Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 37 (2011) 1953–1957

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Regeneration of a solid waste from an edible oil refinery

Chafika Meziti [a,1,*], Abdelhamid Boukerroui [b]

[a] *Faculty of Technology, Laboratory of Materials Technology and Process Engineering, Process Engineering Department, University of Bejaia, DZ-06000 Bejaia, Algeria*

[b] *Faculty of Exact Sciences, Laboratory of Materials Technology and Process Engineering, Chemistry Department, University of Bejaia, DZ-06000 Bejaia, Algeria*

Received 17 December 2010; received in revised form 18 January 2011; accepted 17 February 2011
Available online 31 March 2011

Abstract

This work presents a valorization of a solid waste originating from an edible oil refinery called spent bleaching earth (SBE). The SBE material is first impregnated with an ammonium chloride solution (3 M), then treated directly in furnace at 400 °C during an hour followed by a washing in the cold by HCl 1 M. To elucidate the changes in its crystalline structure, induced by the regeneration method, the obtained material (RSBE) is characterized by several physicochemical methods (X-ray diffraction, FTIR, thermal analysis, BET and SEM). The characterization results show that the heat treatment in furnace and the chemical treatment (decomposition of NH_4Cl) don't affect the structure of montmorillonite of regenerated material (RSBE). The study of porous texture by the nitrogen adsorption technique at −196 °C shows that the specific surface area S_{BET} and the pore volume increased in the RSBE material compared to those of virgin bleaching earth VBE (unused) and their values are respectively of 145.68 against 115.5 $m^2\ g^{-1}$ and of 0.287 against 0.234 $cm^3\ g^{-1}$. Calculations by the adsorption equations using BJH method, applied to both materials, show that the treatment generate an increase in the micropores in the RSBE material. We belonged the values of the micropores area of $S_{mic} = 41.98\ cm^2\ g^{-1}$ and of $V_{mic} = 0.074\ cm^3\ g^{-1}$ for the volume.

Keywords: Regeneration; B. Porosity; D. Clay; D. SiO_2

1. Introduction

The refining process of crude edible oil includes four operations: degumming, neutralization, bleaching and deodorization. The Bleaching operation is carried out by means of a clay (bentonite) activated at hot by sulfuric acid, called bleaching earth and noted VBE [1]. This material eliminates the undesirable elements such as the dyes (the chlorophyll-α and the β-carotene) and other residues (soap residues, traces of heavy metal...), contained in crude oil [2]. After use in the oil bleaching, the material loses its adsorption properties acquired during acid activation, and becomes a waste, called spent bleaching earth (SBE). These solids wastes are thrown in the nature, without undergoing any treatment. The SBE containing up to 20% (w/w) of oil becomes a pollutant; in addition to the release of unpleasant odors, the elements composing the residual oil represent a danger for the environment [3]. Region of Bejaia has two edible oil refineries (COGB-Labelle and Cevital) which generate great quantities of bleaching earth waste which are in rubbish dump without any treatment that would prevent contamination of the environment, which, with time going on, pose an acute problem of management and storage of this solid waste and the harmful effects that they produce.

The regeneration of this waste has aroused a great interest among many researchers who have devoted to it several of their works. It is generally done by heat and chemical treatments [4–6], with solvents extraction [7] or the combination of these various methods [8].

This article, which is a synthesis of the methods previously described, brings back the study of a method of regeneration of the spent bleaching earth impregnated in a solution of ammonium chloride (3 M), followed by a heat treatment in the furnace at 400 °C during an hour and a washing in the cold

* Corresponding author at: Faculté de Technologie, Département de Génie des procédés, Université Abderrahmane Mira, Rue Targa Ouzemour, Béjaia 06000, Algérie. Tel.: +213 668 31 03 53; fax: +213 34 21 57 04.
E-mail addresses: chafikah@yahoo.fr, hamid_602001@yahoo.fr (C. Meziti).
[1] Postal address: Faculté des Sciences Exactes, Département de chimie, Université Abderrahmane Mira, Rue Targa Ouzemour, Béjaia 06000, Algérie.

0272-8842/$36.00 © 2011 Published by Elsevier Ltd and Techna Group S.r.l.
doi:10.1016/j.ceramint.2011.02.016

in a hydrochloric acid solution 1 M. The ammonium chloride having weak acid properties breaks down under the heat action and the release of ammonia gas would involve a displacement of the decomposition balance with hydrochloric acid formation in rather weak concentration. The dissociation, which is catalyzed by the presence of water, is total around 350 °C [9]. The formed protons will release the adsorption sites by increasing the degree of division of clay. The produced acid will attack the alumina of the octahedral layer, thus, creating a porosity responsible for the improvement of the specific surface area of clay and the adsorptions phenomena [10,11]. The chlorides do not bring any change to specific surface area and do not attack the framework [12].

The main aim of this study is a contribution for a reduction of the pollution risk generated by these industrial wastes, which, while accumulating become a threat for our region. However, the characterization of regenerated material (RSBE) by physicochemical methods will make it possible to check the validity of the regeneration method of SBE material, used in this study.

2. Experimental

2.1. Materials

The spent bleaching earth (SBE) used in this study was provided by the unit of edible oil refining, unit of COGB-Label of Bejaia (Algeria). The virgin bleaching earth (VBE) is a bentonite originating from Maghnia activated with sulfuric acid (see Table 1). It is produced and commercialized by the society Bental (Algeria). All reagents used were of analytical grade.

2.2. Spent bleaching earth treatment

A suspension of spent bleaching earth in NH_4Cl solution 3 M is stirred during one night then centrifuged. The recovered solid is dried at 60 °C without washing, then crushed and sieved at 0.04 mm. The impregnated SBE is placed directly in porcelain crucibles then subjected to a heat treatment during 60 min in a furnace (Nabertherm D-2804) regulated at 400 °C, followed by a washing with a normal hydrochloric acid solution (5% (w/w)) at room temperature for 1 h. The obtained material is washed repeatedly with distilled water until negative test with $AgNO_3$, then crushed and sieved at 0.04 mm. The optimization of the physico-chemical parameters (temperature and duration of heating, concentration and solid/solution ratio) has been carried out in previous works [4,11].

2.3. Characterization of materials

The DRX spectra of the VBE and the RSBE have been obtained with monochromatic CuKα radiation using an X Pert Pro Panalytical diffractometer.

The FTIR spectra of different samples (lozenge of KBr 1%) were carried out with SHIMADZU FTRI 8400 spectrometer, in the range 4000–400 cm^{-1}.

SEM Observation of the VBE and the RSBE have been carried out with Quanta 200 scanning electron microscope. The porous texture of the RSBE and VBE is characterized by nitrogen gas adsorption at −196 °C, by using Quantachrome NovaWin2 apparatus. Prior to the determination of isotherm analysis, the sample has been degassed at about 160 °C for 12 h to remove moisture and other volatiles from the sample. BET equation is used in the range of the relative pressures between 0.039 and 0.200. The results of the follow-up of the relative pressure against the nitrogen volume adsorbed have allowed the calculation of the various parameters of texture (by using the equations of BET and BJH, respectively).

3. Results and discussion

The X-ray powder diffraction patterns (see Fig. 1) of VBE, SBE and RSBE show the same diffraction peaks, a characteristic of montmorillonite (M), and the presence of quartz impurities (Q). This confirms the results of the former studies as for the structure of material and proves also that the physicochemical treatment undergone by material doesn't affect its principal structure of montmorillonitic clay, peaks at 8.50°, 19.94°, 34.60° and 61.47°.

The FTIR spectra (see Fig. 2) confirms the presence of the structure of montmorillonite in the materials in particular the band near 3460–3650 cm^{-1} attributable to the stretching vibrations of the interlayer water molecule. The band at 1650 cm^{-1} corresponds to the hydroxyls vibration, 1050 cm^{-1} (Si–O stretching), 792 cm^{-1} (Si–O vibration of quartz impurities), and below 520 cm^{-1} (Si–O–Al bending). The VBE, RSBE and SBE spectra are similar, but the last exhibits the characteristic residual oil bands (spectrum b):

- A large Shoulder at 3250 cm^{-1}, attributable to the stretching vibrations of OH of carboxylic acids (free fatty acids).
- 2850 and 2920 cm^{-1}, stretching vibration of C–H of saturated carbonaceous chains of oil and the free fatty acids.

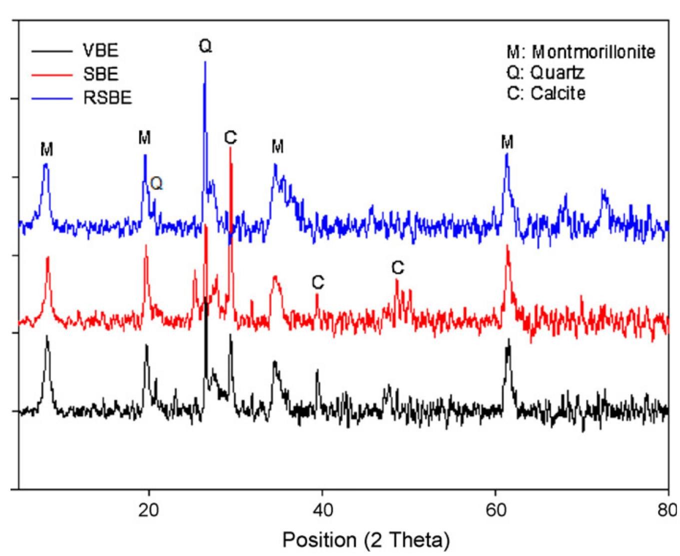

Fig. 1. X-ray diffraction powder of VBE, SBE and RSBE.

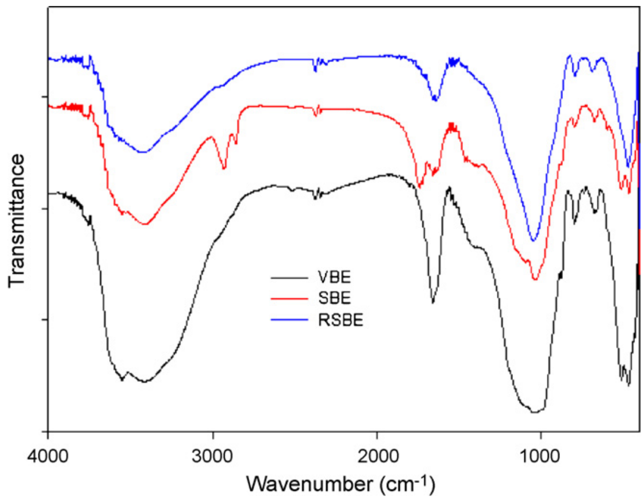

Fig. 2. FTIR spectra of VBE (a), SBE (b) and RSBE (c).

- 1730 cm^{-1}, strong stretching vibration of ester carbonyl of residual oil.
- 1470 cm^{-1}, deformation vibration of C–H of oil and/or deformation vibration of OH of the free fatty acids.

These bands disappear after the heat treatment. What implies that the organic residues adsorbed in the pores are completely eliminated by the physicochemical treatment from regeneration [5].

As for the spectra (a) and (c) they are practically identical what indicates that the heat treatment followed by washing does not seem to modify the structure of montmorillonite of bleaching earth. However, the spectrum (c) presents a broader band IR in the interval ranging between 1250 and 1100 cm^{-1}, a band characteristic of amorphous silica produced by the physicochemical treatment, and which could provide adsorption active sites. The particles of amorphous silica induce the presence of micropores in the RSBE material [13].

The curves of nitrogen adsorption isotherms of VBE and RSBE are presented on Fig. 3. The shape of these isotherms are similar and connected to type IV according to the Brunauer, Demming, Demming and Teller (BDDT) classification with the hysteresis corresponding to type H_3 of the International Union of Pure and Applied Chemistry classification (IUPAC) [14]. It is well known that the type IV isotherms are characteristic of mesoporous materials. The shape of hysteresis characterizes the shape of the pores and the H_3 type indicates that the two materials have slit-shaped pores [14,15]. What can appear at materials composed of plate-like particles or of a layer structure that is typical of clay structures. Also such type of hysteresis is the sign of a particle agglomeration forming the slits with sizes or forms non-uniform [16].

The rise in specific surface area S_{BET} indicates that porous texture has changed. Generally, this rise results from the action of acid which causes the dissolution of the impurities and the replacement of the exchangeable cations by protons. This, associated with heat, results the departure of Al^{3+}, Mg^{2+} and Fe^{3+} elements of the octahedral or tetrahedral sites. Empty spaces which are occupied by these metals gives rise to micropores. This behavior has already been observed in the literature in the case of activation with the sulphuric acid at high temperature [16–20].

The analysis of these results (see Table 2) shows the probable absence of the micropores in VBE material and their strong presence in RSBE material. Indeed, the activation by NH_4Cl has produced amorphous silica causing the increase in the micropores in RSBE material [18–20]. Obtaining a negative value of C in the case of the RSBE indicates a certain degree of microporous character of the sample [21,22].

The microporous volume of the regenerated bleaching earth (RSBE) is determined by starting from the Dubinin-Radushkevich equation, by carrying in diagram the value of log V_{ads} as a function of (log $(P_0/P))^2$.

From Fig. 4, we notice that the experimental points related to RSBE material, for the low pressures, are placed on a line whose ordinate at origin defines the value of the nitrogen volume adsorbed in the micropores (V_{mic}) and thus the volume developed by the micropores of the solid.

The value of C in the P/P_0 field ranging between 0.05 and 0.35 is negative. What implies that the calculation of V_M

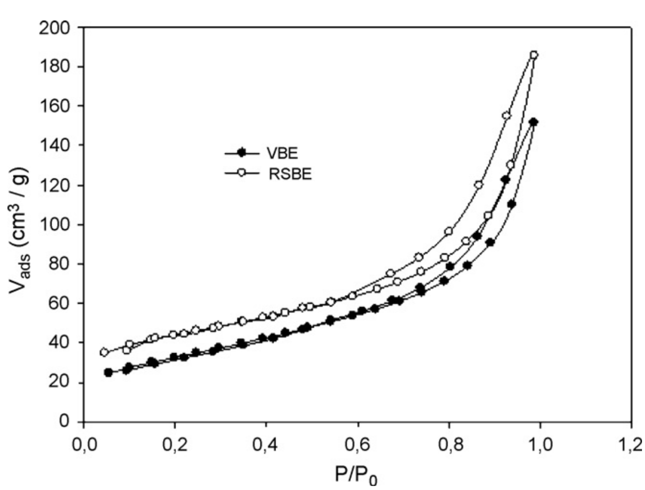

Fig. 3. Isotherms for the adsorption and desorption of nitrogen at 77K on the VBE and RSBE samples.

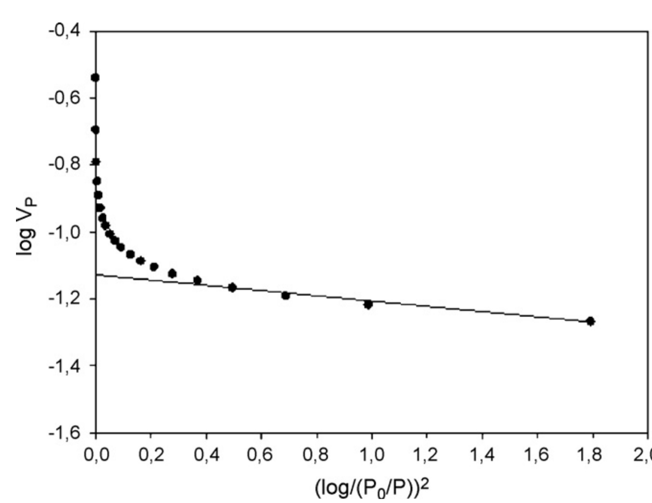

Fig. 4. Dubinin-Radushkevich transformation of the RSBE.

Table 1
Main components of virgin bleaching earth (VBE) (Bental source).

Components	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O
% mass	61.96	9.81	3.51	1.59	2.92	0.05	0.01

Table 2
The textural characteristics of VBE and regenerated material.

Sample	C_{BET}	V_m (cm^3/g)	S_{BET} (m^2/g)	V_P (cm^3/g)	V_{mic} (cm^3/g)	V_{ultra} (cm^3/g)	S_{mic} (m^2/g)	S_{ext} (m^2/g)
VBE	125.67	26.525	115.543	0.234	–	–	–	115.9
RSBE	−150.5	33.445	145.686	0.287	0.074	0.019	41.98	111.14

C_{BET}: BET constant, V_m: monolayer volume, S_{BET}: specific surface area calculated by BET method, V_P: total porous volume, V_{mic}: micropores volume, V_{ultra}: ultramicropores volume, S_{mic}: micropores area, S_{ext}: external surface area.

starting from this value C is incorrect. Moreover, obtaining a negative value of C in the case of the RSBE indicates some degree of microporous character of the sample [21,22]. Indeed, adsorption in the micropores is not governed by the BET equation. To solve these inconsistencies, the literature [22] suggests restricting the field of the relative pressures. However, the value of the BET specific surface area obtained in this case by application of the BET equation is called equivalent BET specific surface area, to mean that this value was calculated by admitting that a monomolecular layer is formed in the micropores in the same way that on the plane surface [22] (Fig. 5).

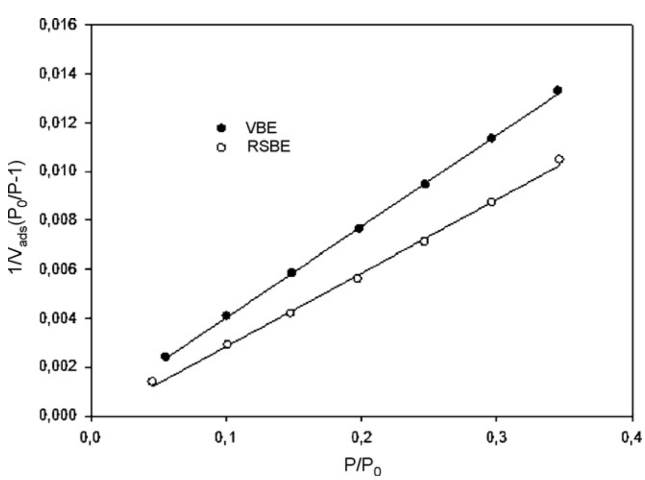

Fig. 5. BET transformation of the RSBE and VBE.

To raise this ambiguity (positive value of C), we must apply the BET law to the restricted field of the relative pressures $0.05 \leq P/P_0 \leq 0.25$. The obtained results in this field are 947.67 and 153.22 m^2/g for C and S_{BET}, respectively.

The porous distribution has carried out by the BJH method. The pore volume and surface distribution curves corresponding to the two adsorbents VBE and RSBE, by using the adsorption isotherm, are plotted on Figs. 6 and 7, respectively.

The pores distribution curve translates a heterogeneous distribution of the slits with a major peak at 18 Å for VBE and 16.8 Å for RSBE and a majority of pores whose size is lower or equal to 100 Å. These two sizes of rays represent the family of mesopores ([14,15].

The SEM observations (see Fig. 8a and b) show that the porous structure of the RSBE is well developed compared to that of VBE. The fitting of the micrograms explains the mesopores volume and the important external surface of both materials.

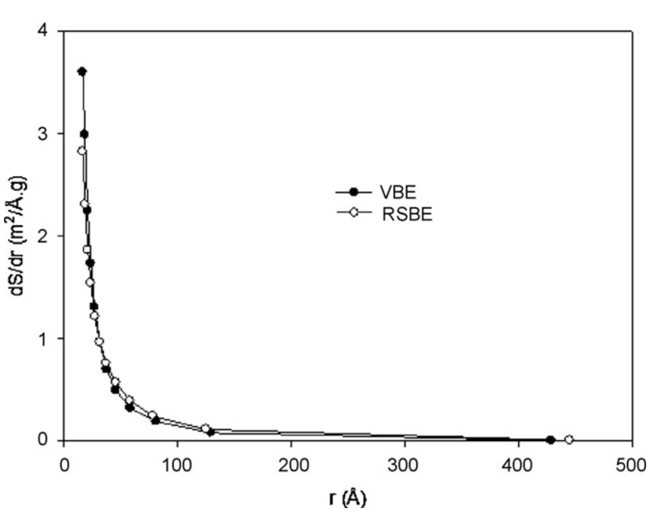

Fig. 6. Pore surface area repartition of samples in adsorption (BJH method).

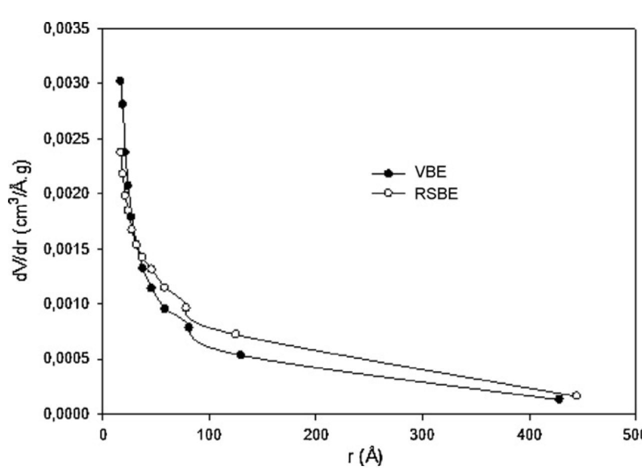

Fig. 7. Pore volume repartition of samples in adsorption (BJH method).

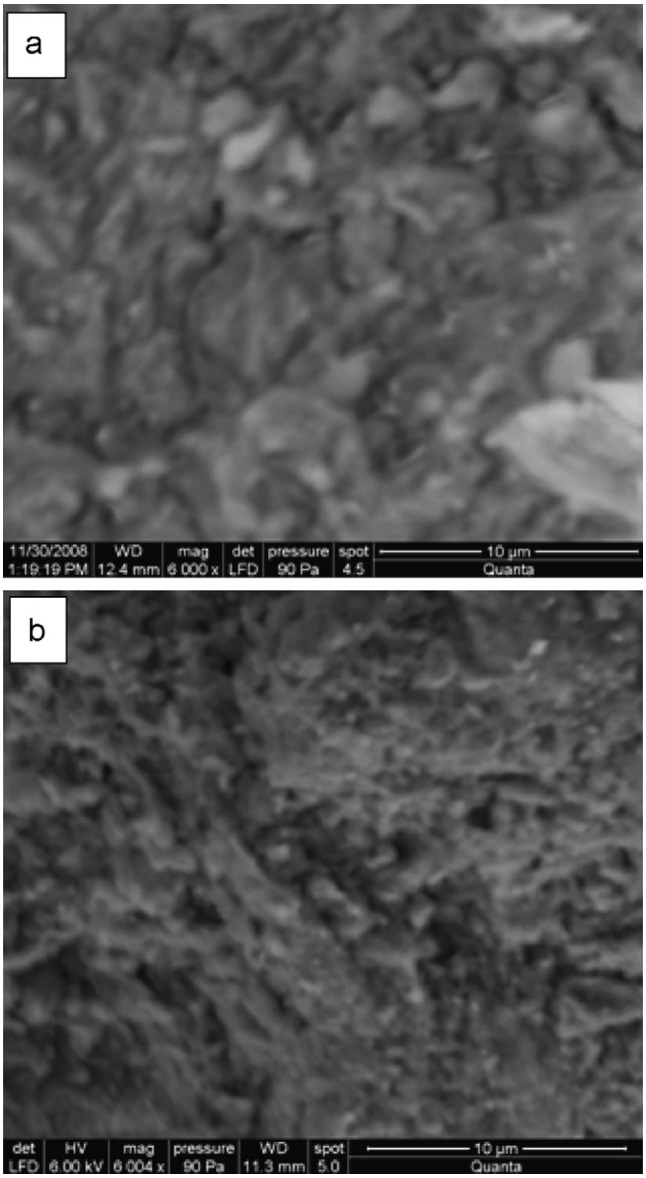

Fig. 8. SEM observations of (a) VBE and (b) RSBE.

4. Conclusions

The impregnation by ammonium chloride solution followed by heat treatment in furnace of solid waste originating from an edible oil refinery have allowed its regeneration without modifying its principal structure of montmorillonite. The analysis of porous texture reveals that the material has recovered its original state (mesoporosity) of before use. Moreover, the decomposition of NH_4Cl under the heat effect caused an increase in microporosity in the regenerated material.

The results of porous texture show that spent bleaching earth, a pollutant industrial waste can be regenerated and reused as a low cost mineral adsorbent.

References

[1] M.A. Didi, B. Makhoukhi, A. Azzouz, D. Villemin, Colza oil bleaching through optimized acid activation of bentonite: a comparative study, Appl. Clay Sci. 42 (2009) 336–344.
[2] E. Sabah, M.C. Inar, M.S.C. Elik, Decolorization of vegetable oils: adsorption mechanism of β-carotene on acid-activated sepiolite, Food Chem. 100 (2007) 1661–1668.
[3] S.J.T. Pollard, C.J. Sollars, R. Perry, The reuse of spent bleaching earth: a feasibility study in waste minimization for the edible oil industry, Bioresour. Technol. 45 (1993) 53–58.
[4] A. Boukerroui, M.S. Ouali, Regeneration of a spent bleaching earth and its reuse in the refining of an edible oil, J. Chem. Technol. Biotechnol. 75 (2000) 773–776.
[5] W.T. Tsai, H.P. Chen, M.F. Hsieh, H.F. Sun, S.F. Chien, Regeneration of spent bleaching earth by pyrolysis in a rotary furnace, J. Anal. Appl. Pyrolysis 63 (2002) 157–170.
[6] M. Mahramanlioglu, O. Ozgen, A. Cinarli, I. Kizilcikli, Adsorption of pyridine by acid treated spent bleaching earth, Asian J. Chem. 22 (2) (2010) 1428–1434.
[7] A. Al- Zahraoui, Y.A. Alhamed, Oil removal from spent bleaching clay by solvent extraction, J. Environ. Sci. Health, Part A 35 (2000) 1577–1590.
[8] E.W. Wambu, G.K. Muthakia, J.K. Wa-Thiong'O, P.M. Shiundo, Regeneration of spent bleaching earth and its adsorption of copper (II) ions from aqueous solution, Appl. Clay Sci. 46 (2009) 176–180.
[9] S. Balci, T. Dogu, H. Yucel, Characterization of activated carbon produced from almond shell and hazelnut shell, J. Chem. Technol. Biotechnol. 60 (1994) 419–426.
[10] A. Boukerroui, M.S. Ouali, Activation d'une bentonite par un sel d'ammonium: évolution de la capacité d'échange et de la surface spécifique, Ann. Chim. Sci. Mat. 25 (2000) 583–590.
[11] A. Boukerroui, M.S. Ouali, Edible oil bleaching with a bentonite activated by microwave irradiation, Ann. Chim. Sci. Mat. 27 (4) (2002) 73–81.
[12] Z. Sarbak, Structural and surface properties of anion-activated clay, Mater. Chem. Phys. 39 (1994) 91–97.
[13] M. Hajjaji, H. El Arfaoui, Adsorption of methylene blue and zinc ions on raw and acid-activated bentonite from Morocco, Appl. Clay Sci. 46 (2009) 418–421.
[14] S. Lowell, J.E. Shields, Powder surface area and porosity, third ed., Chapman & Hall Ltd, London, 1991.
[15] A. Lecloux, Exploitation des isothermes d'adsorption et de désorption d'azote pour l'étude de la texture des solides poreux, Mémoire Société Royale des Sciences de Liège, 6éme série, tome I, Fasc 4 (1971) 169–209.
[16] W.T. Tsai, H.P. Chen, W.Y. Hsien, C.W. Lai, M.S. Lee, Thermochemical regeneration of bleaching earth waste with zinc chloride, Resour. Conserv. Recycl. 39 (2003) 65–77.
[17] S. Korichi, A. Elias, A. Mefti, Characterization of smectite after acid activation with microwave irradiation, Appl. Clay Sci. 42 (2009) 432–438.
[18] P. Kumar, R.V. Jasra, T.S.G. Bhat, Evolution of porosity and surface acidity in montmorillonite clay on acid activation, Ind. Eng. Chem. Res. 34 (1995) 1440–1448.
[19] H. Noyan, O. Userref, S. Yuksel, The effect of sulphuric acid activation on the crystallinity, surface area, porosity, and bleaching power of a bentonite, Food Chem. 105 (2007) 156–163.
[20] J. Temmuujin, Ts. Jadambaa, G. Burmaa, Sh. Erdenechimeg, J. Amarsanaa, K.J.D. MacKenzie, Characterizations of acid activated montmorillonite clay from Tuulant (Mongolia), Ceram. Int. 30 (2004) 251–255.
[21] A. Gervasini, Characterization of the textural properties of metal loaded ZSM-5 zeolites, Appl. Catal., A 180 (1999) 71–82.
[22] F. Rouquerol, L. Luciani, P. Lewellyn, R. Denoyel, J. Rouquerol, Texture des matériaux pulvérulents ou poreux, Techniques de l'ingénieur P1050 (2003).