Response surface modeling of acid activation of raw diatomite using in sunflower oil bleaching by: Box–Behnken experimental design

M. Larouci · M. Safa · B. Meddah · A. Aoues · P. Sonnet

Revised: 11 July 2013 / Accepted: 18 July 2013 / Published online: 25 August 2013
© Association of Food Scientists & Technologists (India) 2013

Abstract The optimum conditions for acid activation of diatomite for maximizing bleaching efficiency of the diatomite in sun flower oil treatment were studied. Box–Behnken experimental design combining with response surface modeling (RSM) and quadratic programming (QP) was employed to obtain the optimum conditions of three independent variables (acid concentration, activation time and solid to liquid) for acid activation of diatomite. The significance of independent variables and their interactions were tested by means of the analysis of variance (ANOVA) with 95 % confidence limits ($\alpha=0.05$). The optimum values of the selected variables were obtained by solving the quadratic regression model, as well as by analyzing the response surface contour plots. The experimental conditions at this global point were determined to be acid concentration = 8.963 N, activation time = 11.9878 h, and solid to liquid ratio = 221.2113 g/l, the corresponding bleaching efficiency was found to be about 99 %.

Keywords Diatomite · Bleaching · Oil · Optimization · Box–Behnken experimental design

Introduction

Crude edible oils obtained by solvent extraction or compression from plants such as soybean, sunflower, sunflower, corn,

cottonseed, rapeseed, mustard seed, sesame, palm, peanut, coconut and olive, contains free fatty acids, gummy materials and coloring matters, known to be detrimental to oil flavor and stability (Boki and Kawasaki 1994). It 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, phosphates, trace metals, and oxidation products are removed from the alkali-refined oils by bleaching process (Falaras et al. 1999; Kheok and Lim 1982; Morgan et al. 1985; Oboh and Aworh 1988; Rossi et al. 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. Different types of adsorbents such as activated earth, activated carbon, kieselguhr or diatomaceous earth and silica-based products are adsorbents commonly used in the edible oil bleaching process.

Bleaching power is dependent on the surface area, surface acidity, catalytic activity, porosity and pore size distribution of the bleaching earth (Breen et al. 1997; Önal et al. 2002; Srasra et al. 1989; Vicente-Rodriguez et al. 1996). These physico-chemical properties of bleaching earths change depending on the mineralogical and chemical composition of the activated bleaching earth, type and concentration of the inorganic acid, used in the process and also temperature and time of activation.

However, Fuller's earth-type activated clay is the most popular bleaching agent of edible oil because of its cheapness price compared to activated carbon- and silica-based products. Since acid-activated bentonites have more ability to bleach coloring matters (Christidis and Kosiari 2003). Although there are other bleaching agent, such as diatomite, considered as low-cost adsorbents with typical desirable properties, e.g. highly porous structure, low density and high surface area, which consists essentially of amorphous silica ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$). It is thus, an alternative material to other sorbents in processes such as wastewater treatment, in the removal of heavy metals

M. Larouci (✉) · M. Safa · B. Meddah · A. Aoues · P. Sonnet
The Faculty of Natural and Life Sciences, Laboratory of BGMSS,
Mascara University, P.O. Box 763, 29000 Mascara, Algeria
e-mail: hamasafa@hotmail.fr

M. Larouci · M. Safa · B. Meddah · A. Aoues
Department of Biology, Laboratory of Experimental Biototoxicology,
Biodepollution and Phytoremediation, University of Es-Senia, Oran,
Algeria

P. Sonnet
Laboratoire des glucides- FRE-CNRS 3517, UFR de Pharmacie,
Université de Picardie, 80037 Amiens, France

such as Pb^{2+} , Cd^{2+} , Zn^{2+} and Cu^{2+} . They have not been much documented in the literature as bleaching agent.

It is therefore the objective of this study to optimize the acid activation of a raw diatomite using three factors, three-level Box–Behnken experimental design combining with RSM and quadratic programming (QP) in order to improve the effectiveness, expressed in terms of bleaching efficiency in the sun flower oil processing. For this purpose, we examined the effects of three independent variables (acid concentration, contact time and solid to liquid ratio) and their interactions upon the activation. The latter ought to be proportional to the effectiveness in the sun flower oil treatment.

Materials and methods

Preparation and characterization of raw diatomite

Natural raw diatomite samples collected from ENOF Sig, Mascara Region, Algeria, were crushed into aggregate sized pieces in roller mills, air dried and gently ground to pass through a 75 μm mesh metal sieve.

The physicochemical characterization of raw diatomite and activated diatomite was performed using standard procedures. Characterization of the raw diatomite and activated diatomite were carried out by chemical composition, surface area analysis and bulk density. The chemical composition of diatomite is determined by X-ray fluorescence; the surface area of diatomite was obtained by using the Brunauer, Emmett and Teller (BET) method. Nitrogen adsorption at 77 K is a standard and widely used method for determining surface area, pore volume and pore size distribution of the adsorbent. The cation exchange capacity (CEC) of the investigated adsorbent was tested using the ammonium exchange method. The density of the samples was determined by specific gravity bottle and the structure was studied using X-ray diffractograms (XRDs).

Preparation and acid activation of diatomite

The activated diatomite was prepared by mixing the raw diatomite with different concentration of H_2SO_4 varying from 2 to 10 N, equilibrated for various contact time 4–12 h and solid to liquid ratio of 100–300 g L^{-1} under continuous whisking at the temperature of 80 ± 1 °C. The residual solid was separated from the mixture by passing the slurry through a filter membrane under vacuum. The crude soil was further washed several times with distilled water. The obtained material was then dried in an oven at 60 °C through 15 h and reground using mesh metal sieve into a particle size 75 μm , the activated samples were stored in tightly closed plastic bottles. These acid activated diatomites were used to bleach the neutralized and dried sunflower oil.

Bleaching

Pretreated, neutralized, washed sunflower oil was provided by Vegetal Oil Refining Enterprise CEVITAL SPA (Bejaia, Algeria). A perfectly dry oil sample has the following features: water: 0.09 %, phosphorus: 60 ppm, chlorophyll: 0.60 ppm, color tests to: yellow = 15, red = 1.9, acidity: 0.39 %, iodine value: 133, peroxide value: 3.4 meq $\text{O}_2/\text{Kg oi}$ and saponification value: 189 mg KOH/g of oil.

The vacuum bleaching tests were performed, in a round bottom for neck round-bottom flask which was connected to a vacuum pump capable of achieving 400 mmHg vacuums. The bleaching method involved placing 100 g of dried sunflower oil and 1 g of activated diatomite into a round-bottom flask of 250 ml. The mixtures were heated under continuous stirring approximately 200 ± 10 rpm at 80 ± 3 °C, for 20 min throughout the bleaching process under reduced pressure.

At the end of the bleaching time, vacuum was stopped and the oil/diatomite slurry was separated by filtration with filter paper (20–25 μm retention) under vacuum suction. Finally, a sufficient amount of bleached sunflower oil was collected for the determination of color index.

Determination of color index of sunflower oil

The color indices of sunflower oil before and after bleaching were measured by a Lovibond tintometer using a 5.25-in. cell. The procedure of AOCS (1997) Official Method Cc 13b-45 was followed. The color index was determined immediately after the bleaching test in order to prevent the oxidation of oil in air.

The bleaching efficiency of activated diatomite was calculated by the following equation:

$$BE = \frac{R_0 - R_1}{R_0} \times 100 \quad (1)$$

where

R_0 red color index of sunflower oil before bleaching

R_1 red color index of sunflower oil after bleaching.

Three runs were conducted under the same experimental conditions, and the average bleaching efficiency was taken from these runs.

Optimization

In this work, to determine the optimum conditions and derive a model for acid activation of a diatomite a 2^3 factorial design was investigated to optimize the analytical conditions that affect the analyte response signals. Three factors were investigated at two levels each, acid concentration (X_1), activation time (X_2) and solid to liquid ratio (X_3) were chosen as independent variables to model, with centre points were employed

to fit the second order polynomial model which indicated that 15 experiments were required for this procedure. The range and the levels of the experimental variables investigated in this study were given in Table 1.

The behavior of the system is explained by the following empirical second-order polynomial regression equation of the following form Eq. (2):

$$Y = \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i=1}^k \sum_{j=1}^K \beta_{ij} x_i x_j + \varepsilon \quad (2)$$

where Y : predicted response, β_o : offset term, β_i : coefficient of linear effect, β_{ii} : coefficient of square effect, and β_{ij} = coefficient of interaction effect. Response surfaces and contour plots were attained using the fitted model by keeping the least effective independent variable at a constant value while changing the other two variables. In this study, the design of the experiment and the data treatment of the Box–Behnken experimental design were performed using statistical software STATISTICA.

Results and discussion

Diatomite characterisation

The elemental composition of the natural raw diatomite and activated diatomite expressed as weight percentages of metal oxide was shown in Table 2. The main components of the natural raw diatomite are oxides of Si, Al and Fe, while the main components of the sample activated with acid are oxides of Si and Al. The acid treatment reduces or eliminates all other oxides relative to SiO_2 raised from 72.1 to 88.6, mainly due to dealumination upon acid treatment. This is well supported by a decrease of the alumina fraction from 5.30 % to 3.19 %.

From XRD patterns (see Fig. 1(a) and (b)), the natural diatomite showed a single diffuse band centered at about $23^\circ 2\theta$ which could be identified as biogenic hydrous amorphous silica and also showed quartz at $2\theta = 26.4^\circ$ and 21.1° and some clay minerals. After acid activation of raw diatomite, the XRD patterns showed formation of a new peak and

Table 2 Chemicals composition of raw diatomite and activated diatomite

Constituents	Percent by weight (%)	
	Raw diatomite	Activated diatomite
SiO_2	72.1	88.6
Al_2O_3	5.30	3.19
CaO	7.20	3.58
Fe_2O_3	3.80	2.14
MgO	2.60	1.32
Na_2O	0.65	0.29
K_2O	0.54	0.13
TiO_2	0.37	0.11

elimination of some peak. It is noted that the absolute intensity of quartz at $2\theta = 26.4^\circ$ and 21.1° increase after acid treatment, this suggested that some impurities and/or sufficient amount of Si–OH in the amorphous silica matrix could promote the transformation of some amorphous silica into crystalline structure. It seemed that quartz still remained even when it was treated with hot acid. However, the XRD pattern of the

Fig. 1 XRD patterns of the raw diatomite (a) and activated diatomite (b)

Table 1 Experimental range and levels of independent variables

Variables	Ranges and levels		
	Low level (−1)	Center level (0)	High level (+1)
Acid concentration X_1 (N)	2	6	10
Contact time X_2 (h)	4	8	12
Solid to liquid ratio X_3 (g/L)	100	200	300

activated diatomite shows reflections characteristic for amorphous silica, as shown by the increase of the broad characteristic band of this compound situated between 15 and 30° 2 θ this due to the deposition of amorphous silica gel caused after the attack on the octahedral layer and the exposure of the tetrahedral layer (Christidis et al. 1997) (Fig. 2).

The BET test was conducted to determine the textural parameters, such as BET surface area, pore volume, and average pore diameter of raw diatomite and activated diatomite. Results are tabulated in Table 3. As shown in Table 3, the BET surface area of activated diatomite is 134.3 m²/g, which is 6.4 fold greater than that of raw diatomite 21 m²/g. The average pore diameter of activated diatomite is estimated to be 2.35 nm, while that of raw diatomite is 5.86 nm, and the total pore volume of activated diatomite relative to raw diatomite increased from 0.181 to 0.0402 cm³/g.

Determination of the regression model and the effects of model components and their interactions on bleaching efficiency

By applying multiple regression analysis on the design matrix and the responses given in Table 4, the following second-order polynomial equation in coded form was established to explain the bleaching efficiency:

$$Y = 82.06 + 14.38x_1 + 4.85x_2 + 4.73x_3 + 3.82x_1x_2 + 7.35x_1x_3 - 3.12x_2x_3 - 11.20x_1^2 + 4.06x_2^2 - 8.50x_3^2 \quad (3)$$

Where Y is the predicted bleaching efficiency, x_1 , x_2 and x_3 are the coded terms for three independent test variables, acid concentration, activation time and solid to liquid ratio respectively. The optimum values of the selected test variables were obtained by solving the Eq. (3) and also by analysing the response surface contour plots. Therefore, the ANOVA was conducted to test the significance of the fit of the second-order polynomial equation for the experimental data as given in Table 5.

As seen in Table 5, the ANOVA of the regression model (Eq. (3)) showed that the quadratic model was highly significant, as was evident from the Fisher's F -test ($F_{\text{model}} = 50.19$) with a very low probability value ($P_{\text{model}} > F = 0.0002$), this indicating that the computed Fisher's variance ratio was large enough to justify a very high degree of adequacy of the quadratic model and also to indicate that treatment combinations are highly significant, as similarly reported by others (Liu et al. 2004; Sen and Swaminathan 2004).

The goodness of fit of the model was checked by the determination coefficient (R^2). In this case, the value of determination coefficient ($R^2 = 0.9891$). In addition, the value of

Fig. 2 3D response surface diagrams showing the effects of the mutual interactions between two independent variables (other variables were held at their respective center levels) on the bleaching capacity of diatomite; **a** acid concentration (X_1) and activation time (X_2), **b** acid concentration (X_1) and solid to liquid ratio (X_3), **c** activation time (X_2) and solid to liquid ratio (X_3)

Table 3 Physicochemical properties of raw and activated diatomite

	Surface area (S_{BET}) (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm)	Bulk density (cm^3/g)	CEC (meq/g)
Raw diatomite	21	0.0402	5.86	0.217	2.31
Activated diatomite	154	0.181	2.35	0.159	1.93

adjusted determination coefficient ($R_a^2=0.9694$) was also very high, showing a high significance of the model, as similarly reported by others (Adinarayana and Ellaiah 2002). Moreover, a very high value of the correlation coefficient ($R=0.9945$) signified an excellent correlation between the predicted values (responses) and the experimental results, the high values of R^2 , R_a^2 and R indicated that the quadratic equation was capable of representing the system under the given experimental domain.

The significance of each coefficient was determined by Student's t -test and p values, which are listed in Table 6. Results showed that the first-order main effects of acid concentration (x_1), and activation time (x_2) were found to be more significant than their respective quadratic effects (x_1^2 and x_2^2), as was evident from their respective t ratios and p values. These values suggest that the different parameters studied have a direct relationship on the bleaching efficiency, except solid to liquid ratio the effect of quadratic term of x_3^2 ($p=0.0016$) are slightly higher than the first-order effect of x_3 ($p=0.0038$). Didi et al. (2008) observed similar phenomenon of acid concentration, activation time and solid to liquid ratio in an optimization based on a 3^3 full-factorial design conducted to optimize bleaching efficiency

of colza oil by bentonite. As seen in Tables 5 and 6, the most significant component of the regression model was found as the acid concentration (x_1) for the present application ($t=15.4597$, $p=2.06\text{E-}5$, $F=239$). Among all model components, the interaction between x_1 and x_3 demonstrated the heights effect on the bleaching efficiency ($t=5.5845$, $p=0.0025$, $F=31.187$). The quadratic terms of x_1^2 , x_2^2 and x_3^2 were also considerably important ($p=0.0004$, $p=0.0312$ and $p=0.0016$ respectively).

The bleaching efficiency measured for the different batches showed a wide variation ranging from a minimum of 45 % to a maximum of 95.50 % (Table 4). Results clearly indicated that the bleaching efficiency was strongly affected by the variables selected for the study.

The TPCi , TPCii , and TPCij are the total percentage contributions (TPC) of first-order, quadratic and interaction terms, respectively. The results indicated that the TPCi of first-order term demonstrated the highest level of significance with a total contribution of 64.64 % as compared to TPC values of quadratic and interaction terms with a total contribution of 25.32 and 10.02 % respectively, this indicating that the interaction components show a low effect in prediction of the bleaching efficiency.

Effects of model components and their interactions on bleaching efficiency

Three dimensional response surface plots as a function of two factors, maintaining all other factors at fixed levels are more helpful in understanding both the main and the interaction effects of these two factors (Adinarayana and Ellaiah 2002). In

Table 4 Box-behnken design matrix with three independent variables expressed in coded units

Batch N°	Acid concentration (mol)		Contact time (h)		Solid to liquid ratio (g/L)		Bleaching capacity (%)	
	X_1 (coded)	X_1 (uncoded)	X_2 (coded)	X_2 (uncoded)	X_3 (coded)	X_3 (uncoded)	Observed Y_0	Predicted Y_p
1	0	6	-1	4	-1	100	63,0	59,51
2	0	6	0	8	0	200	82,0	80,63
3	-1	2	0	8	1	300	45,0	64,91
4	-1	2	0	8	-1	100	50,0	61,56
5	1	10	0	8	-1	100	65,0	84,08
6	0	6	1	12	-1	100	83,0	80,86
7	1	10	1	12	0	200	95,5	88,82
8	-1	2	1	12	0	200	60,0	80,63
9	0	6	1	12	1	300	86,0	97,98
10	0	6	0	8	0	200	82,0	82,06
11	1	10	0	8	1	300	89,4	50,57
12	0	6	0	8	0	200	82,2	82,06
13	-1	2	-1	4	0	200	62,0	64,65
14	0	6	-1	4	1	300	78,5	45,35
15	1	10	-1	4	0	200	82,2	82,06

Table 5 Analysis of variance (ANOVA) of the response surface model for the prediction of bleaching capacity

Factors (coded)	Sum of squares	Degrees of freedom	Mean Sum of squares	<i>F</i> values	Probability (<i>P</i>)
Model	3130,3198	9	347,8133	50,198	0,0002
Linear effect	2023,7325	3	674,5775	97,358	7,44E-05
X_1	1656,0013	1	1656,0013	239,0015	2,06E-05
X_2	188,18	1	188,18	27,159	0,0034
X_3	179,5513	1	179,5513	25,9136	0,0038
Quadratic effect	792,9123	3	264,3041	38,1455	0,0007
X_1^2	442,831	1	442,831	63,9113	0,0005
X_2^2	82,7888	1	82,7888	11,9484	0,0181
X_3^2	267,2926	1	267,2926	38,5768	0,0016
Interaction effect	313,675	3	104,5583	15,0903	0,0061
X_1X_2	58,5225	1	58,5225	8,4462	0,0335
X_1X_3	216,09	1	216,09	31,1871	0,0025
X_2X_3	39,0625	1	39,0625	5,6377	0,0636
Error	34,6442	5	6,9288		
Total	3164,964	14			

this study, 3D response surfaces of fitted second-order Eq. (3) have been used to visualize the effects of independent parameters: acid concentration (x_1), activation time (x_2) and solid to liquid ratio (x_3) on the bleaching efficiency. Figure 2 show the 3D response surfaces as the functions of two variables at the center level of other variables. The nonlinear nature of all 3D response surfaces demonstrated that there were considerable interactions between each of the independent variables and the bleaching efficiency. In Fig. 2a, b and c, in general the bleaching efficiency increased with the increase in acid concentration and activation time.

Optimization studies for maximizing bleaching efficiency

On the basis of the calculation steps defined for the optimization algorithm, the optimal values of the test variables in coded

units were found as $x_1=0.7408$, $x_2=0.995$, and $x_3=0.1121$ with the corresponding $Y=99$. The real values were then determined to be acid concentration = 8.963 N, activation time = 11.9878 h, and solid to liquid ratio = 221.2113 g/l, this results confirming once again the judicious choice of the parameters ranges and the applicability and accuracy of the model developed to describe the correlation between the diatomite activation factors and its performances in bleaching sunflower oil. Under these conditions, a bleaching efficiency value of 99 % was obtained.

A number of characteristics determine the efficiency of a material as a bleaching earth. These properties are: adsorption capacity, acid properties, catalytic properties, ion exchange capacity, particle and pore size distributions. The acid treatment of diatomite removes cations from octahedral and tetrahedral sheets and leaves a large number of highly active

Table 6 Multiple regression results and significance of the components for the quadratic model

Factors (coded)	Parameter	Coefficient	Effect	Standard error	<i>t</i> value	<i>P</i> value	Sum of squares	PC (%)
Intercept	B_0	82,0667						
X_1	β_1	14,3875	28,775	0,9306	15,4597	2,06E-05	1656,0013	52,90
X_2	β_2	4,85	9,7	0,9306	5,2114	0,0034	188,18	6,012
X_3	β_3	4,7375	9,475	0,9306	5,0905	0,0038	179,5513	5,64
X_1^2	β_{11}	-11,2083	-22,446	1,3699	-8,182	0,0004	442,831	14,14
X_2^2	B_{22}	4,0667	8,133	1,3699	2,9686	0,0312	82,7888	2,645
X_3^2	B_{33}	-8,5083	-17,016	1,3699	-6,211	0,0016	267,2926	8,539
X_1X_2	B_{12}	3,825	7,65	1,3161	2,9062	0,0335	58,5225	1,87
X_1X_3	B_{13}	7,35	14,7	1,3161	5,5845	0,0025	216,09	6,998
X_2X_3	B_{23}	-3,125	-6,25	1,3161	-2,3744	0,0636	39,0625	1,248

silanol groups (Si–OH) on the adsorbent sites, and dissolves impurities such as calcite and replaces the exchangeable cations with hydrogen ions. Therefore the adsorptive of the diatomite may be due to effects of surface acidic functional groups found on the diatomite surface. The acid treatment also opens the edges of the platelets and as a consequence of all these changes, the surface area and the pore diameters increase. Also the adsorptive properties of the diatomite are due to the presence of tetrahedrally coordinated Al, formed from exposure of Al which substitutes for Si in the tetrahedral sheet as proposed by Rupert et al. (1987) in the case of bentonite.

Conclusions

The application of a three factor, three-level Box–Behnken experimental design combining with RSM and QP utilized in reaching the global optimal condition of acid activation for maximizing bleaching efficiency of the activated diatomite on dry sun flower oil. The proposed mathematical methodology also provided a critical analysis of the simultaneous interactive effects of independent variables, such as acid concentration, contact time and solid to liquid ratio for better understanding of the bleaching process. The optimum variables were found to be 8.963 N ($x_1=0.7408$) for acid concentration of the H_2SO_4 solution, 11.9878 h ($x_2=0.995$) for contact time and 221.2113 g/l ($x_3=0.1121$) for solid to liquid ratio with a predicted bleaching efficiency of about 99 %, which was also higher than any other bleaching efficiency obtained in the initial 15 experimental tests. The adequacy of the developed mathematical model was checked with the various descriptive statistics. Predicted values obtained using the quadratic model equation were in very good agreement with the observed values ($R^2=0.9891$, $R_a^2=0.9694$, $R=0.9945$ and $C_p=9.9902$ and). The statistical results showed that the first-order main effects of the independent variables (acid concentration, contact time and solid to liquid ratio) were found to be more significant than their respective quadratic effects, indicating that the selected variables had a direct relationship on the bleaching efficiency. The most significant component of the quadratic model was found as acid concentration for the present application ($t=15.4597$, $p=2.06E-05$, $F=239.0015$, $PCi=52.9$ %). Findings of this study also indicated that the total percentage contributions of first-order terms demonstrated the highest level of significance with a total contribution of 64.64 %% as compared to the respective TPC values of quadratic and interaction terms. The three-level Box Behnken experimental design combining with RSM and QP is an effective tool for mathematical modeling and factor analysis of the bleaching oil process.

References

- Adinarayana K, Ellaiah P (2002) Response surface optimization of the critical medium components for the production of alkaline protease by a newly isolated *Bacillus* sp. J Pharma Pharm Sci 5:272–278
- American Oil Chemists' Society (1997) Color wesson method using color glasses calibrated in accordance with the AOCS tintometer color scale, official methods and recommended practices of the American Oil Chemists' Society. AOCS Press, Champaign, Method Cc 13b-45
- Boki KH, Kawasaki N (1994) Bleaching rapeseed and soybean oils with synthetic adsorbents and attapulgit. J Am Oil Chem Soc 71:505–601
- Breen C, Zahoor ED, Madejová J, Komadel P (1997) Characterization and catalytic activity of acid-treated size-fractionated smectites. The J Phys Chem B 101:5324–5331
- Christidis GE, Kosiari S (2003) Decolorization of vegetable oils: a study of the mechanism of adsorption of b-carotene by an acidactivated bentonite from Cyprus. Clays Clay Miner 51(3):327–333
- Christidis GE, Scott PW, Dunham AC (1997) Acid activation and bleaching capacity of bentonites from the Islands of Milos and Chios, Aegean, Greece. Appl Clay Sci 12:329–347
- Didi MA, Makhoukhi B, Azzouz A, Villemin D (2008) Colza oil bleaching through optimized acid activation of bentonite. A comparative study. Appl Clay Sci 42:336–344
- Falaras P, Kovanis I, Lezo F, Seiragakis G (1999) Cottonseed oil bleaching by acid-activated montmorillonite. Clay Miner 34:221–232
- Kheok SC, Lim E (1982) Mechanism of palm oil bleaching by montmorillonite clay activated at various acid concentrations. J Am Oil Chem Soc 59:129–131
- Liu HL, Lan YW, Cheng YC (2004) Optimal production of sulphuric acid by *Thiobacillus thiooxidans* using response surface methodology. Process Biochem 39:1953–1961
- Morgan DA, Shaw DB, Sidebottom TC, Soon TC, Taylor RS (1985) The function of bleaching earths in the processing of palm kernel and coconut oils. J Am Oil Chem Soc 62:292–299
- Mounts TL (1981) Chemical and physical effects of processing fats and oils. J Am Oil Chem Soc 58:51A–54A
- Oboh AO, Aworh OC (1988) Laboratory trials on bleaching palm oil with selected acid-activated Nigerian clays. Food Chem 27:311–317
- Önal M, Sankaya Y, Alemdaroğlu T, Bozdoğan I (2002) The effect of acid activation on some of the physicochemical properties of a bentonite. Turk J Chem 26:409–416
- Rossi M, Gianazza M, Alamprese C, Stanga F (2003) The role of bleaching clays and synthetic silica in palm oil physical refining. Food Chem 82:291–296
- Rupert JP, Granquist WT, Pinnavaia TJ (1987) Catalytic properties of clay minerals. In: Newman ACD (ed) Chemistry of clays and clay minerals. Mineralogical Society, London
- Sen R, Swaminathan T (2004) Response surface modeling and optimization to elucidate and analyze the effects of inoculum age and size on surfactin production. Biochem Eng J 21:141–148
- Srasra E, Bergaya F, Van Damme H, Ariguib NK (1989) Surface properties of an activated bentonite-decolourization of rape-seed oil. Appl Clay Sci 4:411–421
- Temuujin J, Senna M, Jadamba T, Burmaa D, Erdenchimeg S, MacKenzie KJD (2006) Characterization and bleaching properties of acid-leached montmorillonite. J Chem Technol Biotechnol 81:688–693
- Vicente-Rodriguez MA, Suarez M, Lopez-Ganlez JD, Bñares-Munoz MA (1996) Characterization, surface area and porosity analyses of the solids obtained by acid leaching of a saponite. Langmuir 12:566–572
- Zschau W (2001) Bleaching of edible fats and oils. Eur J Lipid Sci Technol 103:505–551