# Adsorption of 4-Toluene Sulfonic Acid on Modified Bentonite : Optimization by Response Surface Methodology

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## Abstract

Adsorption of 4-toluene sulfonic acid (4-TSA) onto modified bentonite (ODTMA-bentonite) was carried out. ODTMA-bentonite was synthesized by placing quaternary ammonium surfactant (octadecyltrimethyl ammonium bromide) on Çankırı sodium bentonite (ÇNa-B) having a cation exchange capacity of 85 meq/100 g clay. Response surface methodology based on a 5-level, 4-variable central composite rotatable was used to evaluate the effects of important parameters on the adsorption of 4-TSA on ODTMA-bentonite. Temperature (25-45 °C), agitation rate (30-170 rpm), the amount of organobentonite (0.1-1.5 g) and initial 4-TSA concentration (100-500 mg/l) were chosen as process variables for the optimization. Of these parameters, initial 4-TSA concentration and the amount of organobentonite had significant effects compared with temperature and agitation rate. The optimum values for the tested variables in selected ranges for the maximum adsorption of 4-TSA onto ODTMA-bentonite were found to be an adsorption temperature of 45 °C, an agitation rate of 170 rpm, an organobentonite level of 1.5 g and an initial concentration of 500 mg/l. The coefficient of determination ($R^2$) for the model is 0.987. Probability value is 1.635 x $10^{-10}$ (P - value < 0.01). This p-value demonstrates a very high significance for the regression model. The predicted maximum adsorption in the selected ranges of 4-TSA on ODTMA –bentonite was 428 mg/l. An actual experimental value of 421 mg/l was obtained.

**Key words:** Adsorption, Smectite, Organobentonite, Response surface methodology

## Introduction

Aromatic waste compounds are generated by a wide variety of sources such as coal conversion plants and the oil and petrochemical industries. The organic contents in these wastewaters usually exceed the level for safe discharge. Hence removal of organic compounds from the wastewater has become an integral part of the wastewater treatment system in the chemical and petrochemical industries. Recently, there has been much interest in using clays, par-

ticularly smectites, because of their high cation exchange capacity (CEC) and surface area for removal of organic pollutants from water. Particularly in the past 10 years, there have been considerable interest and advances in the use of organoclays as adsorbants to remediate 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.*, 1990).

Among the various organoclays, organoben-

tonites are the most widely investigated by researchers (Boyd *et al.,* 1988; Lee *et al.,* 1997; Jaynes and Boyd, 1990; Çelik *et al.,* 2000; Yıldız 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 solutions, primarily because of the electrically charged and hydrophilic characteristics of its surface. With this exchange treatment, the bentonite surfaces are drastically altered. As a result, the organobentonites are turned into strong adsorbents for nonionic organic pollutants compared with natural ones (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 tetrachloromethane sorption to bentonite modified by exchanged small organic cations was characterized by nonlinear isotherms, strong solute uptake, and competitive sorption. In contrast, tetrachloromethane sorption to bentonites modified by relatively large organic cations (C > 10) was characterized by essentially linear isotherms, lower solute uptake and noncompetitive sorption. The authors concluded that the differences between the 2 groups of organoclay sorbents were attributable to different sorption mechanisms: adsorption for bentonite modified with organic cations of small functional groups and partition for bentonite modified with organic cations of relatively large functional groups. The small organic cations (e.g., tetramethyleammonium) create relatively rigid, nonpolar surfaces amenable to nonionic solute uptake by adsorption. The larger organic cations (e.g., hexadecyltrimethylammonium bromide) create an organic partition medium through the conglomeration of their flexible alkyl chains. Although these organoclays find growing usage in environmental applications such as contaminant fixation and fuel spill control, systematic studies to achieve optimum adsorption parameters of adsorption of organic contaminants onto organobentonites have not been carried out extensively and there are few studies on this subject (Yıldız *et al.*, 2000).

In this study, adsorption of the 4-TSA onto ODTMA-bentonite synhesized from Çankırı sodium bentonite was optimized using response surface methodology (RSM) and statistical central composite design. The variables selected for the present study were temperature, agitation rate, amount of organobentonite and initial 4-TSA concentration.

## Materials and Methods

Çankırı (Turkey) sodium bentonite was used in the study. The chemical analysis of the bentonite is given in Table 1. The CEC of original bentonite was determined by the methylene blue test (ANSI/ASTM C 837-76).

The X-ray powder diagrams of the original and ODTMA-bentonite prepared as random powder material, were obtained with a Rikagu D-max 2200 powder difractometer. Montmorillonite was the main mineral in the samples. Minor amounts of quartz, (-cristobalite, albite) were also identified in the raw materials.The particle size distributions of the solid samples were determined using a Malvern Mastersizer 2000 (Hydro 2000 MU) particle analyzer, which is based on the principle of laser ensemble light scattering. The particles are introduced to the analyzer beam in a sample presentation cell located in the optical unit.

Specific surface areas (BET) and pore size distributions of the original and ODTMA-bentonite samples were determined using Quantachrome NOVA 2200 series volumetric gas adsorption instrument. The determination is based on the measurements of the adsorption isotherms of nitrogen at 77 K. Before measurements were started, moisture and gases such as nitrogen and oxygen, which were adsorbed on the solid surface or held in the open pores, were removed under reduced pressure at 150 °C for 5 h.

For the exchange of organic cations with inorganic ions, octadecyltrimethylammonium bromide (ODTMA, Fluka) was used.

**Table 1.** Chemical analyses of the original bentonite.

| Sample | MgO | $Al_2O_3$ | $SiO_2$ | CaO | $Fe_2O_3$ | $SO_3$ | $K_2O$ | $Na_2O$ | $TiO_2$ | KK* |
|---|---|---|---|---|---|---|---|---|---|---|
| Na-B | 0.85 | 15.50 | 70.74 | 0.46 | 2.23 | 0.17 | 0.24 | 2.12 | 0.00 | 6.53 |

*Weight loss at 1000 *C

The organobentonite was prepared as described in detail by Celik *et al.,* (1999). Organic pollutant concentrations in aqueous phase were determined by ultraviolet spectrophotometry (UV-1601, Shimadzu). The measurements were carried out at a wavelength of 261 nm. Solutions of organic contaminant were prepared at selected concentrations. The sorption experiments were carried out as given in detail by Çelik *et al.,* (1999). In the experiments, the quantity of 4-TSA solution and contact time of solution with clay were kept constant at 100 cc and 4 h respectively.

## Experimental Design and Optimization by RSM

RSM is used in the empirical study of relationships between one or more measured responses and a number of input variables, and the objective is to optimize this response (Box and Wilson, 1951; Cochran and Cox, 1957; Myers, 1971; Kazanov, 1976; Box *et al.,* 1978; Khuri and Cornell, 1987; Montgomery, 1996, Kapucu *et al.,* 2002). A 24 full factorial central composite (CCD) for 4 independent variables each at 5 levels was adopted in this study. The fractional factorial design consisting of 16 factorial points, 8 axial points (2 axial points on the axis of each design variable at a distance of 2 from the design center), and 6 replicates at the center points was employed to fit a second order polynomial model. A total of 30 experiments were necessary for the estimation of the 14 coefficients of the model. The quadratic response surface model was fitted to the following equation

$$
\begin{aligned}
Y = &\beta o + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \\
&\beta_5 x_1^2 + \beta_6 x_2^2 + \beta_7 x_3^2 + \beta_8 x_4^2 + \beta_9 x_1 x_2 + \\
&\beta_{10} x_1 x_3 - \beta_{11} x_1 x_4 - \beta_{12} x_2 x_3 + \beta_{13} x_2 x_4 + \\
&\beta_{14} x_3 x_4 + \varepsilon
\end{aligned}
\tag{1}
$$

where $y$ is the measured response for each test (i.e adsorbed 4-TSA, mg/l in this study); $x_1, x_2, x_3, x_4$ are coded independent variables ($x_1$ = initial concentration of 4-TSA, $x_2$ = agitation rate (rpm), $x_3$ = amount of organobentonite $(g)$, $x_4$ = temperature (°C); $\beta o$ is the intercept term; $\beta_1$, $\beta_2$, $\beta_3$, $\beta_4$ are linear coefficients; $\beta_5$, $\beta_6$, $\beta_7$ and $\beta_8$ are quadratic coefficients; $\beta_9$, $\beta_{10}$, $\beta_{11}$ and $\beta_{12}$ are cross-product coefficients; $\varepsilon$ is the experimental error. The range and levels of the variables investigated in this study are given in Table 2.

Selection of these levels was carried out on the basis of results obtained in a preliminary study. In developing the regression equation, the test variables were coded according to the equation

$$
x_i = (X_i - X_i^*)/(X_i) \tag{2}
$$

where xi 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 center point and $X_i$ 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 by the coefficient of determination ($R^2$) and the analysis of variances.

**Table 2.** Experimental range and levels of independent variables.

| Variables | Range and Levels | | | | |
|---|---|---|---|---|---|
| | -2 | -1 | 0 | +1 | +2 |
| Initial concentration of 4-toluene sulfonic acid (mg/l), $X_1$ | 100 | 200 | 300 | 400 | 500 |
| Agitation (rpm), $X_2$ | 30 | 65 | 100 | 135 | 170 |
| Amount of Organobentonite (g), $X_3$ | 0.1 | 0.45 | 0.8 | 1.15 | 1.5 |
| Temperature (°C), $X_4$ | 25 | 30 | 35 | 40 | 45 |

**Table 3.** Properties of original and organobentonite.

| Sample | Total organic carbon content, % | Surface area, $m^2g^{-1}$ | d(001) |
|---|---|---|---|
| Original | 0.7 | 55.37 | 12.40 |
| ODTMA-bentonite | 24.28 | 28.92 | 17.60 |

The contour plots and dimensional surfaces are the most useful approach to predict the response for different values of the test variables and to identify the type of interactions between test variables (Box *et al.,* 1978). Depending on the coefficients, regression equations can take a number of different forms. The corresponding contour systems are obviously of very different kinds, such as a maximum point or a minimum point (elliptical, circular), saddle point (minimax), stationary ridge and rising/falling ridge (Myers, 1971; Kazanov, 1976; Box *et al.,* 1978).

**Results and Discussion**

Total organic carbon content, BET surface areas and basal spacing (d(001)) of the original and the treated bentonite are presented in Table 3. The organic carbon content of the natural clay sample was very low in comparison with ODTMA-bentonite. The organic carbon in the ODTMA-bentonite was almost entirely derived from the exchanged organic cations.

The X-ray diffraction basal spacings d(001) of the original bentonite were 12.4 Å (Table 3). The interlayer spacings of organobentonite increased with the quaternary ammonium cations used in synthesizing and reached 17.6 Å for ODTMA-bentonite. These spacings for ODTMA-bentonite correspond to the formation of bilayers and paraffin complexes in which ODTMA ions are in direct contact with each other, leading to the formation of partition phases derived from the $C_{18}$ hydrocarbon groups.

The BET surface area of original Na-B was 55.37 $m^2g^{-1}$. This decreased to 28.92 $m^2g^{-1}$ for organobentonite (ODTMA-bentonite), which was more aggregated and had lower surface areas than the natural clay. The relatively low surface area of the ODTMA-bentonite indicates the external surface only, no internal surface area was accessible to nitrogen gas (Jaynes and Vance, 1996).

For a textural characterization of any porous solid, the concept of surface area does not give a visual picture of it. Pore size and pore size distributions are necessary if the material is to be fully char-

acterized. The pore size distribution in the mesopore region was obtained by applying the BJH method (Barrett *et al.*, 1951) to the desorption branch of the isotherms of nitrogen at 77 K, assuming the pores to be cylindrical. Figure 1 compares the change of pore size distribution for original and ODTMA-bentonite. As seen from the figure, the samples have almost mesopores whose diameters are between 20 and 500 Å. The original sample exhibited maxima in differential pore volumes at about 39.34 Å in pore diameter. However, ODTMA-bentonite showed maximum differential pore volumes at about 27.64 Å. After that, the differential pore volumes for these samples tend to decrease as the pore diameter decreases. It should be considered that the pores were closed by adsorbed ODTMA cations.
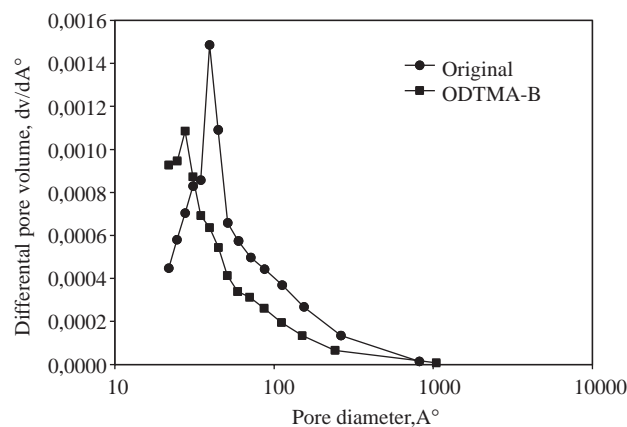


**Figure 1.** Pore size distributions of original and ODTMA-bentonite.

Particle size analysis of the original and organobentonites was also carried out. The particle size distributions for both the original and organobentonites are shown in Figures 2a and b. The distributions are presented in terms of undersize (2a) and in size (2b). Analysis of the original and organobentonites showed that the organobentonites contain many more coarse particles than the original bentonite. It was obvious (Figures 2a and

b) that the whole size range of the original bentonite was finer than the organobentonite. As can be seen from Figure 2a about 80% of the original bentonite is less than 10 $\mu$m, whereas 5% of ODTMA-bentonite is less than 10 $\mu$m. The distributions of the particles in the bulk obtained from organobentonite are more uniform than the original sample size distribution, as shown in Figure 2b.

A second order polynomial model Eq. (3) was fitted to the experimental adsorption of 4-TSA on ODTMA-bentonite. The statistical combinations of the independent variables in coded and natural along with the experimental responses are presented in Table 4.

In order to determine whether or not the quadratic model is significant, it is necessary to conduct an analysis of variance (ANOVA) using the usual Fisher's F-tests etc., in which the regression sum of squares is subdivided into 2 parts: that attributed to linear regression and that attributed to the quadratic model (Myers, 1971). The ANOVA for the quadratic model is presented in Table 5.

**Table 4.** Full factorial central composite design matrix of 4 variables in coded and natural units along with the observed response.

| Obs. No | $X_1$ | $X_2$ | $X_3$ | $X_4$ | Initial concent. of TSA (mg/l) | Agitation (rpm) | Amount of organobentonite (g) | Temperature (°C) | Absorbed TSA (mg/l) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | -1 | -1 | -1 | -1 | 200 | 65 | 0.45 | 30 | 137.91 |
| 2 | 1 | -1 | -1 | -1 | 400 | 65 | 0.45 | 30 | 195.41 |
| 3 | -1 | 1 | -1 | -1 | 200 | 135 | 0.45 | 30 | 137.09 |
| 4 | 1 | 1 | -1 | -1 | 400 | 135 | 0.45 | 30 | 197.94 |
| 5 | -1 | -1 | 1 | -1 | 200 | 65 | 1.15 | 30 | 153.62 |
| 6 | 1 | -1 | 1 | -1 | 400 | 65 | 1.15 | 30 | 305.30 |
| 7 | -1 | 1 | 1 | -1 | 200 | 135 | 1.15 | 30 | 151.36 |
| 8 | 1 | 1 | 1 | -1 | 400 | 135 | 1.15 | 30 | 303.19 |
| 9 | -1 | -1 | -1 | 1 | 200 | 65 | 0.45 | 40 | 135.51 |
| 10 | 1 | -1 | -1 | 1 | 400 | 65 | 0.45 | 40 | 188.43 |
| 11 | -1 | 1 | -1 | 1 | 200 | 135 | 0.45 | 40 | 139.05 |
| 12 | 1 | 1 | -1 | 1 | 400 | 135 | 0.45 | 40 | 190.93 |
| 13 | -1 | -1 | 1 | 1 | 200 | 65 | 1.15 | 40 | 159.21 |
| 14 | 1 | -1 | 1 | 1 | 400 | 65 | 1.15 | 40 | 309.58 |
| 15 | -1 | 1 | 1 | 1 | 200 | 135 | 1.15 | 40 | 157.60 |
| 16 | 1 | 1 | 1 | 1 | 400 | 135 | 1.15 | 40 | 313.96 |
| 17 | -2 | 0 | 0 | 0 | 100 | 100 | 0.8 | 35 | 60.89 |
| 18 | 2 | 0 | 0 | 0 | 500 | 100 | 0.8 | 35 | 315.92 |
| 19 | 0 | -2 | 0 | 0 | 300 | 30 | 0.8 | 35 | 220.8 |
| 20 | 0 | 2 | 0 | 0 | 300 | 170 | 0.8 | 35 | 228.51 |
| 21 | 0 | 0 | -2 | 0 | 300 | 100 | 0.1 | 35 | 38.79 |
| 22 | 0 | 0 | 2 | 0 | 300 | 100 | 1.5 | 35 | 237.45 |
| 23 | 0 | 0 | 0 | -2 | 300 | 100 | 0.8 | 25 | 214.28 |
| 24 | 0 | 0 | 0 | 2 | 300 | 100 | 0.8 | 45 | 227.28 |
| 25 | 0 | 0 | 0 | 0 | 300 | 100 | 0.8 | 35 | 223.84 |
| 26 | 0 | 0 | 0 | 0 | 300 | 100 | 0.8 | 35 | 223.13 |
| 27 | 0 | 0 | 0 | 0 | 300 | 100 | 0.8 | 35 | 218.28 |
| 28 | 0 | 0 | 0 | 0 | 300 | 100 | 0.8 | 35 | 220.24 |
| 29 | 0 | 0 | 0 | 0 | 300 | 100 | 0.8 | 35 | 218.08 |
| 30 | 0 | 0 | 0 | 0 | 300 | 100 | 0.8 | 35 | 218.85 |
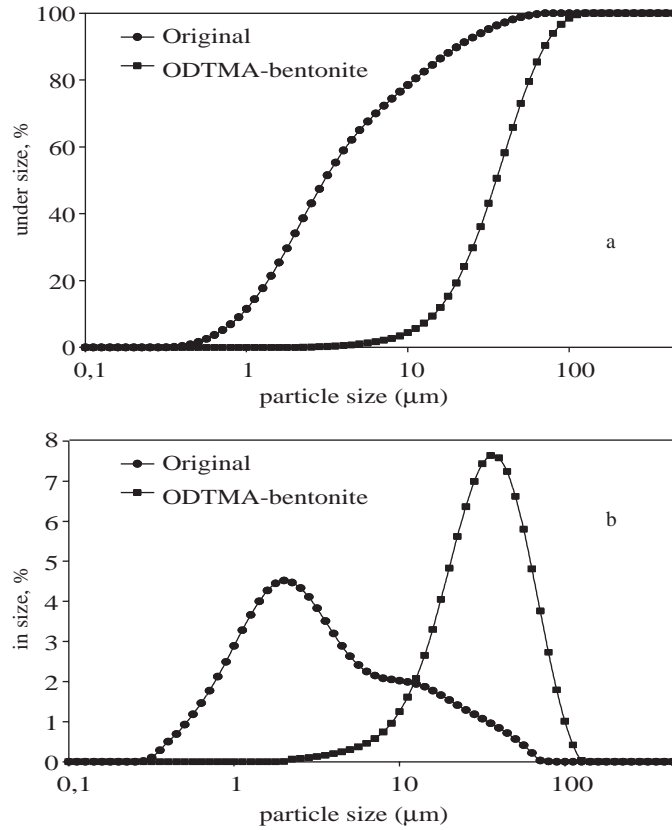
**Figure 2.** Particle size distribution: a) under size, b) in size.

**Table 5.** Analysis of variance (ANOVA) for the quadratic model.

| Sources of variations | Sum of squares | Degreees of freedom | Mean square | F-value | Prob(P) > F |
|---|---|---|---|---|---|
| Model | 1.3305575476e + 05 | 14 | 9503.983 | | |
| Error | 2.482e + 03 | 15 | 165.476 | 57.437 | 0.0001 |
| Total | 135537.765 | 29 | 9669.45 | | |

It is shown that the probability value for the multiple regression is very small (P - value = 1.635 x $10^{-10}$, P < 0.01 when significant). The ANOVA indicated that the model was adequate to represent the actual relationship between the response (adsorption of 4-TSA) and the significant variables. The Fishers F-test with a very low probability value also demonstrates a very high significance for the regression model since the computed F value ($F_{0.01(14,15)}$ = $S_r^2/S_e^2$ = 58.78) is much greater than the tabular $F_{0.01(14,15)}$ value (3.66) at 1.5% level. A good model explains most of the variation in the response. The coefficient of determination is a measure for this criterion and can be calculated by dividing the variation explained by the model by the total variation (Khuri and Cornell, 1987). The closer the value of $R^2$ is to unity the better the correlation between the observed and predicted values. The coefficient of correlation ($R^2$) and the adjusted coefficient of determination ($R_{adj}^2$) of the model were 0.982 and 0.979, respectively. In this case, the value of the $R^2$ indicates that only 1.7% of the total variation is not explained by the regression model, which suggests te high significance of the model. A higher value of the correlation coefficient $R^2$ (0.990) justifies an excellent correlation between the independent variables (Box et al., 1978).

The application of response surface methodology yields, on the basis of parameter estimates, an empirical relationship between the response vari-

ables (adsorbed 4-TSA concentration) and the test variables are related by the following quadratic expression in coded unit

$$Y = 220.4 + 56.217x_1 - 0.6593x_2 + 38.463x_3 +$$
$$1.8415x_4 - 7.1402x_1^2 + 1.9223x_2^2 - 19.711x_3^2 +$$
$$0.9535x_4^2 + 0.88729x_1x_2 + 24.552x_1x_3 -$$
$$1.0048x_1x_4 - 0.94354x_2x_3 + 1.076x_2x_4 +$$
$$2.8733x_3x_4 \qquad\qquad (3)$$

The significance of each coefficient was determined by t-test and P - values, which are listed in Table 6.

Student's t-test was employed to determine the knowledge of the error mean square that is essential in testing the significance of the estimated coefficient of the regression equation Eq. (3). The Student's t-test value can be obtained by dividing each coefficient by its standard error. A large t-value implies that the coefficient is much greater than its standard error. The P - values were used as a tool to check the significance of each of the coefficients. The P - values are necessary to understand the pattern of the mutual interactions between the test variables. The larger magnitude of the t-value and smaller P - value identifies an effect that appears to be very important (Khuri and Cornell, 1987).

The first order main effects of both initial 4-TSA concentration ($x_1$) and the amount of organobentonite ($x_3$) and their second order main effects ($x_1^2$, $x_3^2$) are highly significant since their respective P values are very small. $x_1$ and $x_3$ have a positive influence while $x_1^2$ and $x_3^2$ have a negative effect on adsorption. Among the interactions those between the 4-TSA concentration and amount of organobentonite ($x_1 - x_3$) are modestly significant (P > 0.1) This interaction has a positive effect on adsorption.

The 4-TSA adsorption for different variables can also be predicted from the respective contour plots (Figures 3-8) (Box and Wilson, 1951; Box *et al.*, 1978). Each contour curve represents an infinite number of combinations of 2 test variables with the other 2 maintained at their respective zero levels. A relative comparison between Figure 3 and the regression equation reveals that the slope of each contour curve of initial 4-TSA concentration entirely depends on the amount of organobentonite. The higher the amount of organobentonite and initial 4-TSA concentration, the higher the adsorption obtained. This agrees with the conclusions for the main effects in the above section. In Figures 4 and 5, 4-TSA adsorption is almost independent of agitation and temperature but is dependent on 4-TSA concentration. The nature of the contour plots in Figures 4-6 shows that the mutual interaction between initial 4-TSA concentration and the amount of organobentonite is greater than that between initial 4-TSA concentration and

**Table 6.** Least squares fit and parameters estimates (significance of regression coefficients).

| Model term | Parameter estimate | Standard error | Computed t-value | P - value |
|---|---|---|---|---|
| Intercept | 1189.8 | 5.1908 | 42.461 | 0 |
| $X_1$ | 56.217 | 2.6109 | 21.532 | 1.0805e-12 |
| $X_2$ | 0.65931 | 2.6109 | 0.2525 | 0.8040 |
| $X_3$ | 38.463 | 2.6109 | 14.732 | 2.5033-10 |
| $X_4$ | 1.8415 | 2.6109 | 0.7053 | 0.49142 |
| $X_1*X_1$ | -7.1404 | 2.4288 | -2.9398 | 0.0101 |
| $X_2*X_2$ | 1.9223 | 2.4288 | 0.79147 | 0.44101 |
| $X_3*X_3$ | -19.711 | 2.4288 | -8.1157 | 7.212e-07 |
| $X_4*X_4$ | 0.95358 | 2.4288 | 0.39261 | 0.70013 |
| $X_1*X_2$ | 0.88729 | 3.2071 | 0.2766 | 0.78581 |
| $X_1*X_3$ | 24.552 | 3.2071 | 7.6556 | 1.4742e-06 |
| $X_1*X_4$ | -1.0048 | 3.2071 | -0.3133 | 0.7583 |
| $X_2*X_3$ | -0.94354 | 3.2071 | -0.2942 | 0.7726 |
| $X_2*X_4$ | 1.076 | 3.2071 | 0.3355 | 0.334 |
| $X_3*X_4$ | 2.8733 | 3.4083 | 0.8430 | 0.4125 |
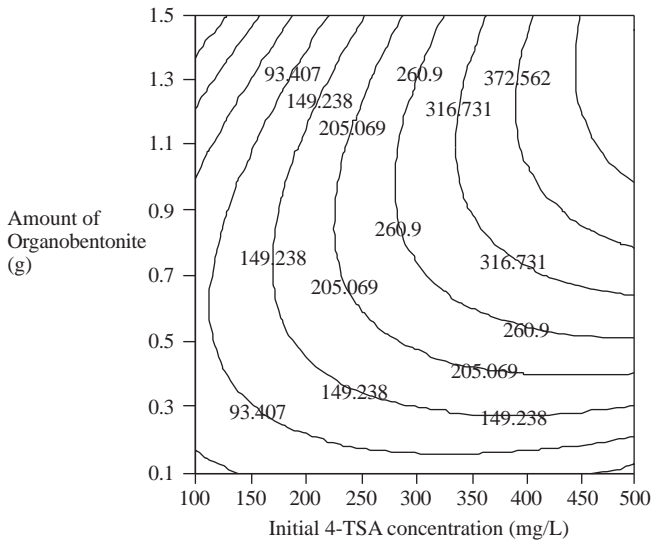
**Figure 3.** Contour plot of 4-TSA adsorption: the effect of amount of organobentonite, initial 4-TSA concentration and their mutual interaction. Other variables are held at zero level.
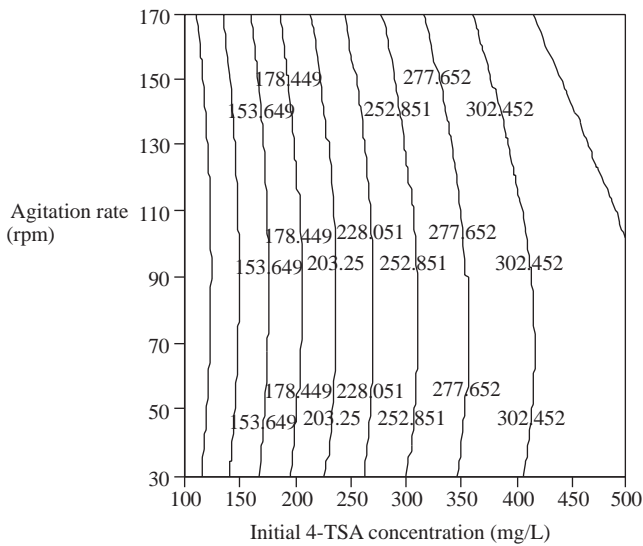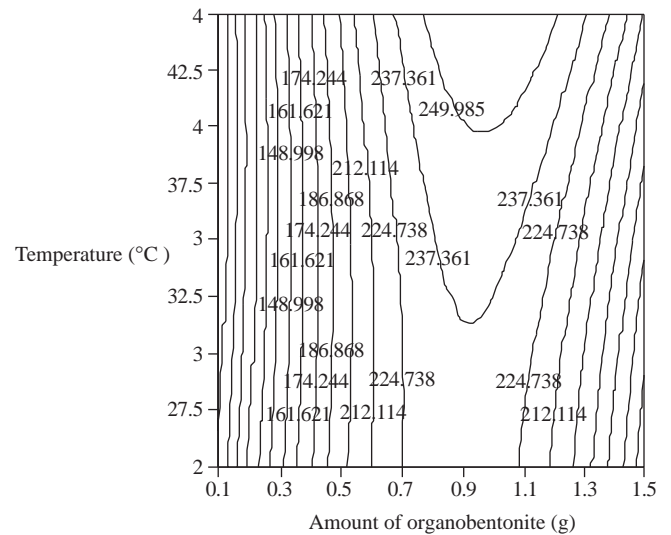


**Figure 4.** Contour plot of 4-TSA adsorption: the effect of agitation, initial 4-TSA concentration and their mutual interaction. Other variables are held at zero level.

agitation or temperature. In Figures 6 and 7 the contour plots show that the interaction between the amount of organobentonite and temperature is greater than that between the amount of organobentonite and agitation. The elliptical contour plot shows that the interaction of the variables is significant (Figure 6). This figure indicates an increase in

adsorption up to an organobentonite level of 0.9 and a decrease in adsorption above this point. Figure 8 shows the mutual interaction between agitation and temperature for 4-TSA adsorption. With a lower temperature and agitation rate (between 70 and 120 rpm) lower adsorption was obtained.
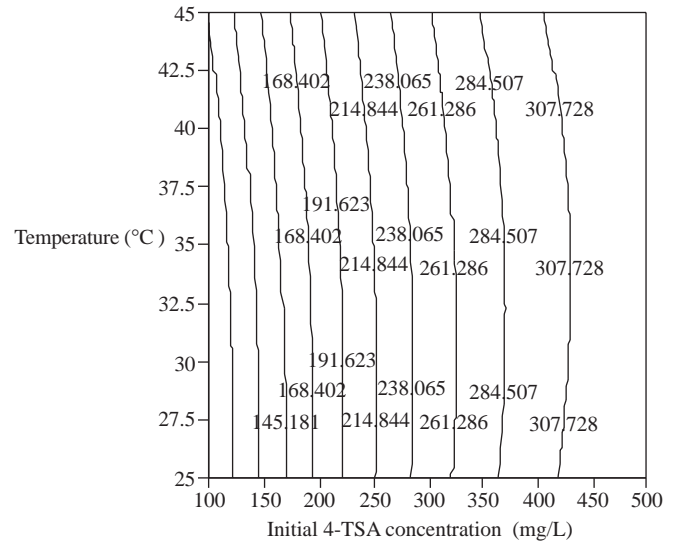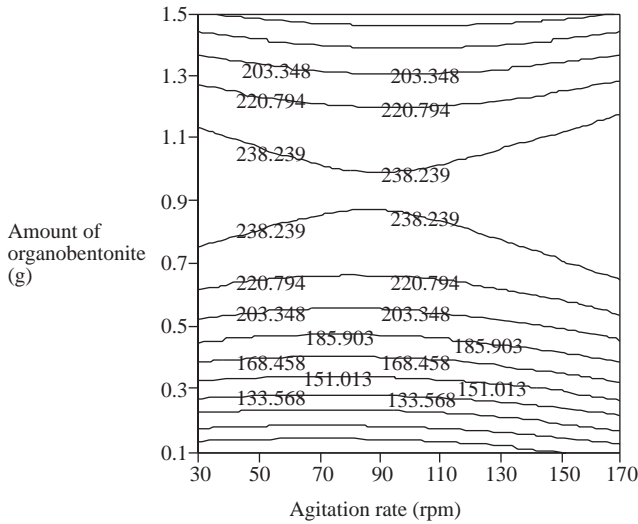


**Figure 5.** Contour plot of 4-TSA adsorption: the effect of temperature, initial 4-TSA concentration and their mutual interaction. Other variables are held at zero level.
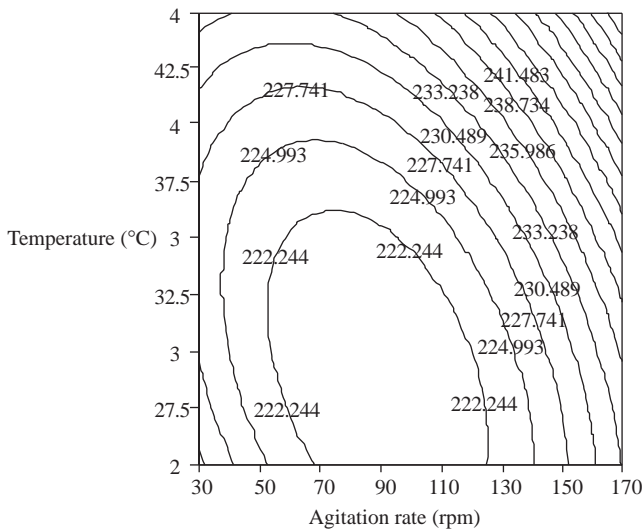


**Figure 6.** Contour plot of 4-TSA adsorption: the effect of temperature, the amount of organobentonite and their mutual interaction. Other variables are held at zero level.

**Figure 7.** Contour plot of 4-TSA adsorption: the effect of the amount of organobentonite, agitation and their mutual interaction. Other variables are held at zero level.



**Figure 8.** Contour plot of 4-TSA adsorption: the effect of temperature, agitation and their mutual interaction. Other variables are held at zero level.

Each of the observed 4-TSA adsorption values is compared with the values predicted from the model in Table 7.

The comparison of the residuals with the error variance ($S_e^2 = 165.467$, Table 5) indicates that none of the individual residuals exceeds twice the square

root of the residual variance. All of the above considerations indicate an excellent adequacy of 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 synthetic condition. The maximum adsorbed 4-TSA concentration predicted by the equation (28.53 mg/g)), agrees well with the experimental verification at the optimum values ($x_1 = 45\ °C$, $x_2 = 170$ rpm, $x_3 = 1.5$ g, $x_4 = 500$ mg/l). This indicates that the generated model adequately predicted the adsorption of 4-TSA on ODTMA-bentonite.

**Table 7.** Observed Responses and predicted values.

| Obs. No | Actual value | Predicted value | Residual |
|---|---|---|---|
| 1 | 137.91 | 126.68 | 11.23 |
| 2 | 195.41 | 190.25 | 5.16 |
| 3 | 137.09 | 125.96 | 11.13 |
| 4 | 197.94 | 193.08 | 4.86 |
| 5 | 153.62 | 159.93 | -6.31 |
| 6 | 305.30 | 312.42 | -7.12 |
| 7 | 151.36 | 146.15 | 5.21 |
| 8 | 303.19 | 311.47 | -8.27 |
| 9 | 135.51 | 124.48 | 11.03 |
| 10 | 188.43 | 184.02 | 4.41 |
| 11 | 139.05 | 128.06 | 10.99 |
| 12 | 190.93 | 191.16 | -0.23 |
| 13 | 159.21 | 159.93 | -0.72 |
| 14 | 309.58 | 317.69 | -8.35 |
| 15 | 157.60 | 159.74 | -2.14 |
| 16 | 313.96 | 321.05 | -7.09 |
| 17 | 60.89 | 79.40 | -18.51 |
| 18 | 315.92 | 304.27 | 11.65 |
| 19 | 220.8 | 226.70 | -5.9 |
| 20 | 228.51 | 229.41 | -0.9 |
| 21 | 38.79 | 64.62 | -25.85 |
| 22 | 237.45 | 218.48 | 18.97 |
| 23 | 214.28 | 220.53 | -6.25 |
| 24 | 227.28 | 227.90 | -0.62 |
| 25 | 223.84 | 220.4 | 3.44 |
| 26 | 223.13 | 220.4 | 2.73 |
| 27 | 218.28 | 220.4 | -2.12 |
| 28 | 220.24 | 220.4 | -0.16 |
| 29 | 218.08 | 220.4 | -2.32 |
| 30 | 218.85 | 220.4 | -1.55 |

## Conclusions

Adsorption of 4-TSA on ODTMA-bentonite was carried out. Central composite design and RSM were used with 4 parameters to evaluate the effects of important parameters. A response equation has been obtained for the adsorbed 4-TSA concentration. From this equation, it is possible to predict adequately the operating conditions required to obtain a well defined adsorption of 4-TSA. It was found that the most effective parameters were the initial concentration of 4-TSA and the amount of organobentonite. These factors have a positive influence on 4-TSA adsorption. Among the interactions, the initial concentration amount of organobentonite interaction is significant and has a positive influence on the adsorption. According to these results the adsorbed 4-TSA concentration of 428 mg/l (28.53 mg/g) predicted by the equation agrees well with the experimental value of 421 mg/l (28.06 mg/g). This indicates that the generated model adequately predicted the adsorbed 4-TSA concentration.

## Nomenclature

| | |
|---|---|
| R | correlation coefficient |
| $R^2$ | coefficient of determination |
| $R^2_{Adj}$ | the adjusted coefficient of determination of the model |
| $S^2_e$ | residual variance |
| $S^2_r$ | variance explained by regression model |
| y | response, adsorbed 4-TSA concentration (mg/l) |
| $\varepsilon$ | random error |
| $\beta_0$ | intercept term |
| $\beta_1 - \beta_4$ | linear coefficients |
| $\beta_5 - \beta_8$ | quadratic coefficients |
| $\beta_9 - \beta_{14}$ | cross-product coefficients |

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