Adsorption of Ethylacetate from Ethyl Acetate – Water Mixture using Activated Clay

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***Abstract*– The adsorption capacity of activated clay produced from ukpor clay on ethyl acetate-water mixture has been investigated. The activated clay was prepared using thermal activation by heating the ukpor clay in the absence of air using a muffle furnace at 200^{o}C, 350^{o}C, 500^{o}C, 600^{o}C for 30, 60, 90,120 minutes respectively. The effect of three factors; temperature of activation, process duration and particle size were carried out using the Analysis of Variance. The optimum conditions were activation of the ukpor clay at 600^{o}C for 90mins. The ash content, iodine number, pH, bulk density and moisture content produced at these condition were 1%, 68.528, 4.80, 1.43mg/ml and 20%, respectively. The adsorptive capacity of the adsorbent was tested using Langmuir and Freundlich isotherm. It was noted that the data fitted better in the Linearized Langmuir adsorption isotherm.**

***Keywords*– Adsorption, Activated Carbon, Sawdust, Ethyl Acetate and Adsorption Isotherms**

I. INTRODUCTION

Industrial production of chemicals involves purification and recovery of the products, by-products and unreacted raw materials. As waste regulations are becoming more stringent, the economical benefits of having recovery systems that allow for recycling and reuse of the solvents within the process are significant. Recovery and reuse of organic solvents is generally practiced because of increased solvent cost and potential solvent shortages and because the disposal often results in the violation of air, water or land pollution regulation.

Ethylacetate are harmful to both human, animals. In human, it causes irritation of the eye and upper respiratory tract at concentration above 400ppm.it also causes eczema and depression of the heart function. At high concentration, it causes narcosis and depression of the heart function in animals [1].

Kaolinite are distinct from other adsorbents in that, for each type, there is no distribution of pore size because the crystal lattice into which the adsorbate molecules can or cannot enter is precisely uniform. For this reason, kaolinite is capable of separating effectively on the basis of molecular size. They are used, among others for the separation of oxygen and argon, separation of normal from branched paraffin, drying of gases and removing water from azeotropic mixtures. The main objective of this research work is to study the adsorption of ethyl acetate from ethylacetate-water mixture using activated clay. Although ethylacetate-water mixture forms a hetroazeotropes but was treated as a homoazeotrope in this study.

II. MATERIALS AND METHODS

A. Materials

The widely available adsorbent used in this study was clay (75-600µm) gotten from Ukpor in Anambra. The adsorbate used in this study was ethyl acetate gotten from Pymotech Laboratories in Enugu State.

B. Activated Clay Preparation

Activated clay was prepared using thermal activation by heating the clay in the absence of air using muffle furnace at 200^{o}C, 350^{o}C,500^{o}C, 600^{o}C for 30,60, 90,120minutes.

C. Characterization of Activated Clay

Determination of Iodine Number

Standard solution of 0.1N iodine solution was prepared. 3 drops of freshly prepared starch indicator was added to 20mls of 0.1N iodine solution and titrated with 0.05N sodium thiosulphate.

Observation– Colourless

For the sample– 0.2g of the activated clay was weighed and poured in the filter paper. 20ml of the standard (Std iodine solution was measured and poured in a filter paper. 2mls of standard (Std iodine solution was measured and poured in the sample in the filter paper). 10mls of the filtrate was pipette and 3 drops of freshly prepared starch indicator added and titrated with 0.005N Sodium thiosulphate.

Observation – Colourless

Moisture Content: The petridish was washed and dry in an oven and was weighed. 1g of the sample was weighed and added in the petridish, put in the oven and dry at 100^{o}C for 2hrs and cooled down in the desiccator and weighed. It was dried in an oven again at 100^{o}C for 30mins, cooled down and weighed again. Drying and weighing continued until a constant weight was obtained.

Bulk Densities: Bulk densities were determined using 50g (VP) of the starch powder. This was gently poured through a short stemmed glass funnel into a 100mls graduated cylinder.

Ash Content: Empty platinum crucible was weighed after which the empty crucible + 1g of the sample were weighed. The platinum Crucible and the content were heated over a flame from a Bunsen burner until the sample turned white colour. The crucible was cooled in desiccators and weighed again.

pH: The pH meter was deep into the samples and the value of the pH was taken.

D. Adsorption Experiment

The 0.4 and 0.05 normal solutions were prepared with the same volume 1000cm^3. Each of these solutions was divided into two equal parts of 500cm^3 each. One part was used to determine the exact concentration C^1 of the ethyl acetate before adsorption (initial Concentration) by titrating an aliquot with NaoH. The other part was used for the adsorption by placing 1g of the activated clay and shaking periodically for about 30mins until equilibrium has been established. The mixture was filtered and aliquot was titrated again with NaoH to determine the final concentration C^{11}.

E. Experimental Design

The experimental design was done using the Latin square experimental design method to determine the effect of the factors, factor X_1 (rows), Factor X_2 (column), Factor X_3 (Latin alphabets) for the Time, Temperature and Particle size respectively on the adsorption of ethyl acetate from ethylacetate- water mixture.

F. FTIR Analysis

The FTIR Analysis was done using the FTIR Spectrometer to determine the type of functional group present in the samples taken and also about the concentration of the bonds.

III. RESULT AND DISCUSSION

A. Characterization Results

From Table 1, the activation condition of Sample E gave the highest iodine number. High moisture contents contribute to low gas heating value. This is because, dry biomass burns at higher temperature and thermal efficiency than wet biomass. Sample E also gave the highest moisture content of 32%. High moisture content contributes to low thermal efficiency since the heat is used for drying purposes. Sample D and F gave the lowest moisture content at 600^{o}C and 200^{o}C within 90 and 120mins respectively.

Flame temperature is directly related to the amount of heat necessary to evaporate in the biomass fuel. Mckendry (2002a, b) reported that biomass fuel with moisture content above 30% is difficult to ignite and reduces the heating value due to the need to evaporate the additional moisture before combustion. Sample D and sample F gave the highest Bulk densities at temperature of 600^{o}C, 90mins and 200^{o}C, 120mins, respectively.

B. ANOVA Results

From Table 2 and Table 3, it was observed that the ANOVA results for Ukpor Clay shows that $F_1 < F_{table}$ for all factors indicating that the factors are insignificant and does not practically affect the uptake of ethylacetate from ethyl acetate – water mixture.

Table 1: Characterization of Activated Clay

SAMPLE	TEMP (^{O}C)	TIME (mins)	IODINE No.	BULK DENSITY (g/mls)	ASH CONTENT (%)	pH	MOISTURE CONTENT (%)
D	600	90	68.528	1.43	1	4.80	20
E	-	-	75.889	1.32	1	4.78	70
F	200	120	60.914	1.43	5	5.91	18

Sample D _____ Activated clay (ukpor clay) at 600^{o}C, 600µm, 90mins

Sample E _____ Raw ukpor clay

Sample F _____ Activated ukpor clay at 200^{o}C, 600µm, and 120mins.

Table 2: ANOVA results ukpor clay 0.05N

Source of Variation	No of Degrees of Freedom	Estimation of Variation	F Ratios
ROWS Q(X1) 1.181 X 10^{-7}	$V_1 = 3$	$S_1^2 = Q(X_1)/V_1$ = 3.935 X 10^{-8}	3.2987
COLUMN Q(X2) 5.031 X 10^{-6}	$V_2 = 3$	1.677 X 10^{-8}	1.4056
TREATMENTS A,B,C,D, Q(X3) 8.841 X 10^{-9}	$V_3 = 3$	2.947 X 10^{-9}	2.47 X 10^{-1}
RESIDUALS Q_{RES} 4.909 X 10^{-6} TOTAL = 8.138 X 10^{-7}	$V_{RES} = 6$ 15	11.93 X 10^{-9}	

Table 3: ANOVA results Ukpor Clay 0.4N

Source of Variation	No of Degrees of Freedom	Estimation of Variation	F Ratios
ROWS Q(X1) 1. 821 X 10^{-8}	$V_1 = 3$	$S_1^2 = Q(X_1)/V_1$ = 6.069 X 10^{-9}	2.352 X 10^{-1}
COLUMN Q(X2) 6.741 X 10^{8}	$V_2 = 3$	2.247 X 10^{-8}	8.7128 X 10^{-1}
TREATMENTS A,B,C,D, Q(X3) 8.059 X 10^{-9}	$V_3 = 3$	2.686 X 10^{-9}	1.0415 X 10^{-1}
RESIDUALS Q_{RES} 1.548 X 10^{-7} TOTAL = 1.348 X 10^{-2}	$V_{RES} = 6$ 15	2.59 X 10^{-8}	

C. Adsorption Isotherms

Freundlich Adsorption Isotherm - Activated Clay

The Linear plots of log A against logC_e shows that the adsorption follows Freundlich Isotherm model. K and n were calculated from the intercept and slope of the plots. K is the adsorption or distribution coefficient and represents the quantity of ethylacetate adsorbed onto activated clay adsorbent for a unit equilibrium concentration. The higher the K, the higher the adsorption efficiency. The Linear plots of log A against log C_e (Fig1) shows that the K value of the plot of Linearized Freundlich Isotherm of ethylacetate onto activated clay at 350^{o}C with initial conc. of 0.4N gave the highest value (0.75mg/g). This shows that the activated clay at 350^{o}C has the highest adsorption efficiency. The slope 1/n ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as it gets closer to zero as observed by Haghscresht, F [4]. According to Treyball, it has been shown using mathematical calculation that values of n between I and 10 represents beneficial adsorption.

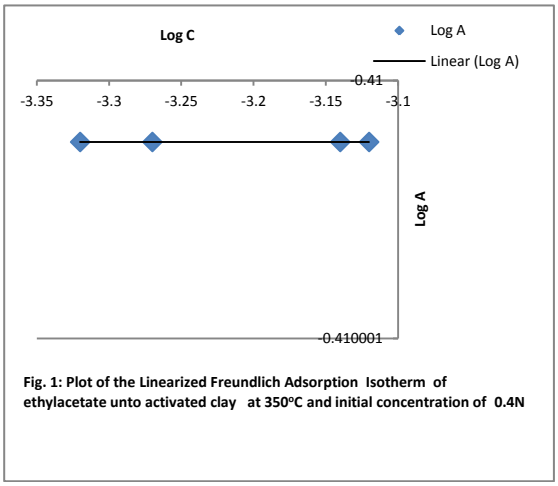

Fig. 1: Plot of the Linearized Freundlich Adsorption Isotherm of ethylacetate unto activated clay at 350^{o}C and initial concentration of 0.4N

Langmuir Adsorption Isotherm - Activated Clay

The linear plots of C_e/q_e Versus C_e shows that the adsorption obeys Langmuir Isotherm model (Fig. 2) q_0 and b were determined from the slope and intercept of the plot Langmuir constant related to the adsorption capacity and energy and presented into adsorption.

R_L values between 0 and I at different concentration indicate favorable adsorption of ethylacetate unto activated clay. The correlation coefficients for the linear plots were good. The best correlation occurred at (Fig. 2), which gives R^2=1 and R_L = 1 indicating the best favourable adsorption.

The plot of Langmuir isotherm for activated clay shows the highest isotherm line at 500^{o}C with initial concentration of 0.05N which indicated best adsorptive capacity as observed by Nester *et al*, 2004 [5].

Table 4: Parameters for Freundlich equation for ukpor clay (0.4N)

AT 350^{0}C

Log A	Log C	K	1/n	n
-0.41	-3.14	0.75	0.23	4
-0.41	-3.12			
-0.41	-3.27			
-0.41	-3.32			

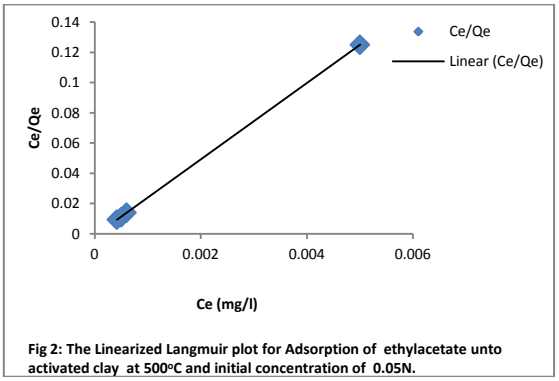

Fig 2: The Linearized Langmuir plot for Adsorption of ethylacetate unto activated clay at 500°C and initial concentration of 0.05N.

Table 5: Parameters for Langmuir Adsorption Isotherm for clay 0.05N

AT 500^{0}C

C_e/Q_e	C_e	Q_o	B	R_L	R^2
			-		
		0.0	0.000039		
0.014	0.0006	4	5	1	1
0.125	0.005				
0.011	0.0005				
0.009	0.00041				
4	7				

D. Infrared Position of Various Bond Variations

Table 5: Tables Showing Infrared Position of Various Bond Variations for different samples

Sample D: (activated clay) at 600^{o}c, 600µm, and 90mins.

Peaks	Bond	Mode	Concentration
3434.28	O-H	Stretch	Strong
2920.00	C-H	Stretch	Strong
1632.38	C-H	Finger print region	Weak
1102.33	C-O	Stretch	Strong
1028.23	C-O	Stretch	Strong
919.98	C-H	Bend	Strong
788.86	C-H	Bend	Strong
689.11	C-H	Bend	Strong

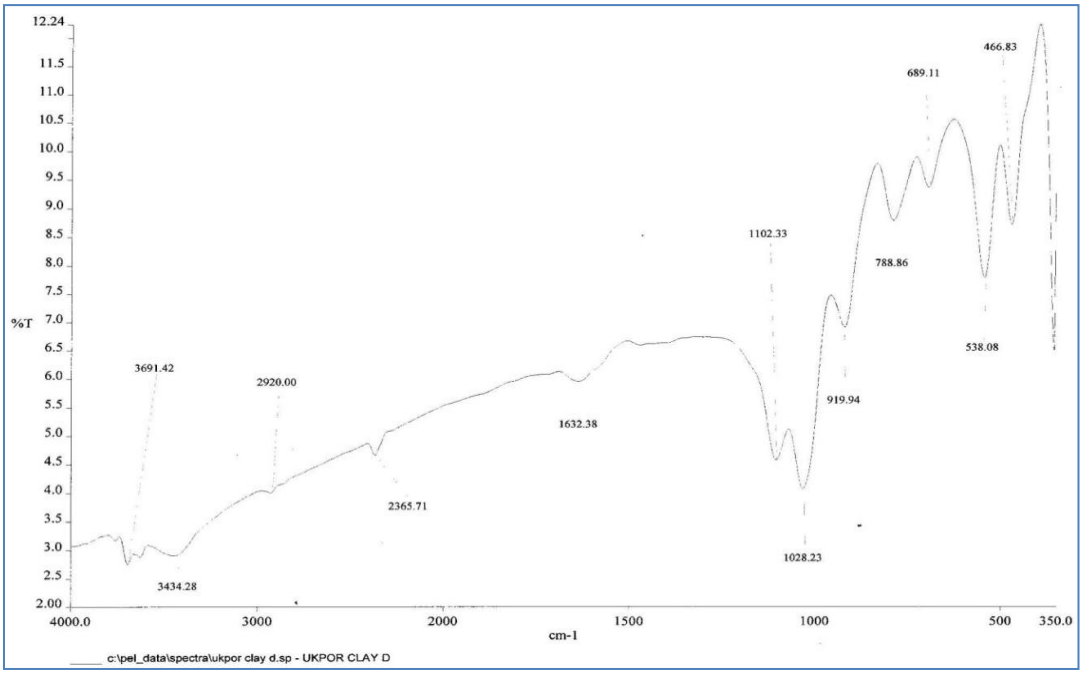

Fig. 3: FTIR Graphical Analysis of Sample D

Sample E: Raw Ukpor clay.

Peaks	Mode	Bond	Concentration
3474.28	Stretch	N-H	Medium
1643.78	Bend	N-H	Medium
1105.18	Stretch	C-H	Medium
1031.08	Stretch	C-H	Medium
922.79	Bend	C-H	Strong
788.86	Bend	C-H	Strong
694.81	Bend	C-H	Strong

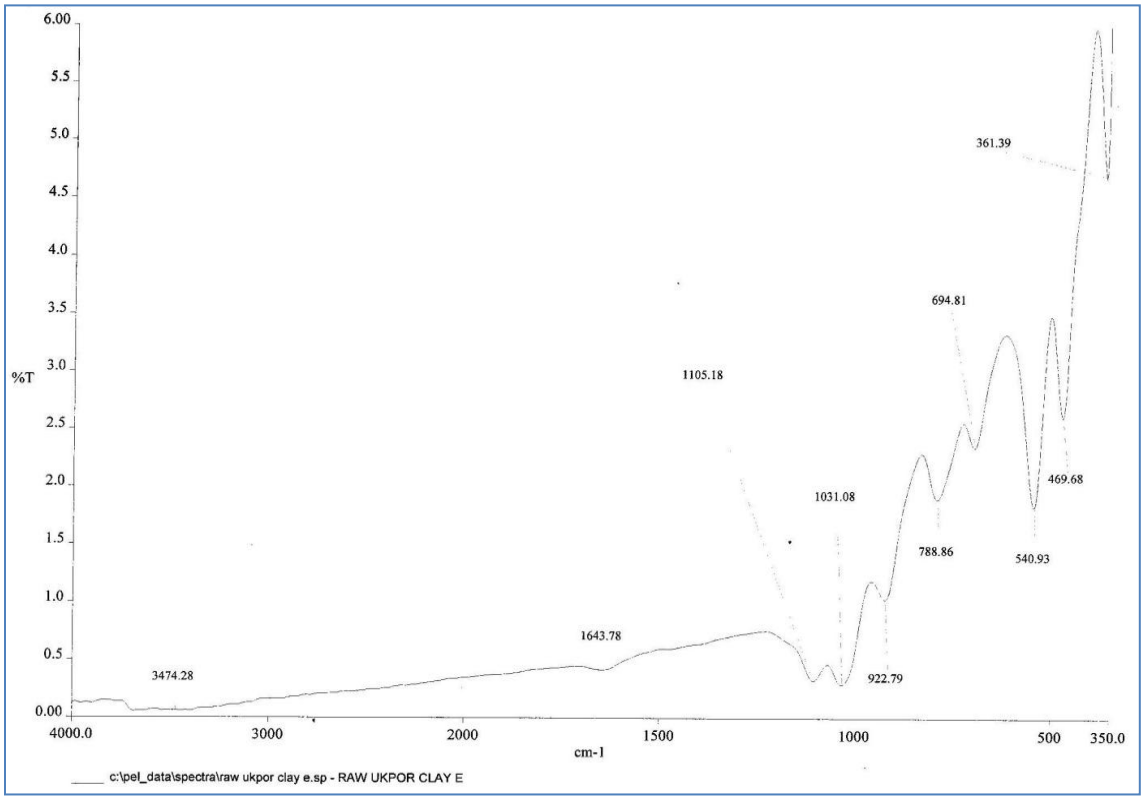

Fig. 4: FTIR Graphical Analysis of Sample E

Sample F: Activated Ukpor Clay at 200^{o}c, 600µm, 120mins.

Peaks	Mode	Bond	Concentration
3474.28	Bend	N-H	Medium
1640.93	Bend	N-H	Medium
1102.33	Stretch	C-N	Medium
1028.23	Stretch	C-N	Medium
919.94	Bend	C-H	Strong
783.16	Bend	C-H	Strong
694.81	Bend	C-H	Strong

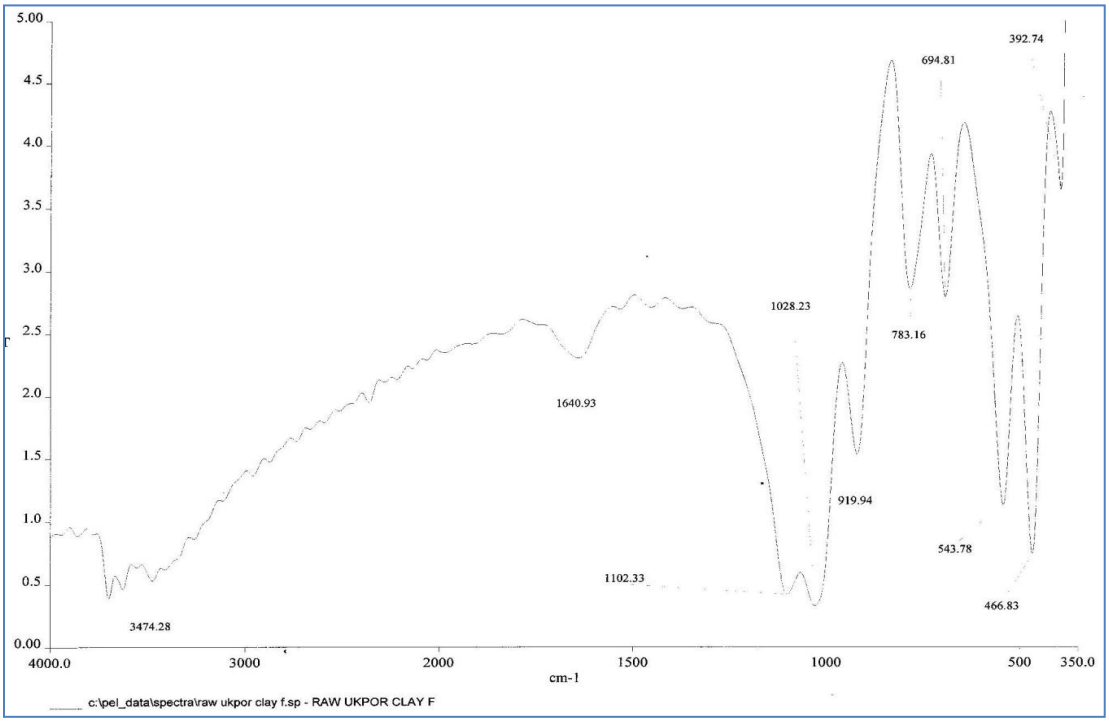

Fig. 5: FTIR Graphical Analysis of Sample F

FTIR of sample D (Fig. 3) shows that the C-H group is mostly present in the sample with strong concentrations at the various wavelengths except for the finger print region where it is showing weak concentrations.

Sample E (Fig. 4) shows that the most abundant group is the amine group. With medium concentration while the C-H group which are also present in the samples are showing strong concentrations.

Sample F (Fig. 5) shows that the C-H group are the ones mostly present in the sample. Though the amine groups are also present showing medium concentrations while the C-H group are showing strong concentrations.

IV. CONCLUSION

Activated clay was shown in this study to be an effective adsorbent in the removal of ethyl acetate from ethyl acetate - water mixture. The optimum conditions were activation of ukpor clay at 600^{o}C for 90mins. The maximum adsorption takes place in the PH of 4.75.The Langmuir and Freundlich isotherms were used for fitting the experimental data in the adsorption studies to understand the extent and degree of favourability of adsorption. The range of n 1 to 10 indicated [7]. . favourable adsorption for the Freundlich plots while R_L values between 0 to 1 indicated favourable adsorption for Langmuir plots. The FTIR analysis on the samples indicated higher wavelengths (cm¯1) for the activated samples.

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