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Investigation of Benzoic Acid Adsorption on to ODTMA-bentonite by Response Surface Optimization

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ABSTRACT: The adsorption of benzoic acid on to a modified bentonite (ODTMA-bentonite) was studied. ODTMA-bentonite was synthesized by the incorporation of a quaternary ammonium surfactant (octadecyltrimethylammonium bromide) on to Çankiri sodium bentonite (ÇNa-B) with a cation-exchange capacity of 85 mequiv/100 g clay. A 2^4 full factorial central composite experimental design followed by multi-stage Monte-Carlo optimization was used in designing the experiments and analyzing the results. This procedure limited the number of actual experiments performed whilst allowing for possible interactions between the four parameters studied.

These parameters were temperature (20–40ºC), agitation rate (30–170 rpm), the amount of organobentonite used (0.1–1.5 g) and the initial benzoic acid concentration (40–200 mg/l). Of these parameters, the amount of organobentonite and the temperature had significant effects in comparison with the agitation rate and initial benzoic acid concentration. To effect the maximum adsorption of benzoic acid on to ODTMA-bentonite, the optimum values for the tested variables over the selected ranges were as follows: initial concentration of benzoic acid = 200 mg/l, agitation rate = 170 rpm, amount of organobentonite = 1.5 g and temperature = 40ºC. The coefficient of determination (R^2) for the model employed was 0.99343 with a probability value of 9.44×10^{-14} (p-value < 0.01). This p-value indicates a very high significance for the regression model. The maximum adsorbed concentration of benzoic acid predicted by the equation (169.05 mg/l) agreed well with the value (163 mg/l) obtained from the experimental data measured under optimum conditions.

INTRODUCTION

Various toxic chemicals have been discharged to the environment as industrial wastes, causing serious water and soil pollution. The removal of organic contaminants from wastewater has been studied extensively using various physicochemical and biological techniques. Of these techniques, there has been much interest recently in using clays (particularly smectites) for the removal of organic pollutants from water because of their high cation-exchange capacity (CEC) and surface areas. In particular, over the past 10 years there has been much interest and advancement in the use of organoclays as adsorbants to remedy organic contamination (Gitipour *et al.* 1997; Lin and Cheng 2000; Koh and Dixon 2001; Carroda 2000; Barrer and Kelsey 1989; Smith and Galan 1995; Smith and Jaffe 1991; Smith *et al.* 1990a,b).

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Of the various organoclays, organobentonites have been the most widely investigated by many researchers (Boyd *et al.* 1988; Lee *et al.* 1997; Jaynes and Boyd 1990; Çelik *et al.* 2000; Yildiz *et al.* 2000). Organobentonites are produced by replacing exchangeable inorganic cations (e.g. Na^+, Ca^{2+}, H^+) on the internal and external mineral surfaces of bentonite with quaternary alkylammonium cations. Naturally-occurring bentonite is not efficient as an adsorbent for the uptake of hydrophobic organic pollutants from aqueous solution, primarily because of the electrically charged and hydrophilic characteristics of its surface. The bentonite surfaces are drastically altered through such an exchange process and the resulting organobentonites behave as strong adsorbents relative to the natural material for non-ionic organic pollutants (Barrer and Kelsey 1989).

The sorption properties of organobentonites depend greatly on the characteristics of the exchanged organic cations. Smith and Galan (1995) demonstrated that the adsorption of tetrachloromethane on to bentonite modified by the exchange of small organic cations was characterized by non-linear isotherms, strong solute uptake and competitive sorption. In contrast, tetrachloromethane sorption on to bentonites modified by relatively large organic cations ($C > 10$) was characterized by essentially linear isotherms, lower solute uptake and non-competitive sorption. The authors concluded that differences between the two groups of organoclay sorbents were attributable to different sorption mechanisms: adsorption for bentonite modified with organic cations with small functional groups and partition for bentonite modified with organic cations with relatively large functional groups. Small organic cations (e.g. tetramethylammonium) create a relatively rigid, non-polar surface amenable to the uptake of non-ionic solutes by adsorption. Larger organic cations (e.g. hexadecyltrimethylammonium bromide) create an organic partition medium through conglomeration of their flexible alkyl chains.

The present study describes the optimization of benzoic acid adsorption on to ODTMA-bentonite synthesized from Çankiri sodium bentonite.

MATERIALS AND METHODS

Materials

Çankiri (Turkey) sodium bentonite (ÇNa-B) was used in the study, the cation-exchange capacity (CEC) of the original material being determined via the Methylene Blue test (ANSI/ASTM C 837-76). X-Ray powder diagrams of the original sample and of the organobentonite, prepared as random powder materials, were obtained using a Rikagu D-max 2200 powder diffractometer. The studies showed that montmorillonite was the main mineral in the samples with minor amounts of quartz, α-cristobalite and albite also being identified in the raw materials.

Octadecyltrimethylammonium bromide (ODTMA, Fluka) was used for the exchange of inorganic ions in the original materials with organic cations. The organobentonite was prepared as described in detail by Çelik *et al.* (2000). The concentration of organic pollutant (benzoic acid) in the aqueous phase was determined by ultraviolet spectrophotometry (UV-1601, Shimadzu) at a wavelength of 238 nm. Solutions of the organic contaminant were prepared at selected concentrations and the sorption experiments were carried out as described by Çelik *et al.* (2000).

Experimental design and optimization by RSM

Response surface methodology (RSM) was used in the empirical study of the relationships between one or more measured responses and a number of input variables with the aim of optimizing such responses (Box and Wilson 1951; Cochran and Cox 1957; Myers 1971; Kazanov 1976; Box *et al.*

1978; Khuri and Cornell 1987; Montgomery 1996). A 2^4 full factorial central composite design (CCD) for four independent variables each at five levels was adopted in this study. A fractional factorial design consisting of 16 factorial points, 8 axial points (two axial points on the axis of each design variable at a distance of 2 from the design centre) and six replicates at the centre points was employed to fit a second-order polynomial model. A total of 30 experiments was necessary for the estimation of the 14 coefficients of this model. The quadratic response surface model was fitted to the following equation:

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_5 x_1^2 + \beta_6 x_2^2 + \beta_7 x_3^2 + \beta_8 x_4^2 + \beta_9 x_1 x_2 + \beta_{10} x_1 x_3 - \beta_{11} x_1 x_4 - \beta_{12} x_2 x_3 + \beta_{13} x_2 x_4 + \beta_{14} x_3 x_4 + \varepsilon \quad (1)$$

where y is the measured response for each test [i.e. adsorbed benzoic acid (mg/l) in this study]; x_1, x_2, x_3, x_4 are coded independent variables [x_1 = initial concentration of benzoic acid (mg/l), x_2 = agitation rate (rpm), x_3 = amount of organobentonite (g), x_4 = temperature (ºC)]; β_0 is the intercept term; β_1, β_2, β_3, β_4 are linear coefficients; β_5, β_6, β_7 and β_8 are quadratic coefficients; β_9, β_{10}, β_{11} and β_{12} are cross-product coefficients; and ε is the experimental error. The range and levels of the variables investigated in this study are listed in Table 1. The selection of these levels was based on the results obtained in a preliminary study. In developing the regression equation, the test variables were coded according to the equation

$$x_i = X_i - X_i^*/\Delta X_i \quad (2)$$

where x_i is the coded value of the ith independent variable, X_i is the uncoded value of the ith independent variable, X_i^* is the uncoded value of the ith independent variable at the centre point and ΔX_i is the step change value.

Macanova software (version 4.07, Minnesota, USA) was used for regression and graphical analyses of the data obtained. The goodness-of-fit of the model was evaluated via the coefficient of determination (R^2) and an analysis of the variances.

The contour plots and dimensional surfaces provide the most useful approach for predicting the response towards different values of the test variables and identifying the type of interactions between these variables (Box *et al.* 1978). The regression equation can take a number of different forms depending on the coefficients. The corresponding contour systems are obviously of very different kinds such as a maximum point or a minimum point (elliptical, circular), saddle point (mini-max), stationary ridge or rising/falling ridge (Myers 1971; Kazanov 1976; Box *et al.* 1978).

TABLE 1. Experimental Range and Levels of Independent Variables

Variables	Range and levels				
	–2	–1	0	+1	+2
Initial benzoic acid concentration (mg/l), X_1	40	80	120	160	200
Agitation rate (rpm), X_2	30	65	100	135	170
Organobentonite amount (g), X_3	0.1	0.45	0.8	1.15	1.5
Temperature (ºC), X_4	20	25	30	35	40

TABLE 2. Full Factorial Central Composite Design Matrix for Four Variables in Coded and Natural Units Together With the Observed Response

Observation No.	X_1	X_2	X_3	X_4	Initial benzoic acid conc. (mg/l)	Agitation rate (rpm)	Amount of organo-bentonite employed (g)	Temperature (ºC)	Conc. adsorbed benzoic acid (mg/l)
1	–1	–1	–1	–1	80	65	0.45	25	50.597
2	1	–1	–1	–1	80	65	0.45	35	50.831
3	–1	1	–1	–1	80	135	0.45	25	45.728
4	1	1	–1	–1	80	135	0.45	35	53.476
5	–1	–1	1	–1	80	65	1.15	25	60.597
6	1	–1	1	–1	80	65	1.15	35	60.953
7	–1	1	1	–1	80	135	1.15	25	56.002
8	1	1	1	–1	80	135	1.15	35	63.836
9	–1	–1	–1	1	160	65	0.45	25	89.680
10	1	–1	–1	1	160	65	0.45	35	90.242
11	–1	1	–1	1	160	135	0.45	25	85.119
12	1	1	–1	1	160	135	0.45	35	92.545
13	–1	–1	1	1	160	65	1.15	25	120.640
14	1	–1	1	1	160	65	1.15	35	121.318
15	–1	1	1	1	160	135	1.15	25	116.367
16	1	1	1	1	160	135	1.15	35	123.437
17	–2	0	0	0	120	100	0.8	20	81.668
18	2	0	0	0	120	100	0.8	40	90.281
19	0	–2	0	0	120	30	0.8	30	84.991
20	0	2	0	0	120	170	0.8	30	86.093
21	0	0	–2	0	120	100	0.1	30	41.744
22	0	0	2	0	120	100	1.5	30	93.813
23	0	0	0	–2	40	100	0.8	30	26.941
24	0	0	0	2	200	100	0.8	30	134.926
25	0	0	0	0	120	100	0.8	30	85.590
26	0	0	0	0	120	100	0.8	30	85.334
27	0	0	0	0	120	100	0.8	30	85.427
28	0	0	0	0	120	100	0.8	30	86.164
29	0	0	0	0	120	100	0.8	30	85.265
30	0	0	0	0	120	100	0.8	30	86.030

RESULTS AND DISCUSSION

The statistical combinations for benzoic acid adsorption on to ODTMA-bentonite are listed in Table 2. In order to determine whether or not the quadratic model was significant, it was necessary to conduct an analysis of variance (ANOVA) using the usual Fisher F-tests, etc., in which the regression sum of squares was subdivided into two parts, i.e. that attributed to linear regression and that attributed to the quadratic model (Myers 1971). The ANOVA for the quadratic model is presented in Table 3. This shows that the probability value for the multiple regressions was very small (p-value = 9.44×10^{-14}, $p < 0.01$ when significant). The ANOVA also indicated that the model

TABLE 3. Analysis of Variance (ANOVA) for the Quadratic Model

Sources of variations	Sum of squares	Degrees of freedom	Mean square	F-value	Probability (p) > F
Model	19795.153714	14	1413.939		
Error	124.367	15	8.291	170.539	0.0001
Total	19919.52071	29	686.88		

represented adequately the actual relationship between the response (the adsorbed benzoic acid concentration) and the significant variables. The Fisher F-test with a very low probability value also demonstrated a very high significance for the regression model since the computed F-value ($F_{0.01(14,15)} = S_r^2/S_e^2 = 170.54$) was much greater than the tabular $F_{0.01(14,15)}$-value (3.66). A good model would explain most of the variation in the response. The coefficient of determination (R^2) provides a measure for this criterion and can be calculated by dividing the variation as explained by the model by the total variation (Khuri and Cornell 1987). The closer the value of R^2 to unity the better is the correlation between the observed and predicted values. In this study, we found that the coefficient of determination (R^2) and the adjusted coefficient of determination (R^2_{adj}) for the model were 0.99343 and 0.992022, respectively. This value of R^2, indicating that only 0.7% of the total variation was not explained by the regression model, was very high and advocated high significance for the model. A higher value of the coefficient of determination R^2 (0.996709) would have provided complete justification for an excellent correlation between the independent variables (Box *et al.* 1978).

The application of response surface methodology based on estimates of the parameters indicated an empirical relationship between the response variables (adsorbed benzoic acid concentration) and the test variables expressed by the following quadratic expression in coded units:

$$\begin{aligned} Y = {} & 85.635 + 2.478x_1 - 0.6871x_2 + 10.78x_3 + 25.985x_4 - 0.0181x_1^2 - \\ & 0.12632x_2^2 - 4.572x_3^2 - 1.2784x_4^2 + 2.4123x_1x_2 + 0.64479x_1x_3 - \\ & 0.6740x_1x_4 - 0.69829x_2x_3 + 0.61704x_2x_4 + 5.1743x_3x_4 \end{aligned} \quad (3)$$

The Student t-distribution and corresponding p-values, along with the parameter estimates, are listed in Table 4. The significance of each coefficient was determined via the p-values and the Student t-test. The Student t-test was employed to obtain a value of the error mean square essential in testing the significance of the estimated coefficient of determination equation [equation (3)]. The Student t-test values could be obtained by dividing each coefficient by its standard error. The p-values were used as a tool to check the significance of each of the coefficients. Such p-values are necessary for understanding the pattern of the mutual interactions between the test variables. A larger magnitude of the t-value and a smaller p-value identifies the effect that appears to be very important (Khuri and Cornell 1987). For our data, it was observed that the first-order main effects of both the amount of organobentonite (x_3) and temperature (x_4) and their second-order main effects (x_3^2, x_4^2) were highly significant since their respective p-values were very small. The quantities x_3 and x_4 had a positive influence while x_3^2 and x_4^2 had a negative effect on the adsorption. Among these interactions, those between the initial concentration of benzoic acid and the rate of agitation (x_1–x_2) and the amount of organobentonite and the temperature (x_3–x_4) were modestly significant ($p < 0.1$). These interactions had a positive effect on the adsorption.

TABLE 4. Least-Squares Fit and Parameter Estimates (Significance of Regression Coefficients)

Model term	Parameter estimate	Standard error	Computed t-value	p-value
Intercept	85.635	1.206	71.005	0
X_1	2.4784	0.60662	4.0856	0.00097421
X_2	–0.68719	0.60662	–1.1328	0.27507
X_3	10.78	0.60662	17.771	$1.7359e^{-11}$
X_4	25.985	0.60662	42.836	0
X_1*X_1	–0.018194	0.56432	–0.032241	0.97471
X_2*X_2	–0.12632	0.56432	–0.22384	0.8259
X_3*X_3	–4.5672	0.56432	–8.0933	$7.4627e^{-07}$
X_4*X_4	–1.2784	0.56432	–2.2655	0.038719
X_1*X_2	2.4123	0.74515	3.2373	0.0055251
X_1*X_3	0.64479	0.74515	0.86531	0.4005
X_1*X_4	–0.67404	0.74515	–0.90456	0.38
X_2*X_3	–0.60829	0.74515	–0.81633	0.42709
X_2*X_4	0.61704	0.74515	0.82807	0.42061
X_3*X_4	5.1743	0.7919	6.534	$9.4553e^{-06}$

Benzoic acid adsorption for different variables could also be predicted from the respective contour plots (Figures 1–6) (Box and Wilson 1951; Box *et al.* 1978). Each contour curve represents an infinite number of combinations between two test variables with the other two being maintained at their respective zero levels. A relative comparison between Figure 1 and the regression equation revealed that the slope of each contour curve for different initial benzoic acid concentrations depended entirely on the amount of organobentonite. The higher the initial concentration of benzoic acid and the amount of organobentonite, the greater the extent of benzoic acid adsorption. This result agrees with the conclusions obtained for the main effects quoted in the above section.

The data depicted in Figures 2 and 3 demonstrate that the adsorption of benzoic acid was virtually independent of the agitation rate and the temperature but dependent on the benzoic acid concentration. The nature of the contour plots depicted in Figures 1–3 indicates that the mutual interaction between the benzoic acid concentration and the amount of organobentonite was more than that between the initial benzoic acid concentration and the agitation rate or the temperature. However, the contour plots shown in Figures 4 and 5 indicate that there was a mutual interaction between the amount of organobentonite, the temperature and the agitation rate, the elliptical nature of the plots indicating that the interactions were significant. As can be seen in Figure 4, the concentration of adsorbed benzoic acid increased with temperature. Mutual interaction between the agitation rate and the temperature for benzoic acid adsorption is demonstrated in Figure 6. Depending on the direction of movement, the concentration of adsorbed benzoic acid concentration either increased or decreased. In this case, a lower temperature and a higher agitation rate resulted in lower benzoic acid adsorption, and a higher temperature and a higher agitation rate led to increased adsorption.

Multi-stage Monte-Carlo optimization was used to solve regression equation (3). The optimum values of the test variables were found to be a temperature of 40ºC, an agitation rate of 170 rpm, an amount of organobentonite equal to 1.5 g and a benzoic acid concentration of 200 mg/l.

In Table 5, each of the observed benzoic acid adsorption values is compared with the values predicted from the model. Comparison of the residuals with the error variance (S_e^2 = 8.291,

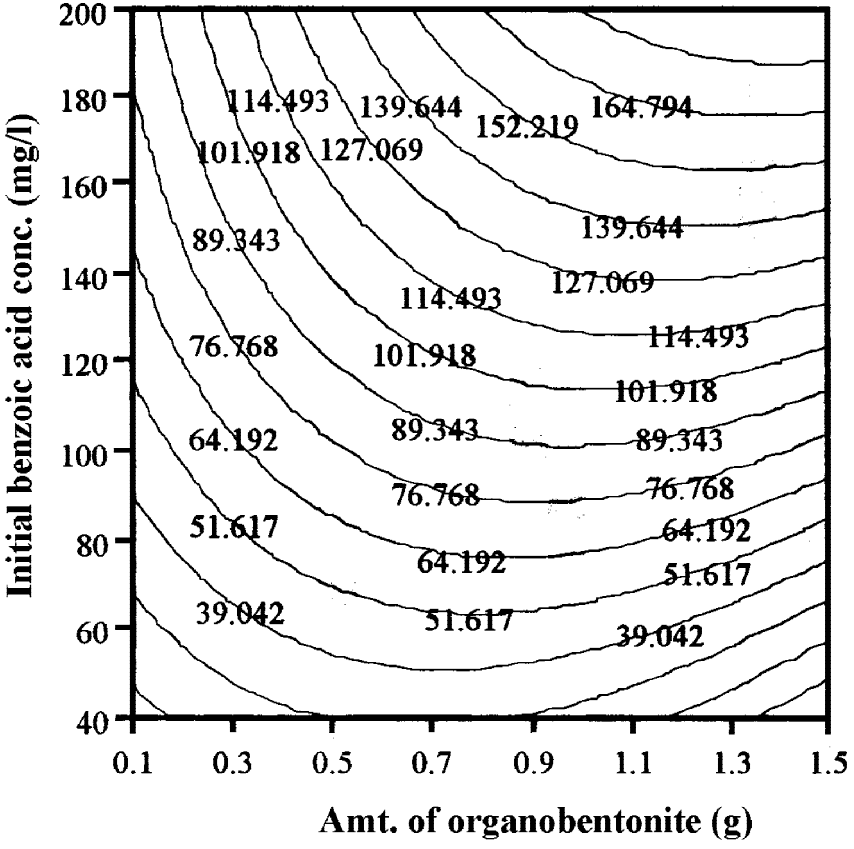


Figure 1. Contour plot of benzoic acid adsorption: influence of amount of organobentonite, initial benzoic acid concentration and their mutual interaction. Other variables held at zero level.

Table 3) indicated that almost none of the individual residuals exceeded twice the square root of the residual variance. All the above considerations indicate excellent adequacy for the regression model (Box *et al.* 1978; Khuri and Cornell 1987). The adequacy of the model was also examined by additional independent experiments at the suggested optimum experimental conditions. The maximum adsorbed benzoic acid concentration predicted by the equation (169.05 mg/l) agreed well with the experimental value (163 mg/l) obtained from experimental verification at the optimum values (x_1 = 200 mg/l, x_2 = 170 rpm, x_3 = 1.5 g and x_4 = 40ºC). This indicates that the model as generated predicted the adsorbed benzoic acid concentration adequately. Thus, the optimum conditions for benzoic acid adsorption on to ODTMA-bentonite were successfully developed by CCD and RSM.

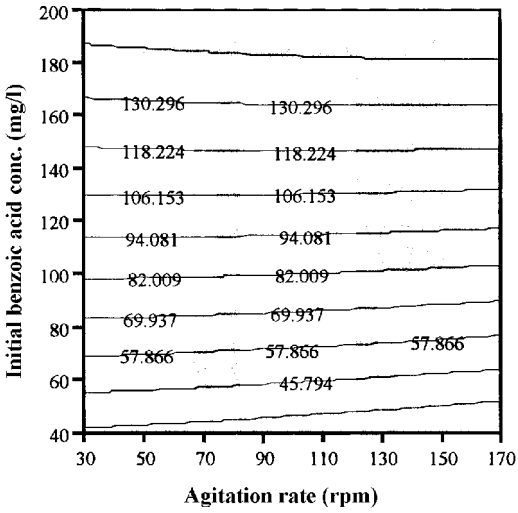


Figure 2. Contour plot of benzoic acid adsorption: influence of agitation rate, initial benzoic acid concentration and their mutual interaction. Other variables held at zero level.

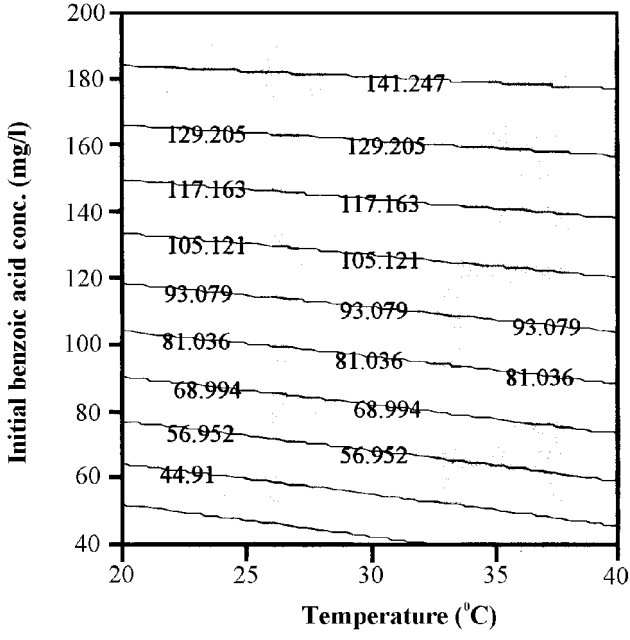


Figure 3. Contour plot of benzoic acid adsorption: influence of temperature, initial benzoic acid concentration and their mutual interaction. Other variables held at zero level.

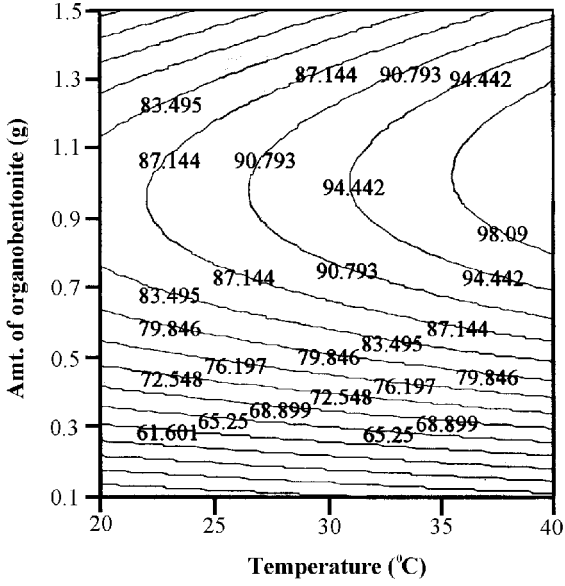


Figure 4. Contour plot of benzoic acid adsorption: influence of temperature, amount of organobentonite and their mutual interaction. Other variables held at zero level.

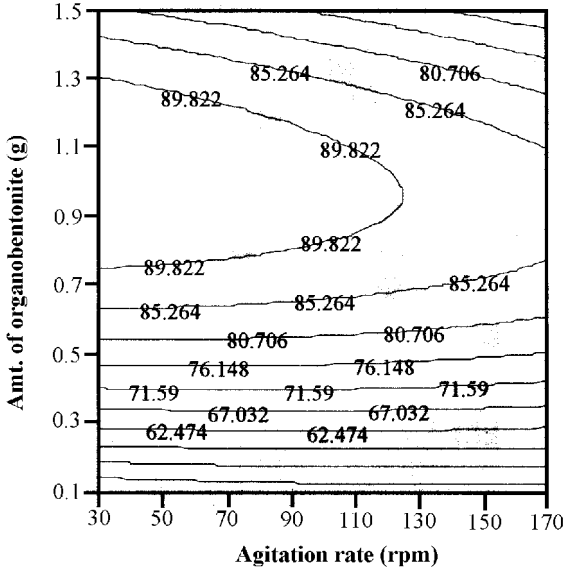


Figure 5. Contour plot of benzoic acid adsorption: influence of amount of organobentonite, agitation rate and their mutual interaction. Other variables held at zero level.

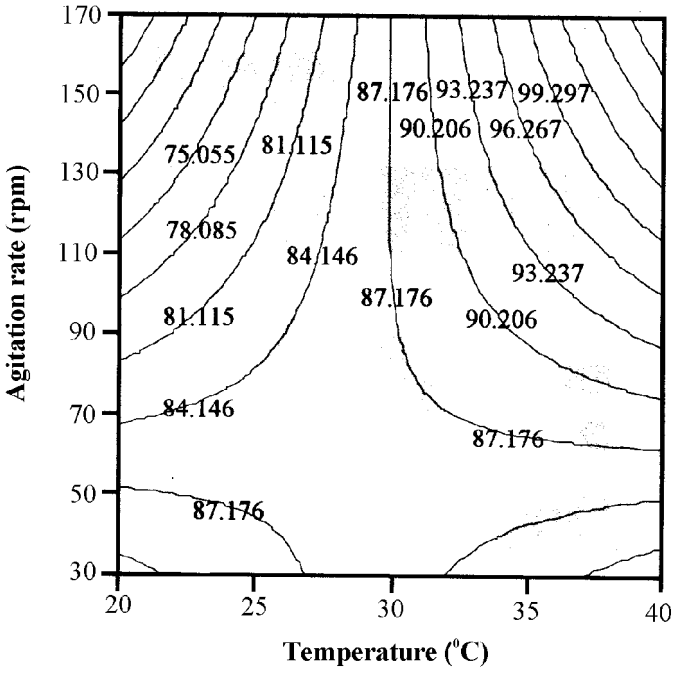


Figure 6. Contour plot of benzoic acid adsorption: influence of temperature, agitation rate and their mutual interaction. Other variables held at zero level.

CONCLUSIONS

Adsorption of benzoic acid on to ODTMA-bentonite was studied. Central composite design and Response Surface Methodology (RSM) were used with four parameters to evaluate the effects of important variables on the adsorption. A response equation was obtained for the adsorbed benzoic acid concentration. From this equation, it was possible to predict adequately the operating conditions required to obtain a well-defined quantity of benzoic acid adsorption.

It was found that the most effective parameters were the amount of organobentonite employed and the temperature. These factors had a positive influence on the concentration of benzoic acid adsorbed. Amongst the interactions, the initial concentration of benzoic acid–agitation rate and the amount of organobentonite–temperature were significant and had a positive influence on the adsorption. As a result, it was found that the adsorbed benzoic acid concentration of 169.05 mg/l predicted by the equation agreed well with the experimental value of 163 mg/l. This indicated that the generated model predicted the benzoic acid concentration adequately.

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TABLE 5. Observed Responses and Predicted Values

Observation No.	Actual value	Predicted value	Residual
1	50.597	48.655	1.942
2	50.831	48.845	1.986
3	45.728	42.438	3.29
4	53.476	52.278	1.198
5	60.597	59.793	0.804
6	60.953	62.563	–1.610
7	56.002	51.144	4.858
8	63.836	63.573	0.263
9	89.680	90.390	–0.710
10	90.242	87.885	2.357
11	85.119	86.642	–1.523
12	92.545	93.786	–1.241
13	120.640	122.226	–1.586
14	121.318	122.299	–0.981
15	116.367	116.044	0.323
16	123.437	125.767	–2.330
17	81.668	80.605	1.063
18	90.281	90.519	–0.238
19	84.991	86.504	–1.513
20	86.093	83.755	2.338
21	41.744	45.806	–4.062
22	93.813	88.926	4.887
23	26.941	28.551	–1.610
24	134.926	132.491	2.436
25	85.590	85.635	–0.045
26	85.334	85.635	–0.301
27	85.427	85.635	–0.208
28	86.164	85.635	0.529
29	85.265	85.635	–0.370
30	86.030	85.635	0.395

NOMENCLATURE

R	correlation coefficient
R^2	coefficient of determination
R^2_{adj}	adjusted coefficient of determination of the model
S^2_e	residual variance
S^2_r	variance as explained by the regression model
y	response, adsorbed benzoic acid concentration (mg/l)

Greek symbols

β_0	intercept term

β_1–β_4 linear coefficients
β_5–β_8 quadratic coefficients
β_9–β_{14} cross-product coefficients
ε random error

REFERENCES

Barrer, R.M. and Kelsey, K.E. (1989) *Clays Clay Miner.* **37**, 385.
Boyd, S.A., Mortland, M.M. and Chiou, C.T. (1988) *Soil Sci. Soc. Am., J.* **52**, 652.
Box, G.E.P. and Wilson, K.B. (1951) *J. R. Statistical Soc. London* **B13**, 1.
Box, G.E.P., Hunter, W.G. and Hunter, J.S. (1978) *Statistics for Experimenters*, John Wiley & Sons, New York, pp. 291–334.
Carrado, K.A. (2000) *Appl. Clay Sci.* **117**, 1.
Cochran, W.G. and Cox, G.M. (1957) *Experimental Designs*, 2nd Edn, John Wiley & Sons, New York, pp. 346–354.
Çelik, A., Yildiz, N. and Çalimli, A. (2000) *Rev. Chem. Eng.* **16**, 301.
Gitipour, S., Bowers, M.T. and Bodocsi, A. (1997) *J. Colloid Interface Sci.* **196**, 191.
Jaynes, W.F. and Boyd, S.A. (1990) *J. Air, Waste Manage. Assoc.* **40**, 1653.
Kazanov, V. (1976) *Cybernetic Methods in Chemistry*, Mir Publishers, Moscow, pp. 510–539.
Khuri, A.I. and Cornell, J.A. (1987) *Response Surfaces: Design and Analyses*, Marcel Dekker, Inc., New York.
Koh, S.M. and Dixon, J.B. (2001) *Appl. Clay Sci.* **18**, 111.
Lee, J.H., Song, D.I. and Jeon, Y.W. (1997) *Sep. Sci. Technol.* **32**, 1975.
Lin, S.H. and Cheng, M.J. (2000) *Environ. Technol.* **21**, 475.
Montgomery, D.C. (1996) *Design and Analysis of Experiments*, 4th Edn, John Wiley & Sons, New York, pp. 575–651.
Myers, R.H. (1971) *Response Surface Methodology*, Allyn & Bacan Inc., Boston, MA, USA, pp. 67–125.
Smith, J. and Galan, A. (1995) *Environ. Sci. Technol.* **29**, 685.
Smith, J. and Jaffe, P.R. (1991) *Environ. Sci. Technol.* **25**, 2054.
Smith, J.A., Jaffe, P.R. and Chiou, C.T. (1990a) *Environ. Sci. Technol.* **24**, 1167.
Smith, J.A., Jaffe, P.R. and Chiou, C.T. (1990b) *Environ. Sci. Technol.* **24**, 1172.
Yildiz, N., Kapucu, H. and Çalimli, A. (2000) *Rev. Chem. Eng.* **16**, 55.