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OPTIMIZATION OF PROCESS PARAMETERS FOR SORPTION OF P-NITROPHENOL FROM AQUEOUS SOLUTION BY HEXADECYLTRIMETHYLAMMONIUM CHLORIDE-TREATED BENTONITE (HDTMA-BENTONITE)

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ABSTRACT

Sorption of p-Nitrophenol from aqueous solution using hexadecyltrimethylammonium chloride treated bentonite (HDTMA-bentonite) clay was investigated using a batch system. The combined effect of four independent variables: contact time, pH, adsorbate concentration and solid:liquid ratio on the sorption process was studied and optimized using the Central Composite Design-Response Surface Methodology. The development of the experimental design as well as the interpretation of results was carried-out using the statistical software MINITAB 16 (Stasoft, USA). It was observed from this investigation that the percentage removal efficiency was influenced by process parameters in the following order: solution pH > Adsorbate concentration > solid:liquid ratio > contact time. Optimum values for pH, adsorbate concentration, solid:liquid ratio and contact time were found to be 7.97, 2.01mg/dm^3, 2.86 and 99 minutes respectively for the maximum p-nitrophenol removal (99.79%). It was also observed that both experimental and predicted values were in good agreement and the model developed was significant. These results indicate the suitability of HDTMA-bentonite for the removal of p-nitrophenol from aqueous solution.

Keywords: Sorption, p-Nitrophenol, HDTMA-bentonite, Response Surface Methodology

INTRODUCTION

The presence of chemicals and dyestuff in aqueous systems as a result of non-/poor treatment of industrial effluents has become a global challenge. Removal of these toxic contaminants from effluents is one of the most significant environmental challenges (Sarkar *et al.,* 2010).

Different treatment techniques and materials, including adsorption, biological treatment, oxidation, ion exchange, organic resin, filtration, precipitation, electrolysis, reverse osmosis, and coagulation, biofoulents, biodegradable nanocomposites, adsorbent coatings, and hybrid materials have been employed to remove dyes from wastewater (Momina *et al.,* 2018). Since synthetic dyes cannot be efficiently decolorized by traditional methods (e.g., activated sludge process, coagulation, oxidation) (Momina *et al.,* 2018). However, adsorption is strongly favored over the other techniques to remove dyes from wastewater because of its simplicity, cost effectiveness, ease of operation, and good efficiency. In addition, proper adsorption has the potential to produce a high-quality treated effluent (Momina *et al.,* 2018).

Recently, several chemical, physical and biological processes have been employed for the remediation of waste effluents. Of these, sorption has proven to be both an attractive and effective option (Sarkar *et al.,* 2010).

Clays are suitable candidates for the removal of organic and inorganic pollutants from waste water as a result of their abundance in nature, low cost, environmental stability, high adsorptive and ion exchange properties (Sarkar *et al.,* 2010). They are used in a wide range of applications including nanocomposites, catalysts, photochemical reaction reagents and adsorbents (de Paiva *et al.,* 2008).

Modified clays have shown great potential as adsorbents for organic pollutants. Organoclays are clays that have been modified to resist the transport as well as increase the retention of pollutants. 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.

p-Nitrophenol (4-NP) is considered as one of the most difficult organic pollutants to decompose because of the water solubility, excellent chemical properties, and biological stability, and is listed as the priority toxic pollutants by the United States Environmental Protection Agency (USEPA) (Liu *et al.,* 2018).

p-Nitrophenol is a common pollutant found especially in effluents discharged from petrochemical, pesticide and pharmaceutical industries. Due to its highly reactive nature and toxicity, its presence in the soil and water bodies is of concern to scientists with interest in environmental issues.

The aim of this work was to investigate the sorption of p-nitrophenol using a bentonite clay modified with HDTMA. The influence of the independent variables and interactions between them were explained using Response Surface Methodology.

MATERIALS AND METHODS

Sample Collection

The bentonite clay used in this study was obtained from local mining sites at Logomani in Borno State, Nigeria. Logomani is precisely located at longitude 14° 01´E and latitude 12° 11´N in Dikwa Local Government Area. The clay was pulverized with an automatic milling machine and sieved with the various Endecotts

Laboratory test sieves on Omron No 17748 (manual timer) sieve shaker.

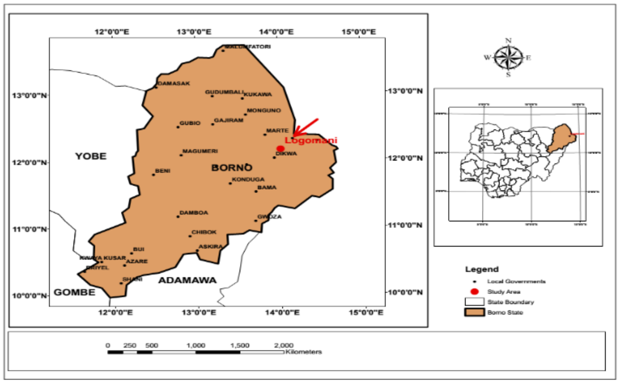


Figure 1: Study map showing area where clay samples were collected

Sample Treatment

The clay sample was dispersed in deionized water contained in a 20 liter plastic bucket. The dispersed clay was agitated vigorously and allowed to settle. The top layer which consisted of plant particles and insoluble impurities were sieved-off. The process of stirring and sieving-off was repeated with the lower layer until it was free of suspended particles. The dispersed clay was allowed to settle for 24 hrs. 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.

Modification of the Clay

The clay sample was dried in an oven at 105 °C for 12hours to remove any moisture and placed in a dessicator. About 15 cm^3 deionized water was measured into a 100 cm^3 beaker. An amount corresponding to twice the cation exchange capacity of clay sample was weighed and transferred into the beaker containing deionized water and stirred for 15 minutes with a magnetic stirrer. The solution was heated up to 27-28 °C and the solution became transparent gradually indicating that the salt was dissolved in the water and $HDTMA^+$ and Cl^- ions were formed in the solution. The solution's temperature was 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 $AgNO_3$. 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.* (2002). 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 carvied 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 p-nitrophenol 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 contact 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. The design matrix showing the experimental plan using the uncoded value of the variables is shown in Tables 2. 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. 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 adsorption process

Variables	Symbol	Range and Levels				
		-α	-1	0	+1	+α
pH	X_1	0.5	2	5	8	10.5
Adsorbate Concentration, mg/dm³	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: Design matrix for the batch adsorption experiments

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

Batch adsorption experiments were carried-out as per the design developed with the response surface central composite design methodology. Concentration of p-nitrophenol in the experimental solution was determined from the calibration curve prepared by measuring the absorbance of various known concentrations at λmax. = 319nm using a UV-Vis spectrophotometer (Jenway).

All experiments were carried out in 120 cm^3 flasks with the working volume of 50 cm^3 of reaction mixture. Mass of adsorbent as specified in the design 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 agitated for the specified time period in the thermostated water bath shaker. After agitation for the desired time of reaction, the flasks were withdrawn from the shaker. The residual concentration of p-nitrophenol was analyzed by centrifuging the reaction mixture at 2,500 rpm, (Labomed, USA) and then measuring the absorbance of the supernatant at the wavelength that corresponds to the maximum absorbance. Concentration of the p-nitrophenol in the reaction mixture was calculated from the calibration curve. Each determination was carried-out in triplicates, and average values recorded. The percentage of p-ntrophenol removal (Removal Efficiency) was taken as a response (Y) of the experimental design and calculated as follows:

$$Re = \frac{(Co - Ct)}{Co} \times 100\%$$

Where,
Co = initial concentration, mg/ dm^3
Ct = concentration at time t, mg/ dm^3
Re = removal efficiency, %

RESULTS AND DISCUSSION

XRF Characterization

XRF analysis was carried-out to determine the chemical composition of the minerals present in the clay sample. From Table 3, it is observed that 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 were found to be in agreement with results obtained by other workers for bentonitic clays; 14 % and 68.20 % (Yildiz and Calimli, 1999), 15.12 % and 65.24 % (Wu *et al.,* 2006) and 14.41 % and 65.13 % (Ikhtiyarova *et al.,* 2012) for alumina and silica oxide respectively in each case, thus confirming that the original clay sample is an aluminosilicate. According to Murray (2007), the theoretical composition without the interlayer material is SiO_2, 66.7 % and Al_2O_3, 28.3 %. The results from the XRF analysis also show a Na_2O content of 0.159 % and CaO content of 1.727 %. According to the formula $K = (E_{Na+} + E_{K+}) / (E_{Ca2+} + E_{Mg2+})$, where K = alkali coefficient, K = 0.39 (< 1), indicating that this bentonite is a typical Ca-bentonite (Wang, 1980). 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_2O/CaO ratio < 1, which indicates the presence of a non-swelling bentonite (Wu *et al,* 2006).

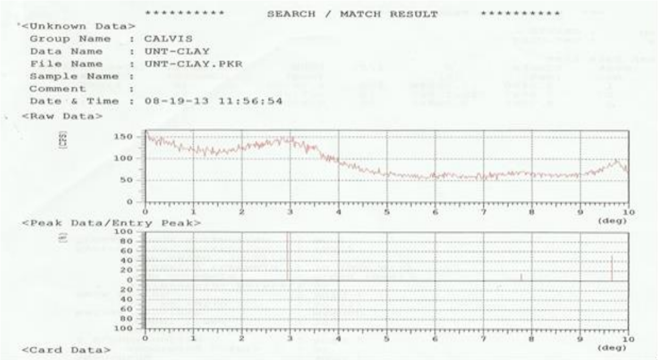
Table 3: Chemical composition of the original clay sample

Element	Content, %
Na_2O	0.159
MgO	1.480
Al_2O_3	21.268
SiO_2	62.687
P_2O_5	0.071
SO_3	0.216
Cl	0.009
K_2O	1.101
CaO	1.727
TiO_2	1.613
Cr_2O_3	0.018
Mn_2O_3	0.124
Fe_2O_3	0.949
ZnO	0.010
SrO	0.025

XRD Characterization

The low angle XRD pattern of the clay sample showed a broad peak appearing at approximately 2θ = 3° which is characteristic of montmorillonites and a basal spacing d(001) value of 11.176Å characteristic of calcium montmorillonites (Wu *et al.,* 2006).

The occurrence of a peak before 2θ = 10 ° 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 (Wu *et al.,* 2006; Tomul and Balci, 2007; Schütz *et al.,* 2013 and dos Santos *et al.,* 2013).



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  File Name    : UNT-CLAY.PKR
  Sample Name  :
  Comment      :
  Date & Time  : 08-19-13 11:56:54
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Figure 2: X-ray Diffractogram of the Original/untreated Clay

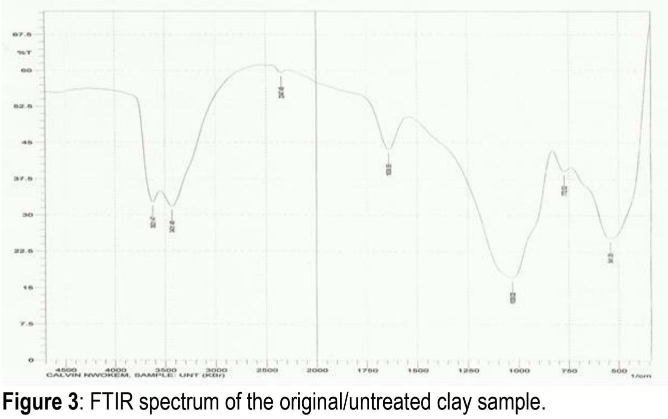

Figure 3: FTIR spectrum of the original/untreated clay sample.

Table 4: Values of the Process Parameters for maximum removal efficiency by HDTMA-bentonite clay

Parameter	Symbol	Value
Removal Efficiency, %	Y	99.79
pH	X_1	7.97
Adsorbate Concentration, mg/dm³	X_2	2.01
Solid: Liquid Ratio, g/ dm³ (S:L)	X_3	2.86
Time, mins	X_4	99

Pareto Analysis

Pareto analysis is a formal technique useful where many possible courses of action are competing for attention. (Khataee *et al.,* 2010).

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).

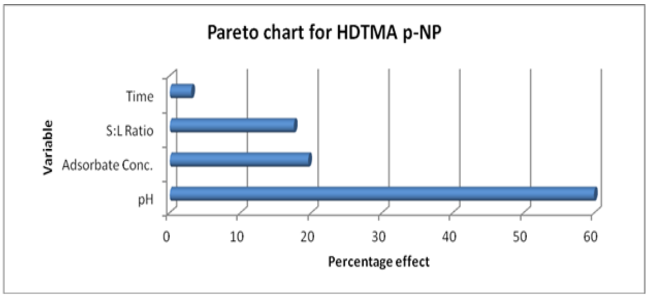

Figure 4: Pareto Chart showing percentage effect of variable for adsorption of p-nitrophenol by HDTMA-bentonite.

From the Pareto chart, it is clearly revealed that pH of the aqueous medium had the highest percentage effect on the adsorption process. This shows that in the removal of p-nitrophenol from aqueous solution using HDTMA-bentonite clay, the pH of the medium is the single most important variable that determines the efficiency of the system. This observation is in consonance with reports by other workers (Badii *et al.,* 2010, Ahamed and Begum 2012) that pH is the most influential parameter in the adsorption process.

Also, 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 (Ponnusamy and Subramaniam, 2013, Kour *et al.,* 2013). p-Nitrophenol can exist in aqueous solution either as an anion or as a molecule, hence it is known as an ionizable organic molecule. It exists as an anion when the solution pH > pKa and as a molecule when the solution pH < pKa. At pH > 9, p-nitrophenol is completely dissociated. The dissociation constant, pKa for p-nitrophenol is 7.16.

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

Maximum removal efficiency (99.79%) was obtained using HDTMA-bentonite clay at a pH of 7.97, as can be seen from Table 4, which is a little above 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-nitrophenol as well as the optimum pH obtained for adsorption involving it, the mechanism for its adsorption is most likely electrostatic attraction since p-nitrophenol 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 is approximately equal to pKa for each compound studied (Ahmaruzzaman, 2008).

Table 5: ANOVA results, regression coefficients and the significance tests and effects for p-nitrophenol adsorption by HDTMA-bentonite

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

Results from Table 5 show that the process is best described by a linear model. This means that interaction by the independent variables during the adsorption process was insignificant. This suggests that the removal of p-nitrophenol by HDTMA- bentonite clay from aqueous medium is one which depends on the linear effects of the independent variables (response surface linear model).

The associated *p*-value is used to judge whether *f* statistics is large enough to indicate statistical significance. A *p*-value less than 0.05 indicate that the model is considered to be statistically significant (Kim *et al.,* 2003). The p-value for the model as can be seen in Table 5 is < 0.0001, meaning that the model is significant. The model terms all had p-values lower than 0.05 except X_4. This indicates that all the terms except X_4, were significant. Results from Table 6 show that interaction effects of the variables all had p-values greater than 0.05, which showed that interaction effect on the removal efficiency was insignificant.

Table 6: Significance Tests and Interaction Effects for P-Nitrophenol Adsorption by Hdtma-Bentonite**.**

Regression	F-value	P-value
Interaction	0.17	0.981
$X_1{*}X_2$	0.00	0.970
$X_1{*}X_3$	0.00	0.997
$X_1{*}X_4$	0.48	0.499
$X_2{*}X_3$	0.53	0.479
$X_2{*}X_4$	0.00	0.983
$X_3{*}X_4$	0.02	0.887

The fit of the model is expressed by the coefficient of determination, R^2, which was calculated to be 0.896. The closer the R^2 value to 1.00, the stronger the model is and the better it predicts response. The calculated R^2 value for this study indicated that the model could explain 89.6% of the variability of the response. Comparing the predicted p-nitrophenol removal (100%) and the experimental results (99.79%) under optimal conditions proved the accuracy and validity of the model.

Conclusion

Response surface central composite design was used to investigate the effects of the process variables on the removal of p-nitrophenol by HDTMA- bentonite clay from aqueous solution. The optimum process conditions obtained were pH of 7.97, adsorbate concentration of 2.01mg/dm^3, solid:liquid ratio of 2.86, contact time of 99 minutes for a removal efficiency of 99.79%. 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 and the adsorption process followed a linear model. This study demonstrates that organically-modified bentonites can be utilized in the remediation of p-nitrophenol pollution.

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