Optimization of Acid-Activated Bentonites on Bleaching of Cotton Oil

ORAL LACIN*, ENES SAYAN AND ELIF GULSAH KIRALI
Atatürk University, Department of Chemical Engineering, Erzurum, TÜRKİYE.
olacin@atauni.edu.tr, molacin69@yahoo.com*

(Received on 19th January 2012, accepted in revised form 18th March 2013)

Summary: Bentonites are commonly used adsorbent on bleaching cotton oil to produce edible oil products. Bleaching capacities of neutralized cotton oil were investigated with acid-activated Arguvan and Kurşunlu bentonites. Two models for acid activation of the bentonites were developed by using a full factorial experimental design and central composite design. The parameters used to develop these models were contact time, solid to liquid ratio, acid concentration and moisture of bentonite. By using a constrained optimization program, the maximum bleaching capacities of neutralized cotton oil were determined as 99.99% and 48.5% for Arguvan and Kurşunlu, respectively. Optimum results showed that Turkish bentonites (especially Arguvan bentonite) have high bleaching ability and they can be used efficiently to bleach neutralized cotton oil by considering the favorable volume weight, capacity of oil adsorbed and filtration rate.

Keywords: Bleaching; activated bentonite; factorial design; optimization neutralized cotton oil.

Introduction

The adsorbent which removes undesirable pollutants such as heavy metals, pigments, phenol compounds, organic compounds, etc., are widely used in industrial activities such as metal finishing, oil refining, electroplating, painting, etc. Most of these pollutants are highly toxic, and their residues in the environment pose a threat not only for human health, but also for the aquatic ecosystem [1-4].

Bleaching of oil in refinery is essential to produce edible light-colored oil with high quality [5,6]. After its degumming and neutralization during the refining process, crude edible oil still contains undesirable impurities such as phospholipids, soap, trace metals, caratenoids, xanthophylls, chlorophyll, tocopherols and gossypol. These impurities not only impair the quality of the oil by altering its taste and color, but also affect its market value by giving it a color that will not be appreciated by the consumer. The removal of these impurities improves the sensory quality and oxidative stability of the deodorized oil [7].

In removal of these impurities, bentonites which consist of hydrated aluminum silicates are by far the most common adsorbents [8-11].

Bentonite, which is predominantly smectite a 2:1 clay mineral, is composed of one Al octahedral sheet placed between two Si tetrahedral sheets. The isomorphous substation of Al^{3+} for Si^{4+} in tetrahedral layer and Mg^{2+} for Al^{3+} in the octahedral layer results in a negative surface charge on the bentonite. This charge imbalance is offset by exchangeable cations (Na^{+} and Ca^{2+}, etc.) at the bentonite surface [12].

Bentonites are highly valued because their high surface area and tendency to absorb water in the interlayer sites. These properties are enhanced with acid activation [13]. Mineral acids treatment of the natural bentonite replaces the cations between the layers of the montmorillonite crystal with protons coming from the acid [14].

$$\text{Ca-bentonite} + 2H^{+} \leftrightarrow \text{H-bentonite} + Ca^{2+}$$

Acid activation of bentonites and the factorial design of this method were reported in several studies [11, 13, 15-20]. Despite numerous studies, no definite relationship exists between the performance of acid activated bentonite and the composition or other properties of the original clay. Therefore, each bentonite has to be specifically activated and tested for its performance [11, 21].

The first aim of the present study was to investigate the bleaching capacity of neutralized cotton by using acid-activated Arguvan and Kurşunlu bentonites. The second aim was to optimize process conditions for the maximum bleaching capacity of neutralized cotton oil. The experiments were designed by using statistical approaches. The contact time, solid to liquid ratio, acid concentration and moisture of bentonite are chosen as process parameters. The regression models obtained were used in a constrained optimization to find optimum process conditions for maximum bleaching capacity of bentonites.

*To whom all correspondence should be addressed.

$$Y_A = 28.34 + 0.06X_1 + 6.67X_2 - 3.58X_3 + 4.40X_4 - 7.77X_1^2 + 11.7X_2^2 + 3.31X_3^2 + 1.64X_4^2 + 3.41X_1X_2 - 9.59X_1X_3 - 0.66X_1X_4 - 9.74X_2X_3 - 1.74X_2X_4 - 1.75X_1X_2X_3 \quad (1)$$

$$Y_Ç = 23.81 + 8.98X_1 - 2.25X_2 + 3.29X_3 - 2.09X_4 - 3.15X_1X_2 + 4.39X_1X_4 - 1.99X_2X_4 - 2.40X_3X_4 + 4.95X_1X_3X_4 + 2.20X_2X_3X_4 \quad (2)$$

where; Y_A and $Y_Ç$ represent the bleaching capacity (%) for Arguvan and Kurşunlu bentonites, respectively.

Results and Discussion

Response Analysis and Interpretation

In order to determine the maximum bleaching capacity and derive a model for acid activation of a Turkish bentonite, a full factorial design of the type 2^4 was used. Contact time (x_1), solid to liquid ratio (x_2), acid concentration (x_3) and moisture of bentonite (x_4), were chosen as independent variables to model and optimize according to previous experiments. Factor levels and coded values are shown in Table-1. The design matrix for four variables is varied at two levels (+1 and -1). The higher level of variable was designed as "+1" and the lower level was designed as "-1". Initially, the 2^4 full factorial experimental designs were used to obtain first-order model with interaction terms effective on bleaching capacity of Arguvan and Kurşunlu bentonites. As usual, the experiments were performed in random order to avoid systematic error. In addition, three central replicates were also added to the experimental design to calculate pure experimental error. As the analysis of variance reveals that quadratic terms were effective on bleaching capacity of Arguvan bentonite, the orthogonal central composite design was planned to estimate quadratic terms separately. With F=16, m_0=3 and n=4, β is calculated as 1.547. The design matrix and results of the auxiliary experiments carried out to calculate first and second order model parameters for Arguvan and Kurşunlu bentonites were given in Table-2. The first order model for Kurşunlu bentonite and full second order model for Arguvan bentonite obtained by variance analysis conducted at 95% confidence interval are given below:

Fig. 1a and b illustrates the graphical representation of 'size effect' of each of parameters upon the bleaching capacities for both bentonites. From Fig. 1a, it can be seen that contact time (X_1), solid to liquid ratio (X_2) and moisture of bentonite (X_4) have a positive effect, while acid concentration (X_3) has a negative effect on the bleaching capacity for Arguvan bentonite. Each of the second orders terms except for contact time (X_1) has positive effect upon the bleaching capacity for Arguvan bentonite. From Fig. 1b, it can be seen that contact time (X_1), acid concentration (X_3) have a positive effect, while solid to liquid ratio (X_2) and moisture of bentonite (X_4) have a negative effect on the bleaching capacity for Kurşunlu bentonite. The interaction terms affect at various ratios for both bentonites.

Table-1: Factor Levels and Coded Values Used In the Experimental Design.

Parameters	$-\beta^*$	-1	0	+1	$+\beta^*$
Contact time (h) (X_1)	**0.91**	**2**	**4**	**6**	**7.09**
Solid to liquid Ratio ($g.mL^{-1}$) (X_2)	**0.01**	**0.1**	**0.3**	**0.5**	**0.59**
Acid concentration (N) (X_3)	**0.01**	**1**	**3**	**5**	**5.99**
Moisture of bentonite (%) (X_4)	**1.81**	**4**	**8**	**12**	**14.19**

*: Used only the orthogonal central composite design to estimate quadratic terms effective on bleaching capacity of Arguvan bentonite.

Optimization Results

The usual final aim of a modeling task is to find the optimum values of some technical and/or economic objective function(s). Besides, imposing constraints is another important step on optimization process in order to obtain sensible results. Apart from the explicit constraints defined naturally by the low and high levels of the process factors, implicit constraints may also be required due to some technical and economic considerations. The main objective of this research is to determine the optimal conditions on the bleaching capacities for both bentonites. Then, using the methodology for experimental design that is mentioned above, the ranges of the parameters required to obtain optimum conditions were determined. In this optimization study, the bleaching capacities for both bentonites were chosen as the objective function. Furthermore, optimum conditions are often calculated in the presence of some constraints, which ensure them to be more realistic. If the model used in the optimization study is an empirical one, high and low levels of the process parameters in the experimental design are considered, inevitably, as explicit constraints, in order to avoid extrapolation

Table-2: Experimental Design And % Bleaching Capacity Of Activated Bentonites.

Experiment no.	Contact time (h)X_1	Solid to liquid ratio (g.mL^{-1})X_2	Acid conc. (N)X_3	Moisture of bentonite (%)X_4	% Bleaching capacity for Arguvan Bentonite	% Bleaching capacity for Kurşunlu Bentonite
1^0	0	0	0	0	30.3	27.0
6	+	+	+	+	28.2	24.1
7	+	+	+	-	26.3	37.2
12	+	-	+	+	28.4	26.0
9	+	+	-	+	73.7	48.5
1	-	+	+	+	41.7	18.3
8	+	-	+	-	23.6	0.5
13	-	+	+	-	42.0	38.3
4	-	+	-	+	43.5	28.8
2^0	0	0	0	0	31.3	5.2
5	+	-	-	+	28.8	12.9
10	+	-	-	-	24.7	24.6
16	-	-	+	-	40.6	37.3
2	-	+	-	-	42.9	29.6
11	-	-	-	+	20.3	32.2
14	-	-	-	-	13.0	19.7
3	+	+	-	-	74.2	13.8
15	-	-	+	+	53.9	3.5
3^0	0	0	0	0	29.7	26.8
19	+1.547	0	0	0	5.0	
17	-1.547	0	0	0	10.6	
23	0	+1.547	0	0	54.3	
20	0	-1.547	0	0	54.7	
18	0	0	+1.547	0	22.0	
22	0	0	-1.547	0	46.6	
24	0	0	0	+1.547	49.8	
21	0	0	0	-1.547	10.8	

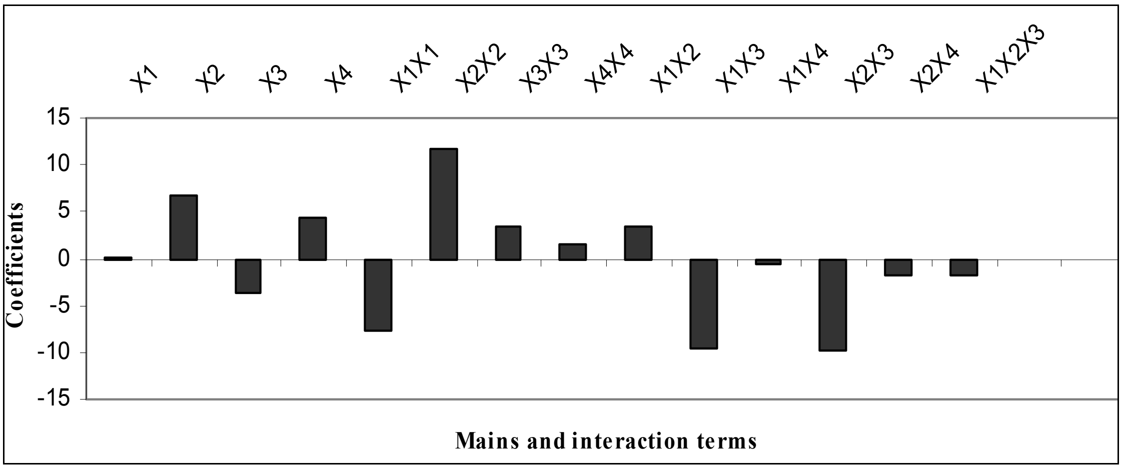

Fig. 1a: Significant Mains, Second And Interaction Terms For Bleaching Capacity Of Arguvan Bentonite..

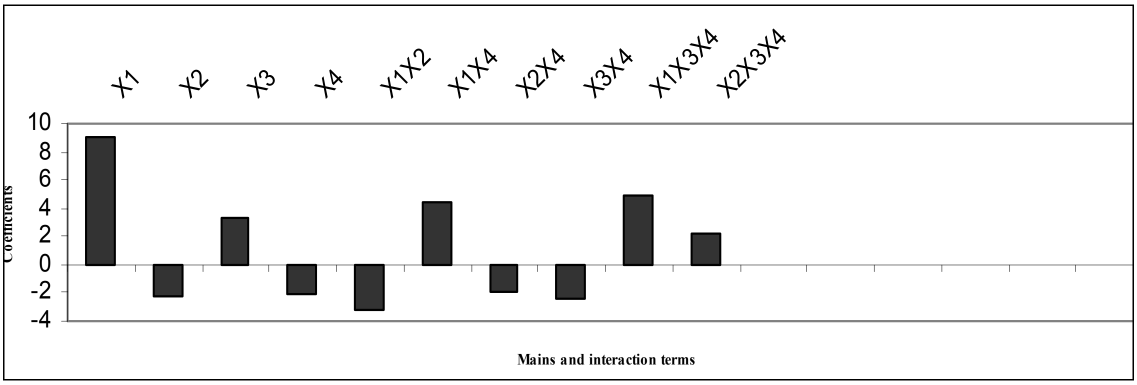

Fig. 1b: Significant Mains and Interaction Terms For Bleaching Capacity Of Kurşunlu Bentonite.

Thus, the optimization problem is defined both responses as;

Maximize $Y_A/Y_Ç$ (3)

Constraints on the parameters X

$-\beta_i<X_i<+\beta_i$ i = 1-4 (4)

$-\beta$ and $+\beta$ values are given in Table-1. The optimization problem (4) is solved using constrained optimization program supplied in the Matlab optimization toolbox. These optimization results show that; contact time (X_1), solid to liquid ratio (X_2) and moisture of bentonite (X_4) is effective on its higher bound on the bleaching capacity for Arguvan bentonite, while acid concentration (X_3) has a negative effect on its lower bound. The contact time (X_1), acid concentration (X_3) and moisture of bentonite (X_4) is effective on its high bound on the bleaching capacity for Kurşunlu bentonite, whereas solid to liquid ratio (X_2) have a negative effect on its low bound. The optimum process conditions are given in Table-3 by considering the models given in Eq. (1-2) established with effective parameters obtained by variance analysis conducted at 95% confidence level.

Experimental

Experimental Design

In industrial experimental design, the factorial experimental design and the orthogonal central composite design methods are widely used to obtain empirical linear models relating process responses to process factors, with a minimum effort of experimentation and with the highest level of statistical confidence [22, 23]. By using this method, modeling is possible and it requires only a minimum number of experiments. It is not necessary in the modeling procedure to know the detailed reaction mechanism since the mathematical model is empirical. Furthermore, the analysis performed on the results is easily realized and experimental errors are minimized.

The design comprises 3 blocks; a factorial design, three central replicates to estimate experimental error and axial (star) experiments block. Thus, each factor is represented by five levels over wide ranges to increase the reliability of the second order regression models obtained. In this paper, the orthogonal central composite design was employed, similar to that described in detail in previous experimental studies [24-27]. The polynomial and optimized conditions were analyzed by using matlab computer software.

Material and Methods

The natural bentonites were collected from Arguvan (Malatya-Türkiye) and Kurşunlu (Çankırı-Türkiye). They were crushed using a jaw crusher and ground to pass through a 75 µm sieve (-200 mesh ASTM) using a porcelain mill. The chemical compositions of the Turkish bentonites determined by X-Ray fluorescence spectroscopy (XRF, ARL 9800 XP) were given in Table-4.

X-ray diffraction patterns of Turkish bentonites were obtained using a Rigaku 2000 JCPDS DMAX (29-1490) diffractometer (XRD) with CuKα radiation (30 kV and 30 mA and automatic monochromator) at a scanning rate 2θ of 2^o min^{-1}. The diffraction patterns of Turkish bentonites before and after activation, which are obtained at the bleaching capacity, are given in Fig. 2a and 2b.

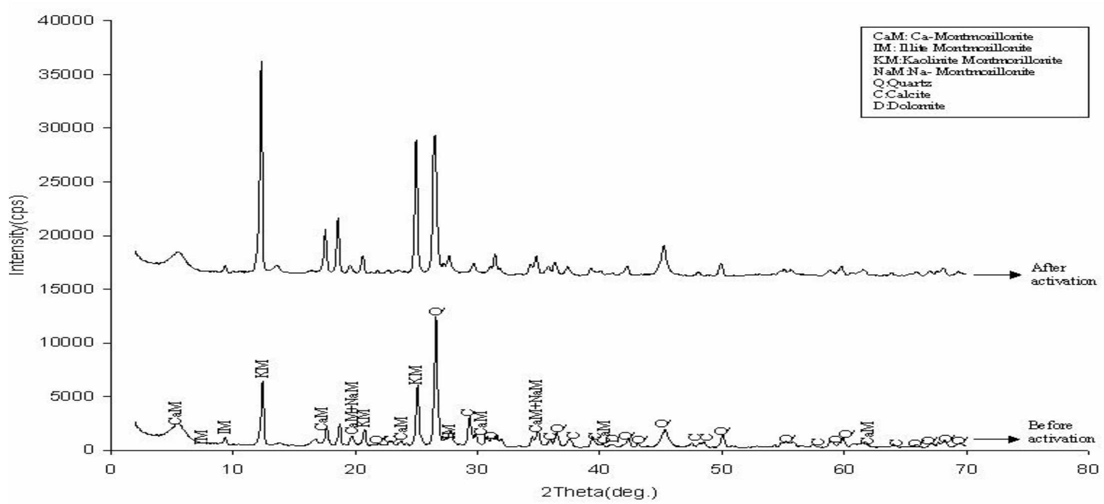

Fig. 2a: The Diffraction Patterns Of Arguvan Bentonite Obtained The Maximum Bleaching Capacity Before And After Activation.

Table-3: Optimum Conditions on The Bleaching Capacity Of Cotton Oil.

Bentonites	Contact time (h)(X_1)	Solid to liquid ratio ($g.mL^{-1}$) (X_2)	Acid concentration (N)(X_3)	Moisture of bentonite (%) (X_4))	Bleaching capacity %
Arguvan	7	0.59	0.01	14.19	99.99
Kurşunlu	6	0.1	5	12	48.5

Table-4: The Chemical Compositions of The Turkish Bentonites.

Sample	SiO_2%	Al_2O_3%	Fe_2O_3%	CaO%	MgO%	Na_2O%	K_2O%	LOI%
Arguvan	45.48	17.70	8.22	6.05	4.01	3.84	2.51	10.95
Kurşunlu	57.93	17.61	3.54	4.84	2.33	4.95	1.57	6.93

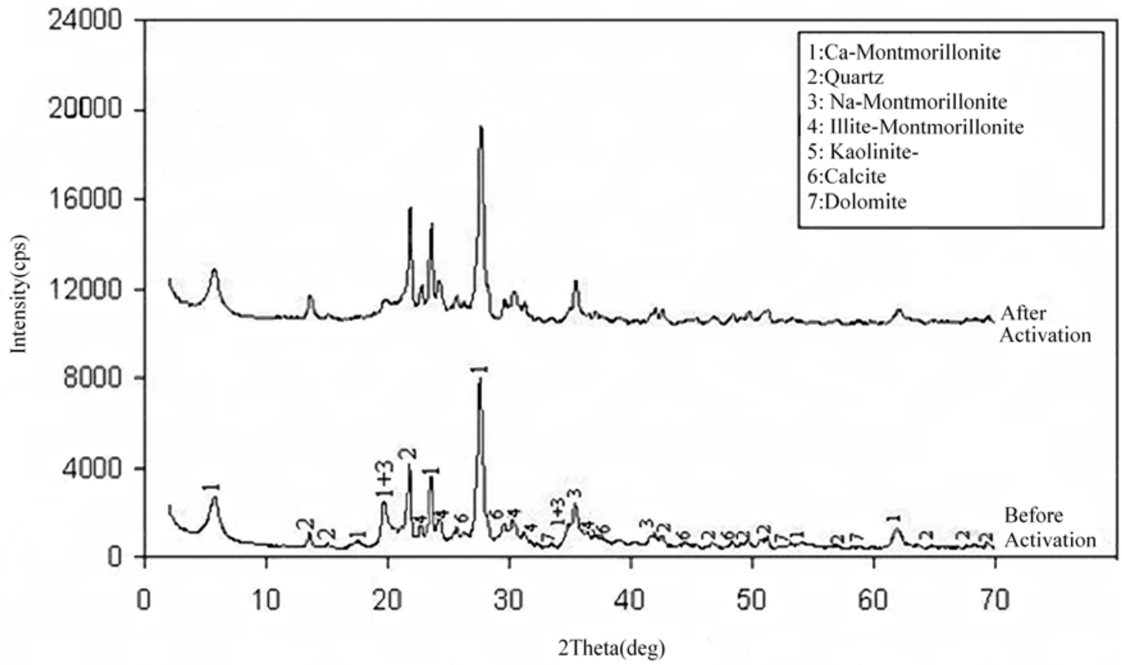

Fig. 2b: The Diffraction Patterns Of Kurşunlu Bentonite Before And After Activation.

The specific surface areas of Turkish bentonites, which are obtained at the maximum bleaching capacity before and after activation, were measured by using the BET-N_2 method. The specific surface areas of Turkish bentonites were given in Table-5.

Table-5: The Specific Surface Areas of Turkish Bentonites.

Sample	Specific Surface Areas ($m^2.g^{-1}$)	
	Before Activation	After Activation
Arguvan	15.64	38.32
Kurşunlu	24.65	39.44

The neutralized cotton oil was provided by Doyasan Oil Comp. in Erzurum (Türkiye). All chemicals used were analytical grade.

The experimental set up consists of a rotary evaporator, round-bottom three-neck flask, mechanic stirrer, vacuum pump, thermometer and a constant temperature circulator.

Activation was carried out in HCI concentrations varying from 1 to 5 N at the temperature of 95 $^oC \pm 1$ ^oC and solid to liquid ratio of 0.1-0.5 $g.mL^{-1}$. Contact time was 2-6 h and moisture of bentonite was 4-12 %. The suspension was cooled in air and filtered off and then washed several times with distilled water to remove excess Cl^- ions and dried in constant weight at 100 ^oC. These acid activated bentonites were used to bleach the neutralized cotton oil. The chemical analyses of the bentonites obtained at the maximum bleaching capacity were given in Table 6.

Table-6: The Chemical Analysis of the Turkish Bentonites at The Maximum Bleaching Capacity.

Sample	SiO_2%	Al_2O_3%	Fe_2O_3%	CaO%	MgO%	Na_2O%	K_2O%	LOI%
Arguvan	69.99	12.53	2.16	1.94	0.22	4.44	2.70	4.40
Kurşunlu	67.54	14.38	2.67	3.02	0.66	5.04	1.47	5.22

Bleaching experiments were performed in a round-bottom three-neck flask equipped with a stirring rod. The acid-activated bentonite was added to the oil for 20 min at about 80 ^{o}C (under reduced pressure). The acid-activated bentonites / oil ratio was 2 % (wt.) (these values are used in factory processing). As soon as bleaching was finished, the bleached oil was separated by filtration at 50 ^{o}C. The samples were kept in coloured bottles. The colour changes in the treated oils were determined spectrophotometrically at the best wavelength of 408 nm (Shimadzu UV160A). Results were calculated as β-carotene equivalents after comparison against a calibration curve prepared with 0-20 mg.L^{-1} β-carotene solutions in petroleum ether.

For this purpose, the bleaching capacity of the activated clays was determined from the following equation: The readings from spectrums were repeated three times and then the average was taken.

$$\text{Bleaching capacity (\%)} = \frac{C_0 - C}{C_0} \times 100 \qquad (5)$$

where C_0 is the initial concentration (mg.L^{-1}) of β-carotene in the neutralized cotton oil at a wavelength of 408 nm and C is final concentration (mg.L^{-1}) of β-carotene in the neutralized cotton oil at a wavelength of 408 nm.

Conclusion

The maximum bleaching capacity of Turkish bentonites were investigated and models were developed for acid-activation of Turkish bentonites by utilizing full factorial experimental design and central composite design in order to bleach neutralized cotton oil. The bleaching capacities of the bentonites were determined with respect to solid to liquid ratio, contact time, concentration and moisture of bentonite. Initially, the 2^4 full factorial experimental designs were used to obtain first-order model with interaction terms effective on bleaching capacity of Arguvan and Kurşunlu bentonites. As the analysis of variance reveals that quadratic terms were effective on bleaching capacity of Arguvan bentonite, the orthogonal central composite design was planned to estimate quadratic terms separately. The maximum bleaching capacities of neutralized cotton oil were obtained 99.99% for Arguvan bentonite and 48.5% for Kurşunlu bentonite under optimal conditions. In conclusions, optimum results show that experimentally investigated Turkish bentonites (especially Arguvan bentonite) may be applicable in the bleaching of neutralized cotton oil by determining on volume weight, capacity of oil adsorbed and filtration rate. It is believed that the model obtained for bleaching capacity of oils may provide background information for a detailed bleaching processes, industrial scale applications and optimization studies.

References

1. E. Srasra and M. Trabelsi-Ayedi, *Applied Clay Science*, **17**, 71 (2000).
2. W. U. Zhansheng, L. I. Chun, S. U. N Xifang, X. U. Xiaolin, D. A. I. Bin, L. I. Jin'e and Z. Hongsheng, *Chinese Journal of Chemical Engineering,* **14,** 253 (2006).
3. C. Bilgiç, *Adsorption Science and Technology*, **26**, 363 (2008).
4. Wu Xiaofu, Zhao Fang, Chen Mingli, Zhang Yangli, Zhao Chong and Zhou Hailan, *Adsorption Science and Technology*, **26**, 145 (2008).
5. Lin Chun-I, and Lin Tse-Li, *Journal of the Taiwan Institute of Chemical Engineers*, **40**, 168 (2009).
6. M. H. Ma and C. Lin, *Seperation and Purification Technology*, **39**, 201 (2004).
7. A. Boukerrouı and M. S. Ouali, *Annales de Chimie - Science des Matériaux,* **27**, 73 (2002).
8. C. C. Harvey and H. H. Murray, *Applied Clay Science*, **11**, 285 (1997).
9. M. Rossi, M. Gianazza, C. Almprese and F. Stanga, *Food Chemistry*, **82**, 291 (2003).
10. D. R. Taylor, D. B. Jenkins and C. B. Ungermann, *Journal of the American Oil Chemists' Society,* **66**, 334 (1989).
11. S. Petrović, T. Novaković and L. Rožić, *Journal of Chemical Technologyand Biotechnology,* **84,** 176 (2009).
12. A. S. Ozcan and A. Ozcan, *Journal of Colloid and Interface Science*, **276,** 39 (2004).
13. G. E. Christidis, P. W. Scott and A. C. Dunham, *Applied Clay Science*, **12**, 329 (1997).
14. Study Group, *Europen. Journal of Lipid Science and Technology*, **103,** 505 (2001).
15. S. Mendioroz, J. A. Pajares, C. Pesquera, F. Gonzales and C. Blanco, *Langmuir,* **3**, 676 (1987).
16. M. A. Didi, B. Makhoukhi, A. Azzouz and D. Villemin, *Applied Clay Science*, **42**, 336 (2009).
17. H. Babaki, A. Salem and A. Jafarizad, *Material Chemistry and Physics*, **108,** 263 (2008).
18. A. Gannouni, A. Bellagi and M. Bagane, *Annales de Chimie - Science des Matériaux,* **24**, 407 (1999).
19. S. Chegrouche and A. Bensmaili, *Water Research,* **36**, 2898 (2002).

20. E. G. Kirali and O. Laçin, *Jouirnal of Food Engineering*, **75**, 137 (2006).
21. F. K. Hymore, *Applied Clay Science*, **10**, 379 (1996).
22. D. C. Montgomery, *Design and Analysis of Experiments*. John Wiley and Sons, New York (1976).
23. R. H, Myers, *Response Surface Methodology*, Allyn and Bacon, New York (1971).
24. E. Şayan and M. Bayramoğlu*, Hydrometallurgy*, **57**, 181 (2000).
25. E. Şayan and M. Bayramoğlu, *Institution of Chemical Engineers*, *Trans IChemE,* B, **79**, 291 (2001).
26. E. Şayan and M. Bayramoğlu, *Hydrometallurgy*, **71**, 397 (2004).
27. E. Şayan, *Chemical Engineering Journal*, **115**, 213 (2006).