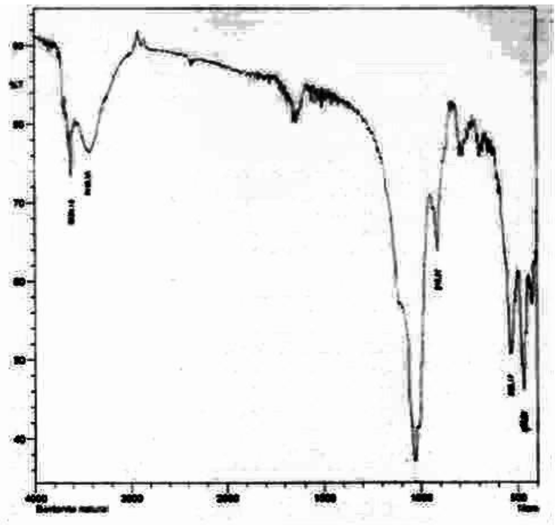

Fig. 3. IR spectrum of pure Bentonite

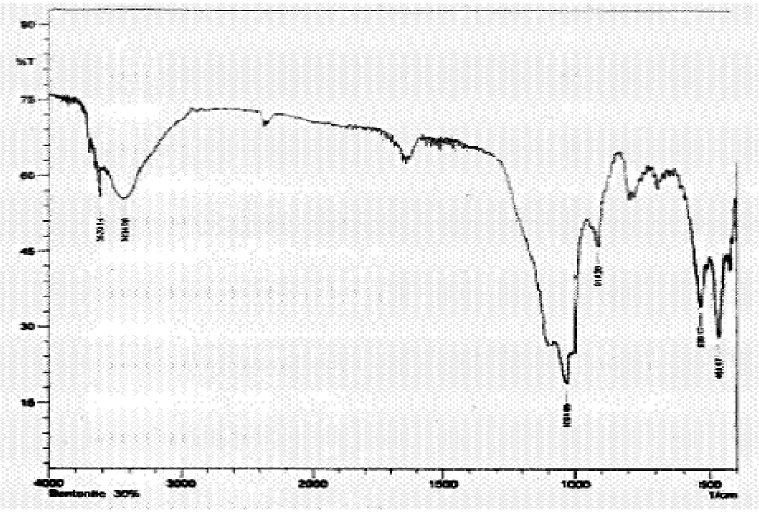

Fig. 4. IR spectrum of Bentonite treated with 30 % acid

It is clear that from Figure 3 that untreated bentonite shows absorption band at 3602, 3447, 1032, 912, 536 and 469cm^{-1}. The absorption at 3620cm^{-1} is attributed to stretching vibration of OH groups[23]. It was reported that the A1-A1-OH stretching frequency is observed at 3620 cm $^{-1}$, while the bending frequency is at 915 cm^{-1}. This can be considered as characteristic of dioctahedral clay[24]. While absorption at the frequencies at 1020 cm^{-1}, 536 cm^{-1} and 469 cm^{-1} are attributed to Si-O stretching, for Si-O-AI bending and Si-O-Mg bending respectively[22,25], while that at 3447cm^{-1} has been assigned to OH groups bonded to absorption water. All bands were shifted after acid treatment (Fig. 4) and their intensities also change, this behavior indicates minimum damage of the crystal structure of bentonite. It is evidence from these figures that there are changes caused by acid activation of bentonite. Temunjin *et al.*[26] reported that a high acid concentration lead to destruction of lamellar structure within clay platelet. The decrease in bleaching ability with increase in acid concentration was attributed to the collapse of clay lattice structure [27]. The results reached by Ozcan[28] show a total change in the IR spectra of bentonite after activation which can be explained by the low acid concentration used in this study (30%), while Ozcan used 50 / 50 (v/v) ratio which gives 65.6 % sulfuric acid by mass (densities of H_2SO_4 and water are 1.90 and 1.00 g.cm^{-3} respectively). Noyan *et al.* [29] reported that bleaching power, specific surface area, specific micro-mesopore volume and mesopore size distribution reached its maximum at 40 % of acid content in activated bentonite. They[29] reported that little change in the crystal structure of the smectite.

Table 3. the effect of the acid concentration on bentonite surface area.

Bentonite					
Sample weight	Untreated	Treated with (H_2 SO $_4$) acid concentration			
		10%	20%	30%	40%

W_a(g)	0.0130	0.0142	0.0151	0.0180	0.0193
W_s(g)	1.06	1.05	1.07	1.06	1.06
Surface area (m^2/g)	42.88	47.88	49.34	59.37	63.66

The specific surface area plays very important role in determining the physical and chemicals properties of clay minerals[30]. It is clear that surface area of the activated bentonite increase by increasing the acid concentration as shown in Table 3. However, the weight of bentonite that was dried with P_2O_5 did change with the acid concentration. It was also observed that the residual ethylene glycol monoethylether in bentonite increased from 0.013g to 0.0193g with the acid concentration.

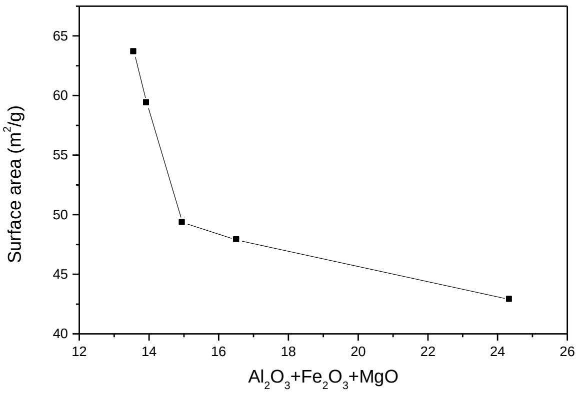

Fig. 5. The variation of surface area by the mass percent of (Al_2O_3 + Fe_2O_3 + MgO)

It is observed from Figure 5 that higher amount of Al_2O_3 + Fe_2O_3 + MgO have lower surface area. Thus the value of surface area increases by the decrease in (Al_2O_3 + Fe_2O_3 + MgO) content i.e. by increasing activation process. The increase in the surface area may be due to unoccupied octahedral spaces resulting from the removal of Mg^{+2}, Fe^{+3} and Al^{+3} ions from the 2:1 layer. Further activation lead to drop in the surface area. This dropping in surface area is due to decomposition of the structure and some location and mesoporous were disappeared.

Table 4. Effect of acid concentration added to bentonite on color absorbances to 100 g cotton seed oil.

Activated bentonite added (g/100g)	Color Absorbance Acid Concentrations				
	10%	20%	30%	40%	References*
0.5	0.504	0.475	0.468	0.468	0.950
1.0	0.494	0.463	0.454	0.455	0.850
1.5	0.486	0.369	0.344	0.348	0.66

2.0	0.405	0.346	0.340	0.350	0.62

* Fuller" s earth import from South Africa

It is clear from Table 4 that the color absorption of bleached cotton seed oil, decreases with increase in the clay added to the oil and also with the acid concentration up to 30 %. The unbleached oil absorbance is 1.88 at wavelength 408nm. The low absorbance value indicates that more colors have been removed from the oil by the activated bentonite.

Table 5 shows that the bleaching efficiency (BE %) of oil increase with increasing the bentonite added. Thus the maximum bleaching efficiency obtained with bentonite treated with 30% (BE%= 81.91) of H_2SO_4 with addition of 2g clay. It was reported that a dosage of 0.5-1.0% clay is the range used internationally[31] which almost agree with the present study.

Table 5. Bleaching efficiency (BE %) for semi-refined cotton seed oil.

Bentonite dosage (g)	Treated bentonite				
	10%	20%	30%	40%	*References*
0.5	73.19	74.73	75.10	75.10	49.41
1.0	73.72	75.37	75.63	75.79	54.73
1.5	74.14	80.42	81.70	81.48	64.73
2.0	76.45	81.54	81.91	80.38	66.91
Si/Al + Fe + Mg	4.3	4.9	5.3	5.6	

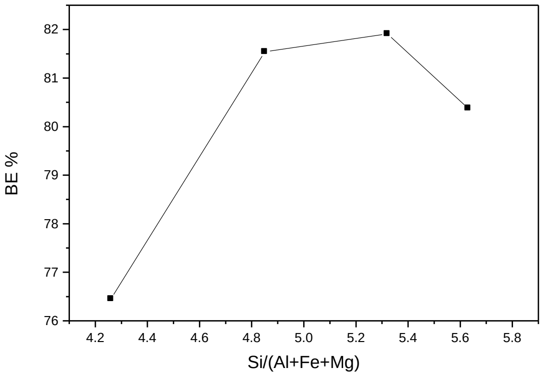

Fig. 5. the relation between bleaching efficiency (BE %) and ratio of Si/ (Al + Fe + Mg)

Figure 5 indicates that the efficiency increases with the loss of octahedral cations of (Al, Fe, and Mg) during the activation process. However, this is a maximum bleaching efficiency, after which a drop in bleaching efficiency is observed. This dropping take place at Si/Al + Fe + Mg value more than 5.2. This also explains the conversion of mesoprous to macroporous. Adsorption of color observed depends on micro and mesoporous in bentonite structure[29].

Conclusions

Acid concentration highly affects the degree of activation of bentonite.The structural change obtained by XRD indicates that the destruction of octahedral sheet is a function of acid concentration. Acid activation of bentonite yielded an adsorbent material that is efficient in bleaching off colors from cottonseed oil and is better than the standard one.

References:

1. E. Gulsah Kirali and Oral Lacin (2006). Statsitical modeling of acid activated on cotton oil bleaching by Turkish bentonite, J. of Food Engineering, **75,** pp. 134 – 141.
2. G. Akkaya, I. Uzun and F. Guzel (2007). Kinetics of the adsorption of reactive **dyes** by chitin Dyes Pigments, **73**, pp. 168 – 177.
3. Adli, A.M.A., 1998. Sudan industrial mineral and rocks. Centre for strategic studies. Khartoum-Sudan.P127.
4. Haydn, M. 2002. Industrial minerals and rocks. 6th edition. Indian university.
5. Gleason, M. H., Daniel D. E. and Eykholt G. R. 1997. Calcium and sodium bentonite for hydraulic contaminant application, J. of Geotech. And Geoenvir. Engineering ASCE VA, 123, pp. 438 – 445.
6. Francisco, R.V. 2001. Studies on the activation of Brazilian smectite clay Quimca. Nova., **24**, pp. 345 – 353.
7. Taylor, D.R. and Jenkins, D.B. 1987 "Acid-activated clays", Society of Mining Engineering of the American Institute of Mechanical Engineers, Transactions **282**, pp. 1901-1910.
8. Wu, Z.S., Li, C., Sun X.F., Xu X. L., Dai B., Li J.E. and Zhao H. S. 2006. Characterization, acid activation and bleaching performance of bentonite from Xinjiang, Chin. J. Chem. Eng. **14**, pp. 253 – 258.
9. Mokaya, R., Jones, W., Davies, M.E.1993. And Whittle, M.E., "Chlorophyll adsorption by alumina pillared acid activated clay", *J. Am. Oil Chem. Soc.* **70**, pp. 241-244.
10. Study Group (2001). Bleaching of edible fats and oils. European J. of Sci. & Tech., **103**, pp. 505 – 551.
11. Tong Junmao, Wu Zhan Sheng, Sun Xifang, Xu Xiaolin and Li Chan 2008. Adsorption Kinetics of *ß*-Carotene and Chlorophyll onto Acid-activated bentonite in Model Oil. Chinese J. of Chemical Engineering, **16**, pp. 270 – 276.
12. Vogel’s, Quantitative chemical analysis 1989, 5th Edition, Longmanns Sci. and Tech., New York.
13. Wu, Z.S., Li, C., Sun X.F., Xu X. L., Dai B., Li J.E. and Zhao H. S. 2005. Study and preparation of activated white clay with bentonite from Wulanlinge, 9th Chinese national chemical process annual meeting, Beijing (in Chinese).

14. Foletto, E.L. Volzone, C. and Porto. L.M. 2003. Performance of an Argentina acid-activation bentonite in the bleaching of soybean oil. Braz. J. Chem. Eng. **20,** pp. 139 - 145.
15. Carter, D. L., Heilman, M. D., and Gonzalez, C. L., 1965, "Ethylene Glycol Monoethyl Ether for Determining Surface Area of Silicate Minerals," *Soil Science,* Vol. 100, No.5, pp. 356-360.
16. Carter, D. L., Mortland, M. M., and Kemper, W. D., 1986, "Specific Surface. Methods of Soil Analysis," Chapter 16, *Agronomy,*No.9, Part 1, 2nd Ed., American Society of Agronomy.
17. Chiou, C. T., D.W. Rutherford, and M. Manes, 1993. “Sorption of N_2 and EGME vapors on some soils, clays, and mineral oxides and determination of sample surface areas by use of sorption data,” *Environ. Sci. Technol*. **27**, pp. 1587–1594.
18. Srasra, E., Bergaya F., Van Damme, H., and Ariguib, N. K. 1989. Surface properties of an activated bentonite decolorization of rape-seed oil, Appl. Clay Sci., 4, pp. 411 – 421.
19. Rodrigues, M. G**.** F., 2003. Physical and catalytic characterization of smectites from Boa-Vista, Paraíba, Brazil, Cerâmica **49,** pp. 146-150.
20. R. Francisco, D. Valenzuela and S. S.Persio 2001. Studies on the acid activation of Brazilian smectitic claysStudies on the acid activation of Brazilian smectitic clays, Quimica. Nova. **24**, pp. 345 – 353.
21. Corma A., Grande M.S., Gonzalez-Alfaro V. and Orchilles A.V. (1996), ‘Cracking activity and hydrothermal stability of MCM-41 and its comparison with amorphous silica-alumina and a USY zeolite, J. Catal., **169**. pp. 375 – 382.
22. B. Benguella, A. Yacouta-Nour, 2009. Adsorption of Bezanyl Red and Nylomine Green from aqueous solutions by natural and acid-activated bentonite, Desalination **235**, pp. 276–292
23. Cailere, S., Henin, S., and Rautureau, M. 1982 Mineralogie des Argiles. I Structure et proprietes physico-chimiques. Ed. Masson, Paris, p. 70-80. (in French).
24. V Van Der Marel, H. W., and Beutelspacher, H. 1976 *Atlas of Infrared Spectroscopy of Clay Minerals and Their Admixtures:* Elsevier, Amsterdam, 31-58.
25. Tavani, E.L, Volzone. C. 1999. Adsorption of sulphuric acid on smetite from acidic aqueous solution. Ceramica, **45**. pp. 133 – 136.
26. Temuujin J., Jadamobaa T., Burmaa G., Erdenechimeg S., Amarsanaa J. and Mackenzie K. J. D. 2004. Characterization of acid activated montmorillonite from Tuulant (Mongolia), Ceram. Int., **30**, pp. 251 – 253.
27. Low s. K., Lee C. K. and Kong L. Y. 1998. Decolorization of crude palm oil by activated spent bleaching earth, J. Of Chem. Tech. Biotechnol, 72, pp. 67 – 73.
28. A. S. Ozcan and A. Ozcan 2004. Adsorption of acid dyes from aqueous solution onto acid activated bentonite, J. Colloid Interface Sci. **276,** pp. 39 – 46.
29. Hula Noyan, Muserret Onal and Yuksel Sarikaya 2007. The effect of sulfuric acid activation on crystallinity, surface area, porosity, surface acidity and bleaching power of bentonite, Food Chemistry, **105**, pp. 156 – 163.
30. Oguz, I., and Fatma, T. 2000. The Measurement of surface area of some Silicates by adsorption. Turk. J. Chem. **24**, pp. 9-19.

31. Ng, K.F., Nair, N.K., Liew, K.Y. and Noor A. M., 1997. A.M.,"Surface and pore structure of deoiled acid- and heat-treated spent bleaching clays", *J. Am. Oil Chem. Soc.* **74**, pp. 963-969.

(Received : 12 November, 2010; Accepted : 01 July, 2011)