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### Removal of p-nitrophenol and p-nitroaniline by benzyldimethylhexadecylammonium -bentonite from single and binary solute systems via response surface methodology.

Nwokem C.O. <sup>1\*</sup>, Gimba C.E.<sup>2</sup>, Ndukwe G.I. <sup>3</sup>, Abechi S.E. <sup>4</sup>

1. National Research Institute for Chemical Technology, Zaria, Nigeria.  
[Email: [onyenwokem@gmail.com](mailto:onyenwokem@gmail.com), Tel: 07080950601]
2. Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria.  
[Email: [gimbace@yahoo.com](mailto:gimbace@yahoo.com), Tel: 08037032495]
3. Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria.  
[Email: [ndukweilogeorge@yahoo.com](mailto:ndukweilogeorge@yahoo.com), Tel: 08036001692]
4. Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria.  
[Email: [abeshus@yahoo.com](mailto:abeshus@yahoo.com), Tel: 08036437394]

Removal of p-nitrophenol and p-nitroaniline from single and binary solute systems by Benzyldimethylhexadecylammonium-bentonite using the response surface methodology was studied. The effect of four independent variables; pH, an adsorbate concentration, solid: liquid ratio (S:L) and Time were investigated; linear and quadratic models were developed for the process. The optimum conditions obtained for the single solute system were pH of 7.99, an adsorbate concentration of 2.00 mg/dm<sup>3</sup>, solid: liquid ratio of 5.0, time of 120 mins and removal efficiency of 42.63% for p-nitroaniline and pH of 7.98, an adsorbate concentration of 2.00 mg/dm<sup>3</sup>, solid: liquid ratio of 5.00, time of 119.62 mins and removal efficiency of 95.10% for p-nitrophenol. The optimum conditions obtained for the binary solute system were pH of 5.08, adsorbate concentration of 1.00 mg/dm<sup>3</sup>, solid: liquid ratio of 5.0, time of 120 mins and removal efficiency of 63.49% for p-nitroaniline and pH of 7.92, an adsorbate concentration of 1.15 mg/dm<sup>3</sup>, solid: liquid ratio of 4.62, time of 119.87 mins and removal efficiency of 93.93% for p-nitrophenol.

**Keyword:** p-Nitrophenol, p-Nitroaniline, Benzyldimethylhexadecylammonium-Bentonite, Response Surface Methodology, Removal Efficiency

#### 1. Introduction

In recent years, industrialization and increased industrial activities have brought about the twin problems of disposal of wastes and the contamination of ground water. Remediation of toxic contaminants from the effluent of industries therefore, has become one of the most significant challenges in the world of environmental science. Aromatics 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. Added 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 <sup>[1]</sup>. 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

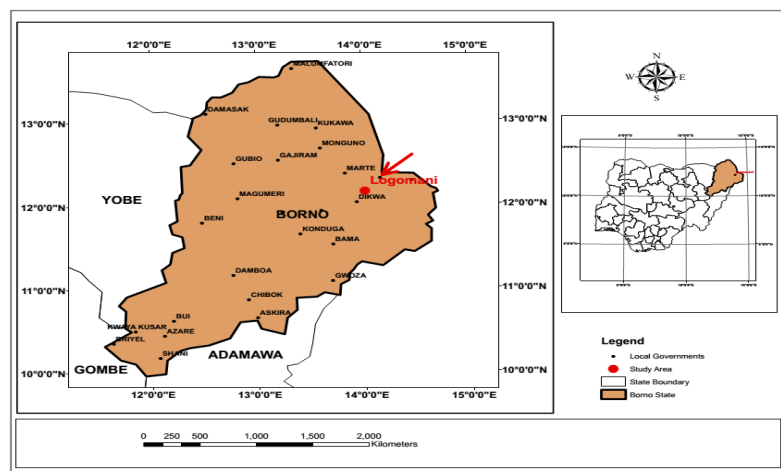
poisoning. However, the presence of p-nitroaniline in water, even at very low concentrations, is extremely harmful to aquatic life and human health in terms of its hemotoxicity, splenotoxicity and nephrotoxicity [2, 3]. In the recent years, several physical, biological and chemical processes have evolved 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 absorptive and ion exchange properties [4]. 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. Organically modified bentonite clays are the most common of the organoclays. They are made by exchanging the naturally occurring  $\text{Na}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  with an organic compound, typically quaternary ammonium cations. The sorption of nonpolar organic pollutants has been found to be several magnitudes greater on organically modified bentonite clay than on the unmodified clay. 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 of

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 BDHDMa-bentonite clay 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.

## 2. 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  $14^{\circ} 01' \text{E}$  and latitude  $12^{\circ} 11' \text{N}$  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.



**Fig 1:** Study map showing area where clay samples were collected.

## 2.1 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.

## 2.2 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 cm<sup>3</sup> deionized water was measured into a 100 cm<sup>3</sup> beaker. An amount corresponding to twice the cation exchange capacity of a 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 BDHDM<sup>+</sup> and Cl<sup>-</sup> ions are formed in the solution. The solution's temperature is kept below 30 °C to prevent crystallization of the salt when left to cool. Two grams of the clay sample were 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 (3 hrs 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 AgNO<sub>3</sub>. 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 63 μm 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.* [5]. 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.

## 2.3 Design of Experiment

The process variables affecting the removal of organic contaminants by the modified bentonite clays were investigated using RSM combined with a 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  $-\alpha$ ,  $-1$ ,  $0$ ,  $+1$  and  $+\alpha$ . The range and levels are shown in Tables 1 and 2. The design matrix showing the experimental plan using the encoded value of the variables is shown in Tables 3 and 4. A total of 31 runs was 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				
		- $\alpha$	-1	0	+1	+ $\alpha$
pH	X <sub>1</sub>	0.5	2	5	8	10.5
Adsorbate Concentration, mg/dm <sup>3</sup>	X <sub>2</sub>	1	2	5	8	11
Solid: Liquid Ratio, g/L (S:L)	X <sub>3</sub>	0.5	1.75	2.75	5	7.25
Time, min	X <sub>4</sub>	15	30	75	120	165

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

Variables	Symbol	Range and Levels				
		- $\alpha$	-1	0	+1	+ $\alpha$
pH	X <sub>1</sub>	0.5	3	5.5	8	10.5
Adsorbate Concentration, mg/dm <sup>3</sup>	X <sub>2</sub>	0.5	1	2.5	4	5.5
Solid: Liquid Ratio, g/L (S:L)	X <sub>3</sub>	0.5	1.75	2.75	5	7.25
Time, min	X <sub>4</sub>	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

**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	30	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

## 2.4 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  $\lambda_{\text{max.}} = 319$  nm and  $\lambda_{\text{max.}} = 381$  nm for p-nitrophenol and p-nitroaniline respectively using a UV-Vis spectrophotometer (Jenway).

The experiments were carried out in 120 cm<sup>3</sup> flasks with the working volume of 50 cm<sup>3</sup> 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 were given 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/ dm<sup>3</sup>

$C_t$  = concentration at time t, mg/ dm<sup>3</sup>

$R_e$  = removal efficiency, %

## 3. Results and Discussion

### 3.1 XRF Characterization

XRF analysis was performed to ascertain the chemical compositions of the minerals present in the clay sample. The data given in Table 5 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%<sup>[6]</sup>, 15.12% and 65.24%<sup>[7]</sup> and 14.41% and 65.13%<sup>[8]</sup> for alumina and silica oxide respectively in each case, thus confirming that the original clay sample is an aluminosilicate. According to Murray<sup>[9]</sup>, the theoretical composition without the interlayer material is SiO<sub>2</sub>, 66.7% and Al<sub>2</sub>O<sub>3</sub>, 28.3%. The results from the XRF analysis also show a Na<sub>2</sub>O content of 0.159% and CaO content of 1.727%. According to the formula  $K = (E_{\text{Na}^+} + E_{\text{K}^+}) / (E_{\text{Ca}^{2+}} + E_{\text{Mg}^{2+}})$ , where K = alkali coefficient,  $K = 0.39 (< 1)$ , indicating that this bentonite is a typical Ca-bentonite<sup>[10]</sup>. 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 Na<sub>2</sub>O/CaO ratio < 1, which indicates the presence of a non-swelling bentonite<sup>[7]</sup>.

**Table 5:** Chemical composition of the original clay sample

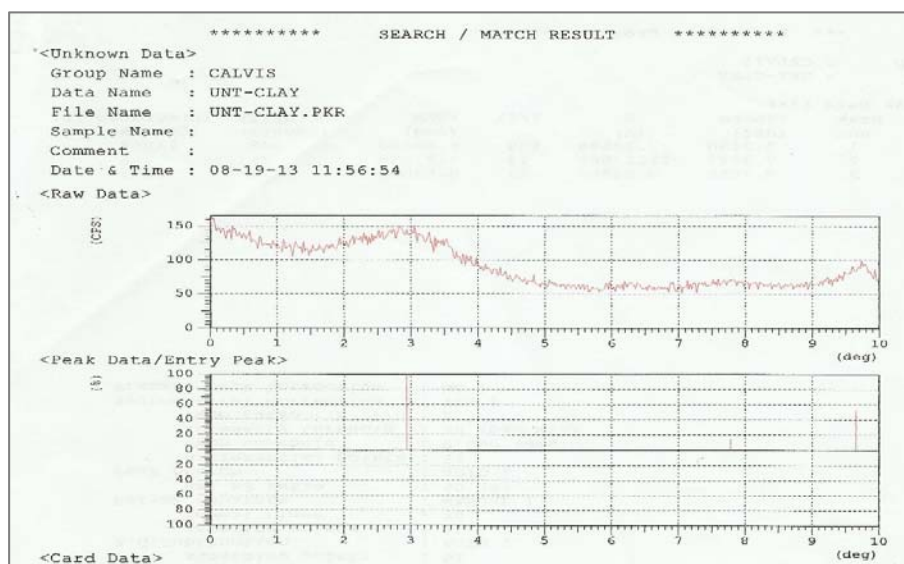
Element	Content, %
Na <sub>2</sub> O	0.159
MgO	1.480
Al <sub>2</sub> O <sub>3</sub>	21.268
SiO <sub>2</sub>	62.687
P <sub>2</sub> O <sub>5</sub>	0.071
SO <sub>3</sub>	0.216
Cl	0.009
K <sub>2</sub> O	1.101
CaO	1.727
TiO <sub>2</sub>	1.613
Cr <sub>2</sub> O <sub>3</sub>	0.018
Mn <sub>2</sub> O <sub>3</sub>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

### 3.2 XRD Characterization

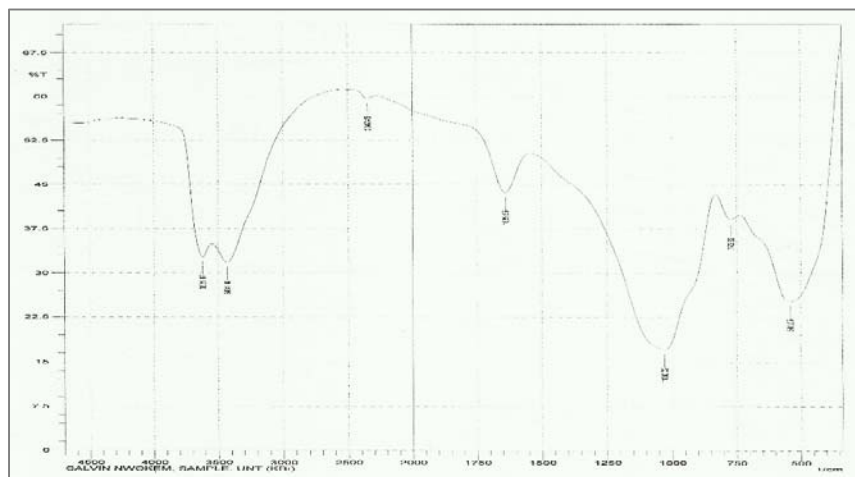
The low angle XRD pattern of the clay sample showed a broad peak appearing at approximately  $2\theta = 3^\circ$  which is characteristic of montmorillonites and a basal spacing  $d(001)$  value of  $11.176\text{\AA}$  characteristic of calcium

montmorillonites [7].

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 [7, 11, 12 and 13].

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





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

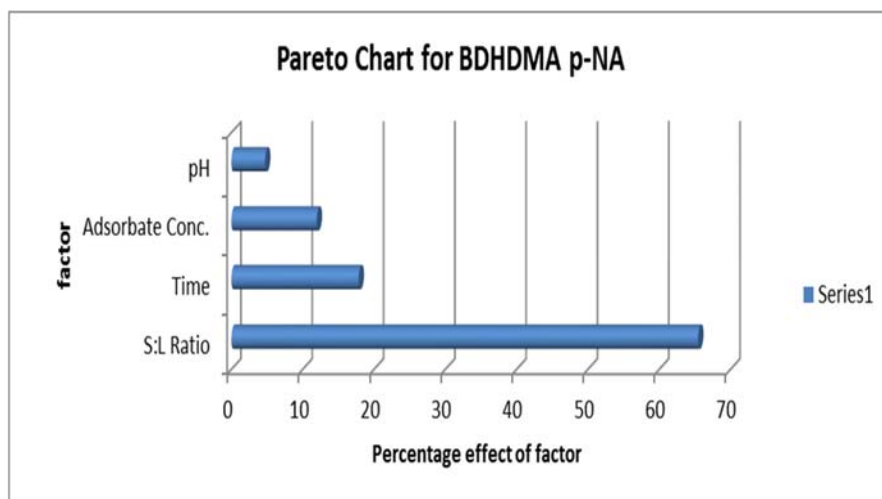
### 3.3 Pareto Analysis

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 [14].

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

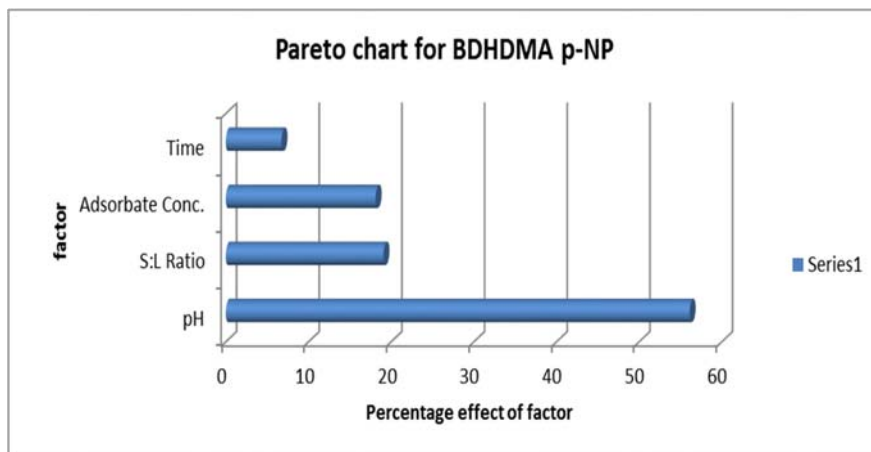
which of the categories comprise the "vital few" and which are the "trivial many." A cumulative percentage line helps you judge the added contribution of each category. Pareto charts can help to identify which variables are most significant so as to focus improvement efforts on areas where the largest gains can be made (Minitab 16).

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

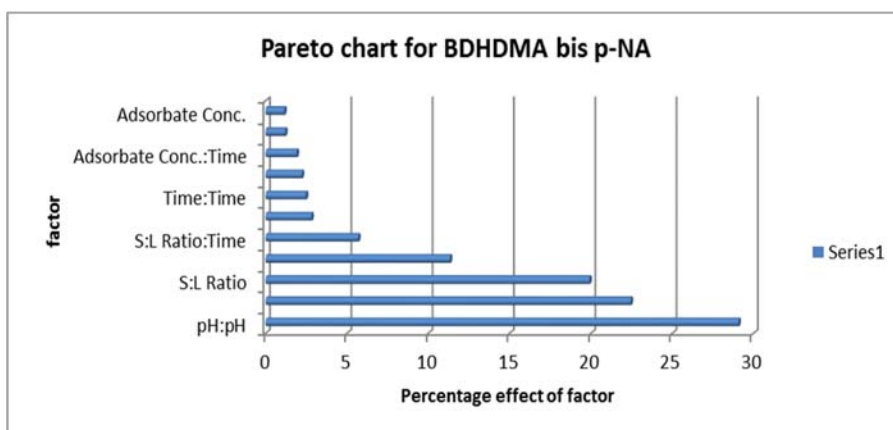


**Fig 4:** Pareto Chart showing the percentage effect of factors for adsorption of p-nitroaniline by BDHDMA-bentonite clay.

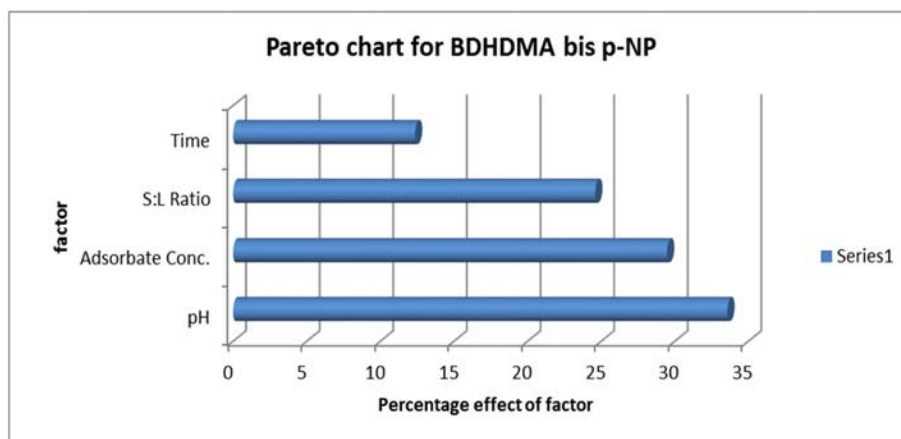




**Fig 5:** Pareto Chart showing the percentage effect of factors for adsorption of p-nitrophenol by BDHDMA-bentonite clay.



**Fig 6:** Pareto Chart showing the percentage effect of factors for adsorption of p-nitroaniline by BDHDMA-bentonite clay (binary solute).



**Fig 7:** Pareto Chart showing the percentage effect of factors for adsorption of p-nitrophenol by BDHDMA-bentonite clay (binary solute)

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 (greatest influence) in three (3) systems. This is followed (though not closely) by the solid-liquid ratio (S:L ratio). This trend is in agreement with previous work carried-out by our research team using Hexadecyltrimethylammonium chloride (HDTMA) bentonite clay. This finding shows that when adsorption of organic contaminants is carried-out using BDHDMA-bentonite clay with simultaneous variation of the four independent variables 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 [15, 16], that pH is the most influential parameter in the adsorption process.

It has also been reported by some workers Ponnusamy and Subramaniam, [17] and Kour *et al.*, [18] 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.

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  $\text{pH} > \text{pKa}$  and as molecule when the solution  $\text{pH} < \text{pKa}$ . At  $\text{pH} > 9$ , p-nitrophenol is completely dissociated. The dissociation constant,  $\text{pKa}$  for p-nitrophenol is 7.16, whereas that for p-nitroaniline is  $\sim 1.11$ .

### 3.4 Effect of the Independent Variables and their interaction on the Removal Efficiency of the BDHDMA-bentonite clay.

Optimum pH values obtained for the removal of p-nitrophenol using the BDHDMA-bentonite clay prepared to range from 5.08 to 7.99. Maximum removal efficiency (93.93%) was obtained using BDHDMA-bentonite clay at a pH of 7.98, which is slightly above the  $\text{pKa}$  of p-nitrophenol. For p-nitrophenol adsorption, the neutral species predominate at pH below  $\text{pKa}$  value and are adsorbed more strongly than the anionic species. Also, the dissociated molecules at pH above  $\text{pKa}$  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 a molecule.

In view of the  $\text{pKa}$  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  $\text{pH} > \text{pKa}$  and the contaminant would exist mainly as an ion under the mentioned pH condition.

These results are in agreement with reports that the extent of adsorption of aromatic is a function of pH and that maximum adsorption for aromatics occurs at a point where  $\text{pH} = \text{pKa}$  for each compound studied [19].

**Table 6:** ANOVA results, regression coefficients and the significance tests and effects for BDHDMA-bentonite p-Nitroaniline.

Source	Coefficient	Sum of Squares	DF	Mean square	F-value	P-value
Model	23.59	4155.46	4	1038.86	15.39	<0.0001
X <sub>1</sub>	0.90	19.63	1	19.63	0.29	0.5946
X <sub>2</sub>	-2.28	125.28	1	125.28	1.86	0.1853
X <sub>3</sub>	12.47	3733.24	1	3733.24	55.29	<0.0001
X <sub>4</sub>	3.40	277.31	1	277.31	4.11	0.0535
Residual		1688.11	25	67.52		
Total		5843.57				

Response Surface Linear model.

**Table 7:** ANOVA results, regression coefficients and the significance tests and effects for BDHDMA-bentonite p-Nitrophenol.

Source	Coefficient	Sum of Squares	DF	Mean square	F-value	P-value
Model	45.72	22859.13	4	5714.78	69.81	<0.0001
X <sub>1</sub>	27.78	18522.19	1	18522.19	226.26	<0.0001
X <sub>2</sub>	-8.97	1932.47	1	1932.47	23.61	<0.0001
X <sub>3</sub>	9.44	2138.24	1	2138.24	26.12	<0.0001
X <sub>4</sub>	3.33	266.23	1	266.23	3.25	0.0834
Residual		2046.58	25	81.86		
Total		24905.71				

Response Surface Linear model.

**Table 8:** ANOVA results, regression coefficients and the significance tests and effects for BDHDMA-bentonite p-Nitroaniline (Binary solute).

Factor	Coefficient	Sum of squares	DF	Mean Square	F-value	P-value
Model	51.39	6272.14	14	448.01	2.99	0.0217
X <sub>1</sub>	-7.96	1518.96	1	1518.96	10.14	0.0062
X <sub>2</sub>	-0.41	3.94	1	3.94	0.026	0.8733
X <sub>3</sub>	7.06	1197.10	1	1197.10	7.99	0.0128
X <sub>1</sub> <sup>2</sup>	-10.31	2916.21	1	2916.21	19.46	0.0005
X <sub>3</sub> <sup>2</sup>	0.79	17.06	1	17.06	0.11	0.7404
X <sub>4</sub> <sup>2</sup>	0.88	21.34	1	21.34	0.14	0.7112
X <sub>1</sub> X <sub>2</sub>	-0.89	12.55	1	12.55	0.084	0.7763
X <sub>1</sub> X <sub>3</sub>	4.02	258.55	1	258.55	1.73	0.2087
X <sub>1</sub> X <sub>4</sub>	-0.43	2.97	1	2.97	0.020	0.8898
X <sub>2</sub> X <sub>4</sub>	-0.68	7.31	1	7.31	0.049	0.8282
X <sub>3</sub> X <sub>4</sub>	2.02	65.01	1	65.01	0.43	0.5201
Residual		149.84	15			
Total						

Response Surface Quadratic model.

**Table 9:** ANOVA results, regression coefficients and the significance tests and effects for BDHDMA-bentonite p-Nitrophenol (Binary solute).

Source	Coefficient	Sum of Squares	DF	Mean square	F-value	P-value
Model	64.30	7386.10	4	1846.52	9.14	0.0001
X <sub>1</sub>	11.22	3022.96	1	3022.96	14.96	0.0007
X <sub>2</sub>	-9.85	2330.36	1	2330.36	11.53	0.0023
X <sub>3</sub>	8.22	1623.49	1	1623.49	8.03	0.0090
X <sub>4</sub>	4.13	409.27	1	409.27	2.03	0.1670
Residual		5051.33	25	247.84		
Total		12437.42				

Response Surface Linear model.

From the results shown in Tables 6-9, it can be seen that only the adsorption processes involving the removal of p-nitroaniline with BDHDMABentonite clay for the binary solute had response surface models in which there were real interactions between independent variables, even though these interactions were insignificant. As can also be seen from the results in Table 6, the interaction of the independent variables had both negative and positive effects on the removal efficiency of the organic contaminant (p-nitroaniline). However, there were interactions with negative effect than positive, making the overall contribution of the interactions between the independent variables possibly negative. The above phenomenon most likely accounts for the relatively low optimal removal efficiency of 63.49% in the system. Findings from previous work conducted by our research team using HDTMA-bentonite clay to show that although interaction between the independent variables could lead to increased removal efficiency, this was not always the case. This again corroborates the results in this present work. That results from three (3) out of the four (4) systems studied in this work depended on the linear effects of the independent variables show that the contribution of the interaction between the independent variables is negligible in adsorption processes involving the removal of p-nitrophenol and p-nitroaniline from single and binary solute systems by BDHDMABentonite clay.

#### 4. 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 BDHDMABentonite clay from single and binary solute systems. The optimum conditions obtained for the single solute system were pH of 7.99, an adsorbate concentration of 2.00 mg/dm<sup>3</sup>, solid: liquid ratio of 5.0, time of 120mins and removal efficiency of 42.63% for p-nitroaniline and pH of 7.98, an adsorbate concentration of 2.00 mg/dm<sup>3</sup>, solid: liquid ratio of 5.00, time of 119.62mins and removal efficiency of 95.10% for p-nitrophenol. The optimum conditions obtained for the binary solute

system were pH of 5.08, an adsorbate concentration of 1.00 mg/dm<sup>3</sup>, solid: liquid ratio of 5.0, time of 120mins and removal efficiency of 63.49% for p-nitroaniline and pH of 7.92, an adsorbate concentration of 1.15 mg/dm<sup>3</sup>, solid: liquid ratio of 4.62, time of 119.87 mins and removal efficiency of 93.93% for p-nitrophenol. These results clearly show that the pH of the aqueous media was the most influential parameter of all the independent variables as it determines whether the organic compound would exist as a molecule or ion.

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