

Process optimization for the removal of p-nitrophenol and p-nitroaniline by hexadecyltrimethylammonium-bentonite from single and binary solute systems

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ABSTRACT

Optimization of the removal of p-nitrophenol and p-nitroaniline from single and binary solute systems by Hexadecyltrimethylammonium chloride (HDTMA) bentonite using the response surface methodology (RSM) was studied. Central composite design was used to determine the effect of four independent variables; pH, Adsorbate concentration, solid:liquid ratio (S:L) and Time. Based on the central composite design used, linear and quadratic models were developed for removal of p-nitrophenol and p-nitroaniline from the single- and binary solute systems respectively. The influence of each factor on the process was determined from the analysis of variance (ANOVA). The optimum conditions obtained for the single solute system were pH of 7.99, adsorbate concentration of 2.02mg/dm³, solid: liquid ratio of 5.0, time of 120mins and removal efficiency of 27.07% for p-nitroaniline and pH of 7.97, adsorbate concentration of 2.01mg/dm³, solid: liquid ratio of 2.86, time of 99mins and removal efficiency of 99.79% for p-nitrophenol. The optimum conditions obtained for the binary solute system were pH of 6.10, adsorbate concentration of 1.00mg/dm³, solid: liquid ratio of 5.0, time of 120mins and removal efficiency of 71.33% for p-nitroaniline and pH of 7.17, adsorbate concentration of 1.00mg/dm³, solid: liquid ratio of 5.00, time of 120mins and removal efficiency of 94.74% for p-nitrophenol.

Keywords: Optimization, p-nitrophenol, p-nitroaniline, Hexadecyltrimethylammonium chloride, bentonite, Central composite design

INTRODUCTION

In recent years, there has been increasing concerns about waste disposal and the contamination of ground water resulting from industrialization. Removal of toxic contaminants from the effluent of various industries therefore, has become one of the most significant environmental challenges in the world of science. Aromatic compounds such as p-nitrophenol and p-nitroaniline are common contaminants in waste water discharged from petroleum refining and petrochemical industries, coal processing plants, fertilizer and chemical plants, pesticides and dye manufacturing companies, pulp and paper manufacturing companies etc. in addition to these, the compounds are also synthesized for laboratory and industrial applications. Both compounds have been listed among the priority pollutants by the US Environmental Protection Agency [6]. p-Nitrophenol is considered toxic and has been implicated in carcinogenesis, teratogenesis and mutagenesis. It is toxic to plant, animal and human health. In case of acute exposure, it is known to cause blood disorder (methenoglobinemia) liver and kidney failure, anaemia, skin and eye irritation and systemic poisoning. However, the presence of p-nitroaniline in water, even at very low concentrations, is extremely harmful

to aquatic life and human health in terms of its hematoxicity, splenotoxicity and nephrotoxicity [3 and 4]. In the recent years, several physical, biological and chemical processes have evolved for the remediation of effluents. Of these, contaminant immobilisation by adsorption has proven to be an attractive and effective mechanism. In this context, the use of clay materials has gained considerable attention in the recent years. Clays are suitable candidates to remove organic and inorganic pollutants from waste water due to their abundance in nature, inexpensiveness, environmental stability and high adsorptive and ion exchange properties [10]. Modified clays have shown great potential as adsorbents for organic pollutants. Organoclays are clays that have been organically modified to increase pollutant retention and resist pollutant transport. Organobentonites are the most common of this of organoclays. They are made by exchanging the naturally occurring Na^{2+} , Ca^{2+} and Mg^{2+} with an organic compound, typically quaternary ammonium cations. The sorption of nonpolar organic pollutants has been found to be several magnitudes greater on organobentonites than unmodified clays. This process changes the clay from a hydrophilic, or “water loving” to a hydrophobic, or “water hating” clay.

The conventional method of studying a process by changing one variable at a time and keeping the other variables at a constant level does not depict the combined effect of all the factors involved. Moreover, this method is time-consuming and also requires a large number of experiments to determine optimum levels, which may or may not be reliable. These limitations of the conventional method can be eliminated by simultaneously varying all the affecting parameters by using a statistical experimental design such as the response surface methodology (RSM).

The main objective of this investigation therefore, is the utilization of HDTMA-bentonite for the removal of the organic contaminants p-nitrophenol and p-nitroaniline from single and binary solute systems and the determination of optimal operating conditions for their removal using the response surface methodology. The central composite design was used to determine the influence of the experimental variables and their interaction on the removal efficiency of the modified clay adsorbent.

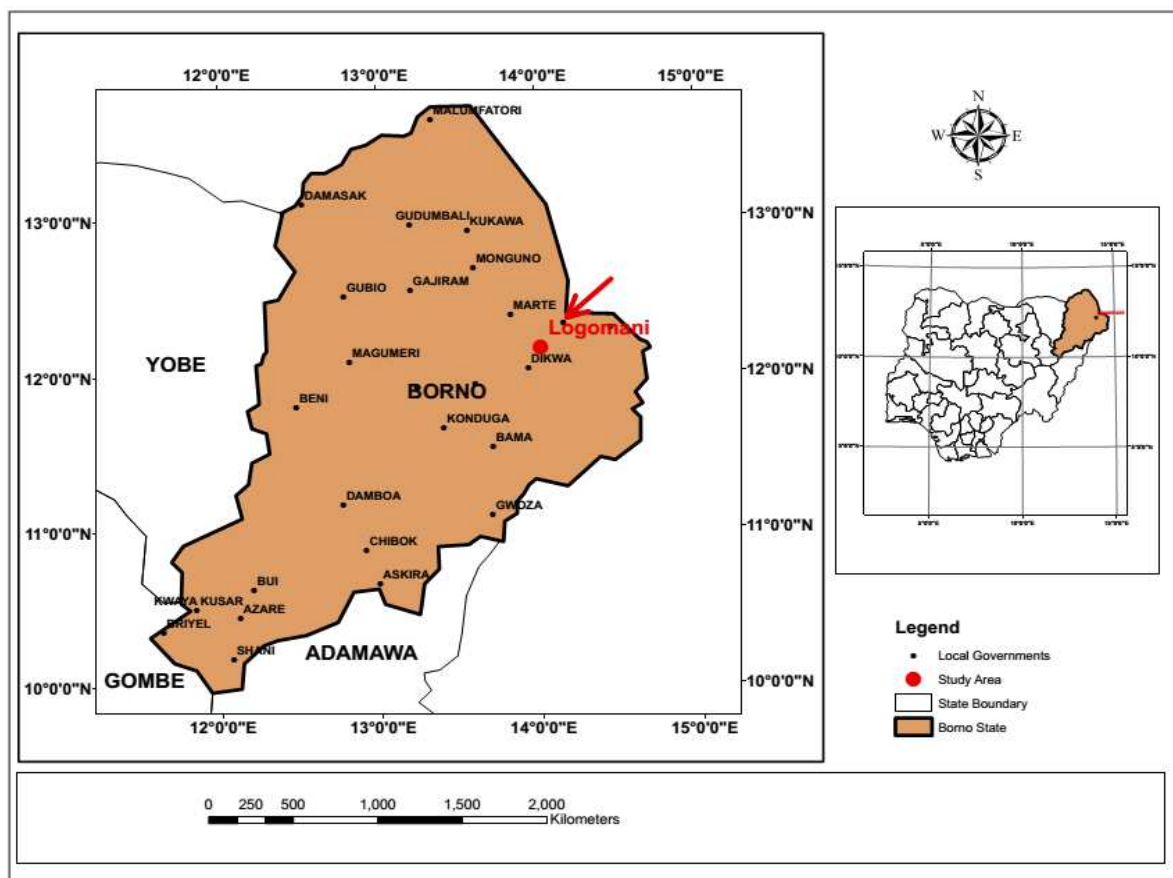


Figure 1: Study map showing area where clay samples were collected

MATERIALS AND METHODS

The bentonite clay used throughout this study was obtained from local mining sites at Logomani in Borno State. Logomani is precisely located at longitude 14° 01'E and latitude 12° 11'N in Dikwa Local Government Area. The clay was milled with Automatic milling machine and sieved with the various Endecotts Laboratory test sieves on Omron No 17748 (manual timer) sieve shaker.

Pretreatment of the raw bentonite

The clay sample is dispersed in the deionized water contained in a 20 liter plastic bucket. The dispersed clay is stirred vigorously and allowed to settle. The upper layer which consists of insoluble impurities and plant particles are sieved-off. The process of stirring and sieving-off is repeated with the lower layer until it becomes free from suspended particles. The dispersed clay is then allowed to settle for 24 hrs to allow the sedimentation process since different clay particle sizes are present. The top layer was collected via decantation and the remainder was washed with deionized water, allowed to settle for 24 hrs (for further sedimentation) and decanted to collect the top layer. All reagents and chemicals used in the study were of analytical grade and were used without further purification.

Preparation of the Organoclay

The clay sample is dried in an oven at 105 °C for 12 hours to remove any moisture and placed in a dessicator. 15 cm³ deionized water was measured into a 100 cm³ beaker. An amount corresponding to twice the cation exchange capacity of clay sample was weighed and transferred into the beaker containing distilled water and stirred for 15 minutes with a magnetic stirrer. The solution was heated up to 27-28 °C and the solution becomes transparent gradually indicating that the salt is dissolved in the water and HDTMA⁺ and Cl⁻ ions are formed in the solution. The solution's temperature is kept below 30 °C to prevent recrystallization of the salt when left to cool. Two gram of the clay sample was weighed and transferred into a centrifuge tube and the prepared solution was poured into this tube. The tube was capped and hand-shaken for 1 minute. Then the sample was placed onto a laboratory shaker and laterally shaken for 12 hours at room temperature (3hrs at 80 °C). After shaking, the suspension was centrifuged for 15 minutes at 3000 rpm. Then, the solution in the tube was decanted and some deionized water was added into the tube to wash the sample and again the solution was centrifuged for 15 minutes at 3000 rpm. This process of washing was repeated for three times to remove the excess of the salt as indicated by test for halide with AgNO₃. After washing, the clay sample was transferred into a porcelain dish with a glass rod and the sample was dried at 80 °C. Finally, the sample was ground and sieved through 63µm mesh.

The cation exchange capacity of the bentonite was determined by the European Standard spot test (Methylene blue (MB) test) as outlined by Santamarina *et al.*, [9]. The MB test is a method based on the principle of replacing original cations at the external and internal structure of the clay minerals by organic molecules. Maximum absorption of methylene blue corresponded to complete exchange of the inorganic ions by the organic ions is used to estimate the cation exchange capacity.

Characterization of both the raw and the modified clay samples was carried via Fourier Transform Infra-red Spectroscopy (FTIR), X-ray fluorescence (XRF) and X-ray Diffraction (XRD) analyses.

Design of Experiment

The process variables affecting the removal of organic contaminants by the modified bentonite clays were investigated using RSM combined with five-level, four-factor fractional factorial design as established by Minitab 16 software, Statsoft, U.S.A. The process variables were pH, adsorbate concentration, solid/liquid (S:L) ratio and reaction time. The response variable was chosen as percentage removal efficiency. The factor levels were coded as - α , -1, 0, +1 and + α . The range and levels are shown in Tables 1 and 2. The design matrix showing the experimental plan using the uncoded value of the variables is shown in Tables 3 and 4. A total of 31 runs were carried out to optimize the process variables and experiments were performed according to the actual experimental design matrix shown in Tables 1 and 2. The experiments were performed randomly to avoid systemic error. The results were analyzed using the coefficient of determination, analysis of variance (ANOVA), and response plots.

Table 1: Range and levels of variables for the single solute system

Variables	Symbol	Range and Levels				
		- α	-1	0	+1	+ α
pH	X ₁	0.5	2	5	8	10.5
Adsorbate Concentration, mg/dm ³	X ₂	1	2	5	8	11
Solid:Liquid Ratio, g/L (S:L)	X ₃	0.5	1.75	2.75	5	7.25
Time, min	X ₄	15	30	75	120	165

Table 2: Range and levels of variables for the binary solute system

Variables	Symbol	Range and Levels				
		- α	-1	0	+1	+ α
pH	X ₁	0.5	3	5.5	8	10.5
Adsorbate Concentration, mg/dm ³	X ₂	0.5	1	2.5	4	5.5
Solid:Liquid Ratio, g/L (S:L)	X ₃	0.5	1.75	2.75	5	7.25
Time, min	X ₄	15	30	75	120	165

Table 3: Experimental design matrix for single solute adsorption studies

Run Order	pH	Adsorbate Concentration (mg/L)	S:L Ratio (g/L)	Time (min)
1	8.0	8	5.00	30
2	3.0	2	5.00	120
3	8.0	2	0.50	30
4	3.0	2	5.00	30
5	3.0	2	0.50	120
6	3.0	8	5.00	120
7	8.0	2	5.00	120
8	8.0	2	5.00	30
9	5.5	5	2.75	75
10	3.0	8	5.00	30
11	5.5	5	2.75	165
12	5.5	5	2.75	75
13	5.5	5	2.75	75
14	5.5	5	2.75	75
15	8.0	8	5.00	120
16	5.5	5	2.75	75
17	5.5	1	2.75	75
18	5.5	5	2.75	15
19	8.0	8	0.50	30
20	5.5	11	2.75	75
21	5.5	5	2.75	75
22	5.5	5	7.25	75
23	10.5	5	2.75	75
24	3.0	8	0.50	120
25	5.5	5	1.75	75
26	5.5	5	2.75	75
27	0.5	5	2.75	75
28	8.0	8	0.50	120
29	8.0	2	0.50	120
30	3.0	8	0.50	30
31	3.0	2	0.50	30

Experimental procedure

Adsorption experiments for the single and binary organic solute systems were conducted as per the design developed with the response surface central composite design methodology. Concentration of the organic contaminant in the experimental solution was determined from the calibration curve prepared by measuring the absorbance of various known concentrations of the organic contaminant at $\lambda_{\text{max.}} = 319\text{nm}$ and $\lambda_{\text{max.}} = 381\text{nm}$ for p-nitrophenol and p-nitroaniline respectively using a UV-Vis spectrophotometer (Jenway).

Table 4: Experimental design matrix for binary solute adsorption studies

Run Order	pH	Adsorbate Concentration (mg/L)	S:L Ratio (g/L)	Time (min)
1	5.5	5.5	2.75	75
2	5.5	2.5	2.75	75
3	3.0	1	0.50	120
4	8.0	4	5.00	30
5	5.5	2.5	2.75	75
6	3.0	4	5.00	120
7	5.5	2.5	1.75	75
8	10.5	2.5	2.75	75
9	5.5	2.5	2.75	165
10	5.5	2.5	2.75	75
11	8.0	4	0.5	30
12	3.0	4	5.00	30
13	0.5	2.5	2.75	75
14	3.0	1	0.5	30
15	3.0	1	5.00	30
16	8.0	1	5.00	30
17	5.5	2.5	2.75	75
18	3.0	4	0.5	30
19	5.5	2.5	2.75	75
20	5.5	2.5	2.75	75
21	8.0	4	5.00	120
22	5.5	2.5	7.25	75
23	8.0	1	5.00	120
24	8.0	4	0.50	120
25	8.0	1	0.5	120
26	5.5	2.5	2.75	75
27	3.0	1.0	5.00	120
28	5.5	2.5	2.75	15
29	8.0	1	0.50	30
30	3.0	4	0.50	120
31	5.5	0.5	2.75	75

The experiments were carried out in 120 cm³ flasks with the working volume of 50 cm³ of reaction mixture. The specified mass of adsorbent was added to the flask and the initial pH of the solution adjusted to the desired value by adding either 0.1 M NaOH or 0.1 M HCl as the case may be. The pH of the solution was measured with a pH meter (Jenway 3505) using a combined glass electrode. The flasks were shaken for the specified time period in the thermostated water bath shaker. The flasks were withdrawn from the shaker after the desired time of reaction. The residual concentration of the organic contaminant in the reaction mixture was analyzed by centrifuging at 2,500 rpm, (Labomed, USA) the reaction mixture and then measuring the absorbance of the supernatant at the wavelength that corresponds to the maximum absorbance of the organic contaminant. Concentration of the organic contaminant in the reaction mixture was calculated from the calibration curve. Each determination was carried-out in triplicates, and the results given were their average value. The percentage of organic contaminant removal (Removal Efficiency) was taken as a response (Y) of the experimental design and calculated as follows:

$$R_e = \frac{(C_o - C_t)}{C_o} \times 100\%$$

Where,

C_o = initial concentration, mg/ dm³

C_t = concentration at time t, mg/ dm³

R_e = removal efficiency, %

RESULTS AND DISCUSSION

XRF Characterization

XRF analysis was performed to ascertain the chemical compositions of the minerals present in the clay sample. The data given in Table 1 show that the alumina and silica oxide are present in major quantities with percentage content

of 21.268% and 62.687% respectively, while other minerals are present in trace amounts. These values obtained for alumina and silica oxide are in agreement with those obtained by other workers for bentonitic clays; 14% and 68.20% [14], 15.12% and 65.24% [13] and 14.41% and 65.13% [7] for alumina and silica oxide respectively in each case, thus confirming that the original clay sample is an aluminosilicate. According to Murray [8], the theoretical composition without the interlayer material is SiO₂, 66.7% and Al₂O₃, 28.3%. The results from the XRF analysis also show a Na₂O content of 0.159% and CaO content of 1.727%. According to the formula $K = (E_{Na^+} + E_{K^+}) / (E_{Ca^{2+}} + E_{Mg^{2+}})$, where K = alkali coefficient, $K = 0.39 (< 1)$, indicating that this bentonite is a typical Ca-bentonite. Also, the higher percentage of Ca as compared to Na confirms that the sample is a calcium bentonite. In addition, the bentonite shows a moderate content of CaO (1.727%) and Na₂O/CaO ratio < 1, which indicates the presence of a non-swelling bentonite [13].

Table 1: Chemical composition of the original clay sample

Element	Content, %
Na ₂ O	0.159
MgO	1.480
Al ₂ O ₃	21.268
SiO ₂	62.687
P ₂ O ₅	0.071
SO ₃	0.216
Cl	0.009
K ₂ O	1.101
CaO	1.727
TiO ₂	1.613
Cr ₂ O ₃	0.018
Mn ₂ O ₃	0.124
Fe ₂ O ₃	0.949
ZnO	0.010
SrO	0.025

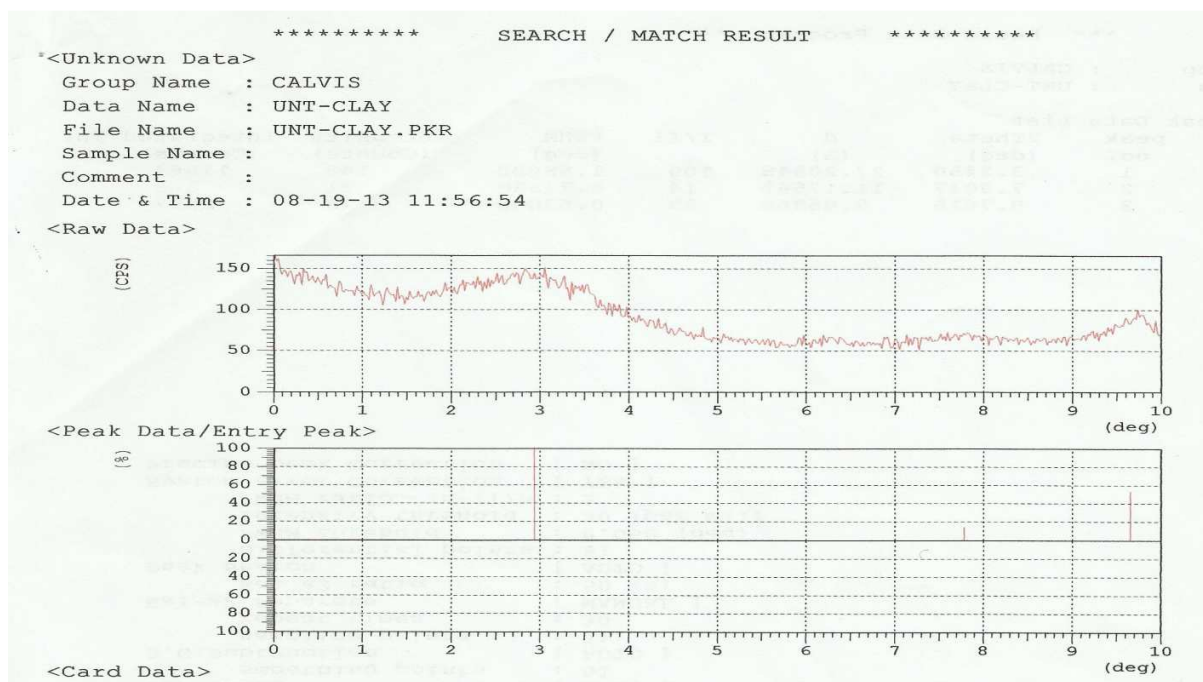


Figure 2: X-ray Diffractogram of the Original/untreated Clay

XRD Characterization

The low angle XRD pattern of the clay sample showed a broad peak appearing at approximately $2\theta = 3^\circ$ which is characteristic of montmorillonites and a basal spacing $d(001)$ value of 11.176Å characteristic of calcium montmorillonites [13].

The occurrence of a peak before $2\theta = 10^\circ$ is representative of the basal distance (d_{001}) for smectite clays. This peak tends to be intense, which enables their detection even in small quantities [5, 11, 12 and 13].

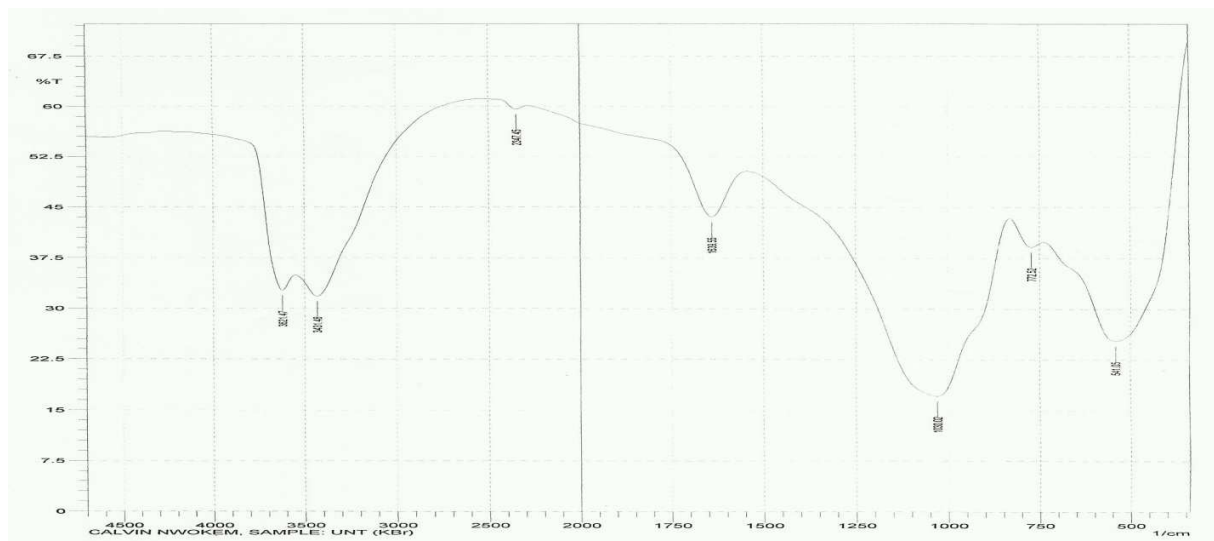


Figure 3: FTIR spectrum of the original/untreated clay sample.

Pareto Analysis

Pareto analysis is a formal technique useful where many possible courses of action are competing for attention. In essence, the problem solver estimates the benefit delivered by each action, then selects a number of the most effective actions that deliver a total benefit reasonably close to the maximal possible one [15].

A Pareto chart is a tool used by quality control scientists for planning. Pareto charts are a type of bar chart in which the horizontal axis represents categories of interest, rather than a continuous scale. By ordering the bars from largest to smallest, a Pareto chart can help you determine which of the categories comprise the "vital few" and which are the "trivial many." A cumulative percentage line helps you judge the added contribution of each category. Pareto charts can help to identify which variables are most significant so as to focus improvement efforts on areas where the largest gains can be made (Minitab 16).

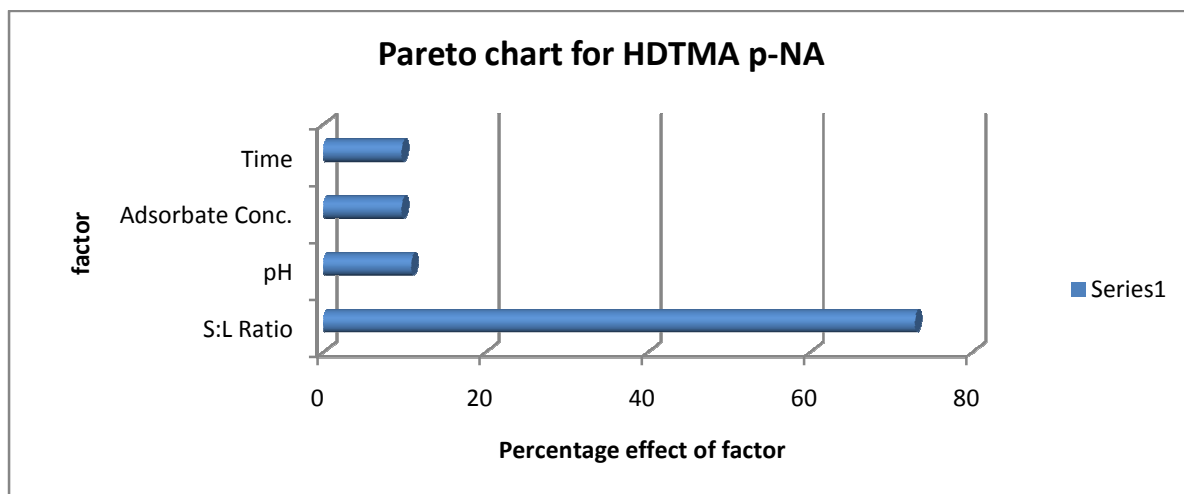


Figure 4: Pareto Chart showing percentage effect of factors for adsorption of p-nitroaniline by HDTMA-organoclay

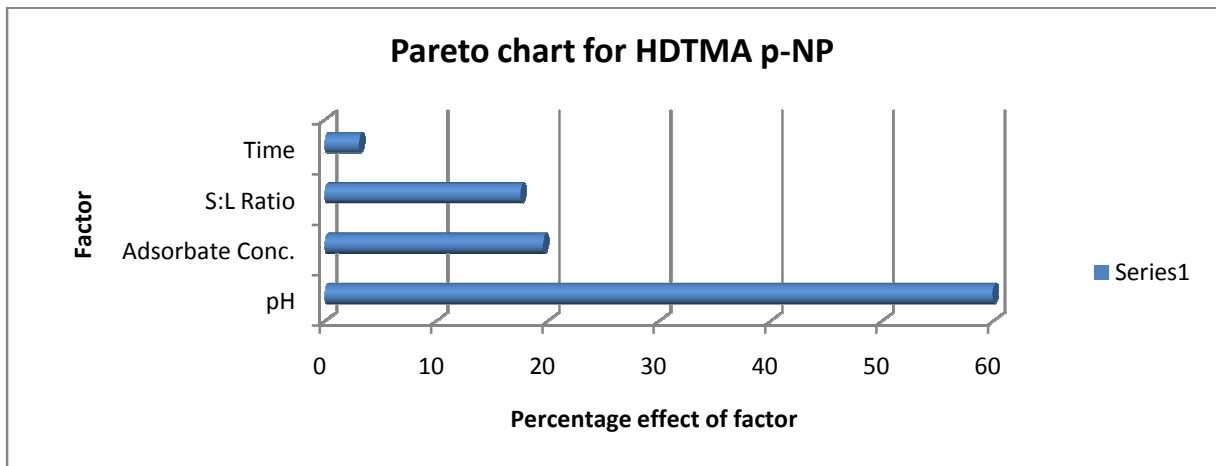


Figure 5: Pareto Chart showing percentage effect of factors for adsorption of p-nitrophenol by HDTMA-organoclay

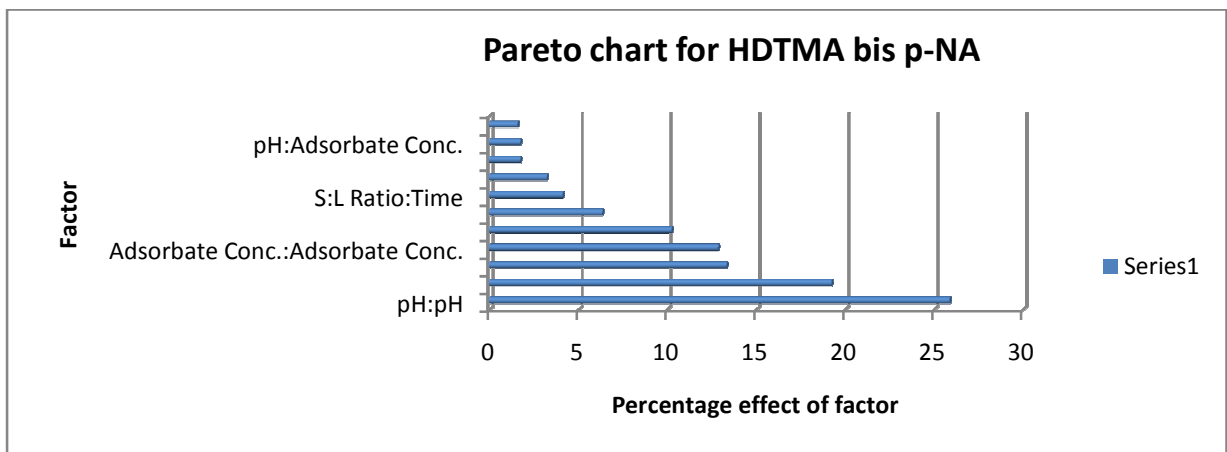


Figure 6: Pareto Chart showing percentage effect of factors for adsorption of p-nitroaniline by HDTMA-organoclay (bisolute)

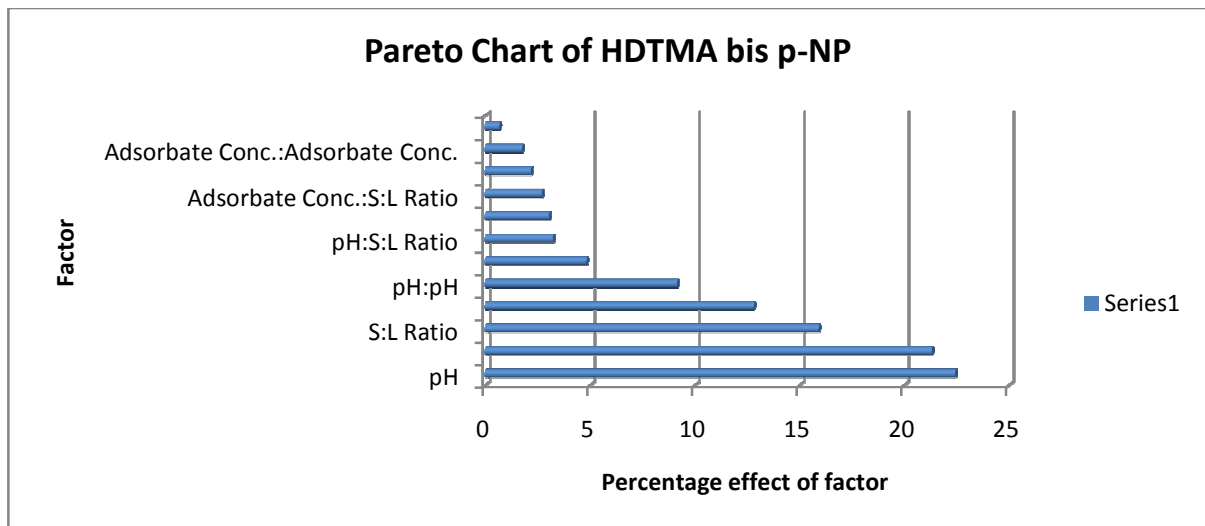


Figure 7: Pareto Chart showing percentage effect of factors for adsorption of p-nitrophenol by HDTMA-organoclay (bisolute)

The Pareto graphic analyses for organoclays, are summarized in Figures (4-7). Where X_a represents main effect of an independent variable and $X_a : X_b$ represents interaction effect, that is the effect of interaction between the independent variables X_a and X_b .

From the Pareto graphs of the above four (4) systems that is, Figures 4 to 7, pH of the system had the highest percentage effect in three (3) systems. This is followed (though not closely) by the solid-liquid ratio(S:L ratio). This shows that when adsorption of organic contaminants is carried-out using HDTMA-bentonite clay with simultaneous variation of the four factors for optimization, the single most important factor that determines the efficiency of the system is the pH of the aqueous medium; this could be either singly or in interaction with another factor(s). This observation is in agreement with reports by several workers [1 and 2], that pH is the most influential parameter in the adsorption process.

It has been reported that the initial pH of the aqueous medium has great influence on the surface properties of the organoclay and the ionization/dissociation of the organic molecule [16 and 17]. p-Nitrophenol and p-nitroaniline can exist in aqueous solution either as an anion or as a molecule, hence they are known as ionizable organic molecules. They exist as anion when the solution pH > pKa and as molecule when the solution pH < pKa. at pH>9, p-nitrophenol is completely dissociated. The dissociation constant, pKa for p-nitrophenol is 7.16, whereas that for p-nitroaniline is ~1.11.

Effect of the Independent Variables and their interaction on the Removal Efficiency of the HDTMA-bentonite clay

Optimum pH values obtained for the removal of p-nitrophenol using the HDTMA-bentonite clay prepared ranged from 7.17 to 7.99. Maximum removal efficiency (94.74%) was obtained using HDTMA-bentonite clay at a pH of 7.17, which is approximately equal to the pKa of p-nitrophenol. For p-nitrophenol adsorption, the neutral species predominate at pH below pKa value and are adsorbed more strongly than the anionic species. Also, the dissociated molecules at pH above pKa are less strongly adsorbed than the undissociated form. As a result, the adsorption process is usually affected by the competing influence of p-nitrophenol ion and p-nitrophenol molecule. There are two main mechanisms for the adsorption of p-nitrophenol on clays. The first being electrostatic attraction when the p-nitrophenol exists as anion and the second partition when p-nitrophenol exists as molecule.

In view of the pKa of p-nitroaniline as well as the optimum pH obtained for adsorption involving it, the mechanism for its adsorption is most likely electrostatic attraction since p-nitroaniline dissociates at pH>pKa and the contaminant would exist mainly as an ion under the mentioned pH condition.

These results are in agreement with report that the extent of adsorption of aromatics is a function of pH and that maximum adsorption for aromatics occurs at a point where pH = pKa for each compound studied [18].

Table 4.8: ANOVA results, regression coefficients and the significance tests and effects for HDTMA p-nitroaniline

Source	Coefficient	Sum of Squares	DF	Mean square	F-value	P-value
Model	14.69	1440.51	4	360.13	10.21	<0.0001
X_1	1.12	30.16	1	30.16	0.86	0.3639
X_2	-0.68	11.13	1	11.13	0.32	0.5792
X_3	7.57	1374.10	1	1374.10	38.97	<0.0001
X_4	1.02	25.12	1	25.12	0.71	0.4067
Residual		881.54	25	35.26		
Total		2322.05				

Response Surface Linear model.

Table 3: ANOVA results, regression coefficients and the significance tests and effects for HDTMA Single Solute p-nitrophenol

Source	Coefficient	Sum of Squares	DF	Mean square	F-value	P-value
Model	58.00	27731.79	4	6932.95	62.32	<0.0001
X_1	31.10	23217.82	1	23217.82	208.71	<0.0001
X_2	-10.15	2473.84	1	2473.84	22.24	<0.0001
X_3	9.09	1981.27	1	1981.27	17.81	0.0003
X_4	1.57	58.85	1	58.85	0.53	0.4738
Residual		2781.12	25	111.24		
Total		30512.90				

Response Surface Linear model.

Table 4: ANOVA results, regression coefficients and the significance tests and effects for HDTMA Binary Solute p-nitroaniline

Factor	Coefficient	Sum of squares	DF	Mean Square	F-value	P-value
Model	52.66	6186.30	14	441.88	3.68	0.0087
X ₁	-2.42	140.66	1	-2.42	1.17	0.2965
X ₂	-3.93	370.45	1	-3.93	3.08	0.0996
X ₃	7.38	1308.33	1	7.38	10.88	0.0049
X ₄	1.23	36.29	1	1.23	0.30	0.5908
X ₁ ²	-9.94	2712.37	1	-9.94	22.56	0.0003
X ₂ ²	4.93	666.00	1	4.93	5.54	0.0326
X ₄ ²	-0.60	9.77	1	-0.60	0.081	0.7795
X ₁ X ₂	-0.65	6.69	1	-0.65	0.056	0.8167
X ₁ X ₃	5.11	417.68	1	5.11	3.47	0.0820
X ₁ X ₄	-0.65	6.69	1	-0.65	0.056	0.8167
X ₃ X ₄	1.58	39.88	1	1.58	0.33	0.5732
Residual		1803.39	15			
Total		7989.69				

Response Surface Quadratic model.

Table 5: ANOVA results, regression coefficients and the significance tests and effects for HDTMA Binary Solute p-nitrophenol

Factor	Coefficient	Sum of squares	DF	Mean Square	F-value	P-value
Model	67.10	13208.74	14	943.48	12.30	<0.0001
X ₁	13.71	4509.77	1	4509.77	58.80	<0.0001
X ₂	-13.03	4071.83	1	4071.83	53.09	<0.0001
X ₃	9.72	2269.80	1	2269.80	29.59	<0.0001
X ₁ ²	-5.60	861.21	1	861.21	11.23	0.0044
X ₂ ²	1.06	31.05	1	31.05	0.40	0.5342
X ₃ ²	1.33	48.68	1	48.68	0.63	0.4381
X ₄ ²	0.41	4.57	1	4.57	0.060	0.8105
X ₁ X ₂	7.82	977.85	1	977.85	12.75	0.0028
X ₁ X ₃	1.98	62.74	1	62.74	0.82	0.3801
X ₂ X ₃	1.65	43.57	1	43.57	0.57	0.4627
X ₂ X ₄	1.86	55.14	1	55.14	0.72	0.4098
X ₃ X ₄	2.95	139.21	1	139.21	1.82	0.1979
Residual		1150.47	15			
Total		14359.21				

Response Surface Quadratic model.

From Tables 2-5, it can be seen that only the adsorption processes involving the removal of p-nitroaniline with HDTMA-bentonite clay for both single and binary solute systems and p-nitrophenol with HDTMA-bentonite clay for the binary solute systems had response surface models in which interaction between independent variables were significant. As can also be seen from the results in tables, the interaction of the independent variables had both negative and positive effects on the removal efficiency of the organic contaminants studied except in the case of p-nitrophenol removal using HDTMA- bentonite clay for the bisolute system, in which case, the interaction effect is positive. This phenomenon, most likely explains the reason why the latter system had the highest optimal removal efficiency of 94.74% of all the system models in which interaction between independent variables were significant. However, the results also show that although interaction between the independent variables could lead to increased removal efficiency, this was not always the case. This can also be seen from the Tables 2 - 5, as the system with the highest optimal removal efficiency of 99.79%; that is, removal of p-nitrophenol by HDTMA- bentonite clay from the single solute system was one which depended on the linear effects of the independent variables (response surface linear model).

CONCLUSION

The Response surface central composite design was used to investigate the effects of the process variables on the removal of p-nitroaniline and p-nitrophenol by HDTMA- bentonite clay from single and binary solute systems. The optimum process conditions obtained for the single solute system were pH of 7.99, adsorbate concentration of 2.02mg/dm³, solid:liquid ratio of 5.0, time of 120mins and removal efficiency of 27.07% for p-nitroaniline and pH of 7.97, adsorbate concentration of 2.01mg/dm³, solid:liquid ratio of 2.86, time of 99mins and removal efficiency of 99.79% for p-nitrophenol. The optimum conditions obtained for the binary solute system were pH of 6.10, adsorbate concentration of 1.00mg/dm³, solid:liquid ratio of 5.0, time of 120mins and removal efficiency of 71.33% for p-

nitroaniline and pH of 7.17, adsorbate concentration of 1.00mg/dm³, solid:liquid ratio of 5.00, time of 120mins and removal efficiency of 94.74% for p-nitrophenol. Furthermore, results from this study also reveal that the pH of the aqueous media was the most influential parameter of all the independent variables in determining the removal efficiency. This is due to the fact that the pH determines whether the organic compound would exist as a molecule or ion.

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