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Optimization of H_2SO_4-Modification of ITU Bentonitic Clay under Box Behnken Design

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ABSTRACT

Bentonite clay from Itu, Akwa-Ibom State, Nigeria was modified using sulfuric acid (H_2SO_4). The chemical composition of the raw (RI) and H_2SO_4 modified (HI) Itu clay was determined using the X-ray fluorescence (XRF) technique. The Box Behnken Design (BBD) was used to optimize the H_2SO_4 and clay modification process using the wet acidification method. The process parameters considered for the optimization were H_2SO_4 concentration (0.1-6.0 M), activation temperature (60-100 °C) and activation time (5-10 mins). The optimum yield of 6.12 g was obtained in 7.5 min and at 60 °C when 6 M H_2SO_4 concentration was used for the clay modification. The predicted value of the modified clay (Itu/H_2SO_4) yield agrees with its observed values (R^2 = 0.9681 and Adj R^2 = 0.9271), statistically. These results revealed that the process parameters significantly influenced the clay modification process. The XRF analysis of the samples revealed that the RI and HI are calcium montmorillonite with SiO_2/Al_2O_3 ratio values of 3.20 and 5.48 respectively.

INTRODUCTION

Clays are largely abundant phyllosilicate materials that occur naturally. They consist of fine-grained materials that turn plastic when in contact with water and harden when dried. Clays are environmentally friendly, recyclable and economical. The properties of clay minerals such as acidity, high surface area and cation exchange capacity make them useful as catalysts, catalyst supports (Salawudeen *et al.* 2018) and adsorbents (Anumata *et al*., 2021; Salihu and Suleiman, 2018; Ahmed *et al*., 2012). Clays are modified for the manufacture of value-added materials applied in drilling fluids formulation (Adeleye *et al*., 2009), ligands on casting moulds and precursor materials for the synthesis of other value-added materials (Salam *et al*., 2022; Oke *et al*., 2024). They are applicable in vegetal and mineral oil decolouration and deodorization (Mannu *et al*., 2019; Hmeid *et al*., 2020). Clays are categorized into montmorillonite-smectite, kaolinite, illite, and chlorite groups (Manukaji, 2013). The classification which determines their area of application is done based on their structural arrangements and chemical compositions.

Nigeria is blessed with large clay deposits which if well harnessed will reduce its importation and cost. The proven reserve of bentonite in Nigeria has been modestly estimated to be above 700 million metric tons (Bilal *et al*., 2015; Abdullahi *et al*., 2017) with over 70 to 80 million metric tons of the clay found

in Afuze, Edo State, Nigeria (Nweke *et al*., 2015). Apugo-Nwosu *et al*., (2011) identified bentonitic clay deposits in the Northeastern quadrant of Borno, Yobe, Taraba and Adamawa states. The elemental contents of some bentonitic clay in Akwa-Ibom State were determined by Okorie *et al*., (2015). With regards to bentonite's vast deposits in Nigeria, the Federal Government in 2003 issued a restriction order on the importation of foreign bentonite with a view of exploiting its local deposits (Oriji *et al*., 2014). Bentonite clay is averagely valued at $41.33 per ton (Mamudu *et al*., 2020). Bentonites may be referred to as calcium or sodium bentonite depending on the dominant exchangeable cations present in the clay (Christidis and Scott 1997; Hmeid *et al*., 2020;). During its formation, a variety of accessory minerals such as feldspars, quartz, calcite, dolomite, gypsum, biotite, crystobalite, plagioclase, etc. occur with montmorillonites. They are characterized by thin layers and small particle sizes that contribute to their high absorptive properties for water, oil, and chemicals (Ahmad and Yasin, 2018). They mostly display characteristics like swelling, shrinkage, and high Cation Exchange Capacity (CEC) (Sun *et al*., 2016; Idoko *et al*., 2019). The presence of interlayer cations affects their swelling behavior, with sodium-containing clays demonstrating higher expansion capacity (Muhammad and Siddiqua, 2022).

Bentonites possess valuable properties such as catalytic activity, high CEC, specific surface area, sorption capacity, and surface reactivity, making them useful in various industries (Kgabi and Ambushe, 2023).

Properties such as charge density, surface charges and surface area, the type of exchangeable cations, silanol groups of crystalline defects or broken surfaces with hydroxyl groups on the edges and Lewis and Bronsted acidity make it have a great sorption capacity (Djomgoue and Njopwouo, 2013; Quero-Jiménez *et al*., 2021). These characteristics make them suitable for various industrial applications such as their use as sealants, fillers for paper, pharmaceutical products, catalysts, adsorbents, drilling fluids, etc. (Bilal *et al*., 2016).

Several research studies have been done on the characterization of bentonitic clays. Kpagi *et al*., (2023) investigated the mineralogical and morphological properties of South African bentonite and kaolin clays using powered X-ray diffraction (PXRD), FTIR, SEM and BET, Aroke and Hamidu, (2020) studied the instrumental characterization of unmodified and HDTMA-Br modified kaolin clay while Olaseinde *et al.*, (2020) characterized Pretoria clay soil using XRF, XRD and SEM. In addition, Oniya *et al*., (2020) characterized clay that was modified with alkali extracted from plantain peels using SEM, XRF and FTIR and Ahmed *et al*., (2012) studied the mineral and chemical characteristics of Pindiga bentonitic clay. The work of Okorie *et al*., (2015) was limited to the characterization of raw Itu clay using XRF analysis. The results obtained from the above-mentioned works of literature suggested that clays had interesting features that could be useful in various industries. Meanwhile, there is no research work on the optimization of the modification process of indigenous Itu clay using H_2SO_4. This paper focused on enhancing the chemical composition of Itu clay to increase its commercial value and improve its suitability as a catalyst support.

MATERIALS AND METHODS

Materials

Itu clay was collected from a mining site located at Itu (Longitude: 7° 59' 1.43" E; Latitude: 5° 12' 4.72" N), in Itu Local Government Area of Akwa-Ibom State. Ten kilograms (10 kg) of the sample was mined through digging of 20 cm deep hole. The

sample was kept in a polyethylene bag, labeled and carried to the laboratory for further analysis. Analytical grade sulfuric acid (H_2SO_4; 98%) was procured from the Central Research laboratory, Ilorin and used as received for clay activation.

Beneficiation of raw clay sample

The clay sample was weighed and crushed down from lumps to fine powder using a spice and herb grinder (HR-16B, 2400W). The sample was purified using methods described by Salahudeen *et al*., (2012). One kilogram (1 kg) of the clay was soaked in water using an experimentally determined optimum mixing ratio of 0.1kg: 1 liter (clay to water) and stirred for 3 h at room temperature. The stirred mixture was left undisturbed in the container for 24 hours to allow sedimentation, resulting in the separation of suspended particles at the bottom and leaving a colloidal solution at the top. The colloid was collected and separated from the quartz sediments by scooping.

The colloids were further sieved through a 230 mesh Tyler sieve (63μm sieve opening) to remove coarse impurities. The clay obtained was allowed to settle and thickened in a filter bag. The thickened clay was pressed under a hydraulic press to squeeze out water and the resulting cake was dried in an electric oven (NYC-101) at 300 ^oC to remove moisture and volatile organics. The dried clay was crushed to powder using a spice and herb grinder and stored in a polyethylene bag for subsequent experiments.

Clay calcination

The crushed beneficiated clay (BC) was calcined in a muffle furnace (FB1315M, 120 V, 1100 ^oC) at 800 ^oC and allowed to remain at this temperature for 3 h. The temperature was selected because the hydroxyl group (chemically combined water or water of hydration) in clay structure gets destroyed at temperatures between 600 ^oC and 700 ^oC (Ahmed *et al.*, 2012).

Clay activation using sulfuric acid (H_2SO_4)

Seventeen (17) experimental runs were designed for clay activation with H_2SO_4 using the Box Behnken Design (BBD) of the Response Surface Methodology (RSM) in Design Expert Software (DOE_13). Varying acid concentrations (0.1-6.0 M) (Salahudeen *et al*., 2012; Mara *et al*., 2016; Tarmizi *et al*., 2018), activation temperatures (60-100 ^oC) (Ahmed *et al*., 2012; Mara *et al*., 2016; Onukwuli *et al*., 2018; Tarmizi *et al*., 2018) and activation time (5-10 minutes) (Ahmed *et al.*, 2012; Salahudeen *et al*., 2012) were considered as limits/range for the activation process. Table 1 simplifies the experimental ranges and process parameters considered. The modification was carried out in a 500 ml flat bottom flask that was placed on a hot plate magnetic stirrer. Respective calcined clay was sieved using a Tyler sieve of mesh size 230 (63 μm aperture opening), weighed and introduced into the flask. Twenty (20) mL prepared H_2SO_4 solution with varying concentrations, activation temperatures and activation times were introduced gradually to 5 g clay powder already contained in the flask for a specific experiment. The stirrer speed was set and maintained at 400 rpm to achieve thorough mixing (Tsakiri *et al*., 2022). At the end of the process, the acid-modified clay (HI) was separated from the mixture by decantation; the supernatant was discarded while the modified clay slurry layer was washed with distilled water. The modified clays were dried in an electric oven (NYC-101) operated at 110 ^oC for 120 mins (Onukwuli *et al*., 2018). The samples collected from the oven were ground, weighed and stored in sample bottles. The HI yield (response) was used to develop an empirical model that correlated the dependent variables with the independent variables using Equation 1.

$$Y = b_o + b_1A + b_2B + b_3C + b_{12}AB + b_{13}AC + b_{23}BC + b_{11}A^2 + b_{22}B^2 + b_{33}C^2 \quad (1)$$

Where Y is the response of HI yield; b_i is the regression coefficient for linear effect; b_{ii} is the quadratic effects, respectively, while A, B and C are the coded experimental variables Acid concentration, Activation temperature and Activation time.

Table 1: Factors considered for H_2SO_4 activation of calcined Itu clay

Factors	**Unit**	**Level**	
		Low	High
Acid concentration	M	0.10	6.00
Activation temperature	^oC	60.00	100.00
Activation time	Min	5.00	10.00

Characterization of raw and modified Itu clays

The chemical composition of the samples was determined using the PAnalytical MagiX PRO XRF instrument (Kgabi *et al*., 2023). About 1.02 g of each of the samples were weighed into the crucibles and heated at 930 ^oC for 30 min in a muffle furnace. After the ignition process, the samples were cooled in a desiccator containing anhydrous silica gel. The loss on ignition (LOI) was calculated by subtracting the mass of the sample after ignition from the initial mass of the clay sample.

The procedure for the X-ray fluorescence (XRF) analysis was according to Kgabi *et al*., (2023). Approximately, 0.7 g of the ignited clay sample was mixed with 0.1 g of lithium nitrate ($LiNO_3$) and 6.0 g of 50/50 flux (Malvern PANalytical, South Africa) in Pt–Au crucibles. The mixture was subjected to fusion at a temperature of 1100 ^oC for 5 min using a Claisse TheOx Advanced fusion instrument. Afterward, the mixture was allowed to cool while the resulting fused sample was cast into a glass bead within the crucible and analysed using the PAnalytical MagiX PRO XRF instrument.

RESULTS AND DISCUSSION

Results of clay activation using H_2SO_4

The BBD of design expert software (version 13) was used to generate data for the analysis (Table 2). It was observed from the Table that modified Itu clay (HI) yield ranges between 4.23 and 6.12 g. The correlation between the factors considered for clay modification using H_2SO_4 and the yield is expressed by the second-order polynomial equation given in Equation 2.

$$HI\ yield = +5.15 + 0.5788 - 0.0825B - 0.0313C - 0.0025AB - 0.2850AC + 0.0125BC + 0.2010A^2 + 0.1535B^2 - 0.2990C^2 \quad (2)$$

The positive signs in front of the terms indicate a synergetic effect while negative signs indicate an antagonistic effect (Agarry *et al*., 2024). The responses obtained from the analysis are also presented in Table 2. The predicted HI yields were determined by Equation (2) and shown in the table. The actual yield values obtained from the experiments are in concordance with their respective predicted yield values. The correlation between the actual and predicted yield values was evaluated using the correlation coefficient (R^2). The R^2 value measures the strength and direction of the relationship between two responses (Yusuff, 2019). It shows the perfectness of a model as it fits the experimental data. An R^2 value of 0.9681 was obtained in this analysis, indicating that the responses (actual and predicted) were well correlated and 96.81% of the total variations for HI yield were described by the model while just 3.19% variations could not be accounted for.

Table 2: Result of responses from Itu Clay activation with Sulfuric acid (H_2SO_4)

Run	Acid Concentration (M)	Activation Temperature (ºC)	Activation Time (min)	Predicted Modified Clay yield	Modified Clay (HI) (g)
1	3.05	80.00	7.50	5.15	5.22
2	3.05	60.00	10.00	5.04	5.10
3	0.10	80.00	10.00	4.72	4.67
4	3.05	100.00	5.00	4.94	4.88
5	0.10	60.00	7.50	5.00	5.00
6	6.00	100.00	7.50	6.00	6.00
7	6.00	60.00	7.50	6.17	6.12
8	0.10	100.00	7.50	4.84	4.89
9	3.05	80.00	7.50	5.15	5.32
10	3.05	80.00	7.50	5.15	5.09
11	6.00	80.00	10.00	5.31	5.30
12	3.05	60.00	5.00	5.13	5.12
13	3.05	80.00	7.50	5.15	4.90
14	6.00	80.00	5.00	5.95	6.00
15	3.05	80.00	7.50	5.15	5.21
16	3.05	100.00	10.00	4.90	4.91
17	0.10	80.00	5.00	4.22	4.23

Since its value in this research is close to unity, it signifies that the experimental data fits in the model equation 2. In addition, the R^2 value agree reasonably with the values obtained for adjusted R^2 (0.9271) and the predicted R^2 (0.8829) (Table 3). The difference between the R^2 and adjusted R^2 values (0.0041) is lower than the maximum allowable difference of 0.2 (Dhawane *et al*., 2016). These values were used to measure the fitness of the model.

The result of the analysis of variance (ANOVA) is presented in Table 3. ANOVA was used to evaluate the adequacy of the model as it expresses the significance of the three (3) process parameters on HI yield. From the table, the model Fischer's statistical test (F-value) was 23.63. This confirms the adequacy of the model as the value is greater than the tabulated F (11.82 at 95% significance). In addition, the probabilities of the model and those of each parameter otherwise referred to as the probability distribution function (Prob.>F) are used to check the significance of each of the model terms. When values of Prob.>F are less than 0.05, the corresponding model term is significant (Agarry *et al*., 2024). Hence, A, AC, A^2, B^2 and C^2 are the significant parameters of the model. HI with the highest yield value (6.12 g) was characterized using the analysis as discussed earlier.

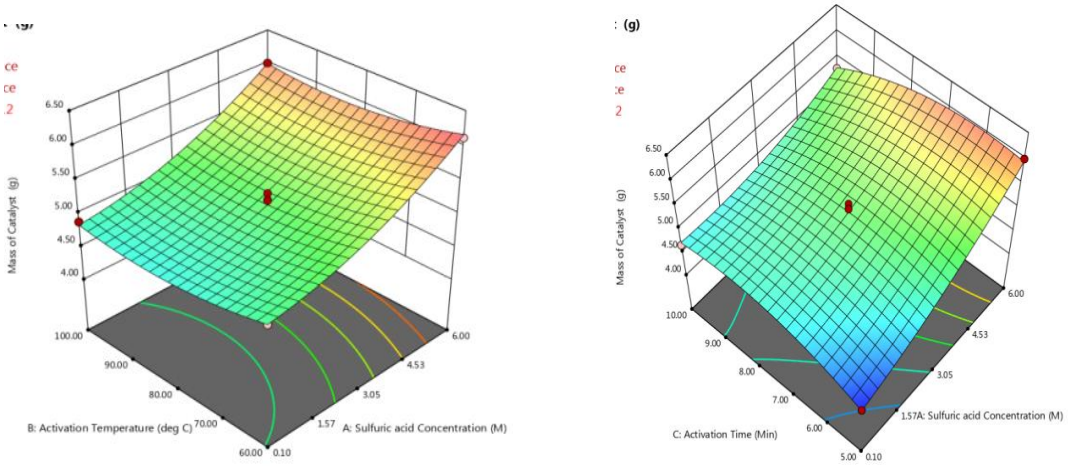
Interaction effect between H_2SO_4 concentration (A) and activation temperature (B) on HI yield

From Figure 1a (interaction between H_2SO_4 concentration (A) and activation temperature (B)) for HI, it was observed that the HI yield increases when H_2SO_4 concentration increases and at low

Table 3: Analysis of Variance (ANOVA) for Quadratic Modeling of Itu Clay Activation with H_2SO_4

Source	Sum of squares	df	Mean square	F-value	p-value
Model	3.68	9	0.4091	23.63	< 0.0002*
A- H_2SO_4 Concentration	2.68	1	2.68	154.76	< 0.0001*
B- Activation Temperature	0.0544	1	0.0544	3.14	0.1195
C- Activation Time	0.0078	1	0.0078	0.4512	0.5233
AB	0.0000	1	0.0000	0.0014	0.9708
AC	0.3249	1	0.3249	18.76	0.0034*
BC	0.0006	1	0.0006	0.0361	0.8547
A^2	0.1701	1	0.1701	9.82	0.0165*
B^2	0.0992	1	0.0992	5.73	0.0479*
C^2	0.3764	1	0.3764	21.74	0.0023*
Residual	0.1212	7	0.0173		
Lack of Fit	0.0177	3	0.0059	0.2284	0.8725
Pure Error	0.1035	4	0.0259		
Cor Total	3.80	16			
R^2: 0.9681; Adj R^2: 0.9271; Pred R^2: 0.8829					

*=significant at $p < 0.05$; **= significant at $p < 0.1$



1a 1b

Figure 1: a) 3D plot showing the interactive effect of H_2SO_4 Concentration and Activation temperature and (b) effect of H_2SO_4 Concentration and Activation time on HI yield

activation temperature. This was also observed in Figure 1b, for the interaction effects between H_2SO_4 concentration (A) and activation time (C).

Perturbation plot of catalyst yield

The result of the statistical analysis in the form of a perturbation plot at the center point for Itu/ H_2SO_4 is shown in Figure 2. This plot illustrates the comparative effects of the variables across the studied range for acid-activated Itu cay on HI yield. Flat or semi-flat curvatures in the curves suggest less sensitivity or insensitivity of HI yield while a sharp curvature in the plot indicates high sensitivity

of the yield (Salam *et al*., 2023). From Figure 2, it can be deduced that the factors possess sharp curvatures with H_2SO_4 concentration having the most effect on HI yield. Initially, the H_2SO_4 concentration was 2 M. The concentration increased gradually to the center point (3.05 M) until it reached 6 M concentration. Meanwhile, activation temperature and time were held constant. The HI yield increases from 4.77 g to 5.21 g as H_2SO_4 concentration increases from 2 M to the center point (3.05 M; 5.21 g) and further increased to 5.93 g at 6 M. Therefore, acid concentration had the strongest effect on the catalyst yield. The effect of activation temperature (B, ^oC) on HI yield can be deduced from the figure. Increasing the temperature B, from 60 ^oC through the center point (80 ^oC) to 100 ^oC linearly increases the HI yield from 5.38 g to 5.41 g. Furthermore, increasing the activation time from 5 min to 10 min at a constant acid concentration and activation temperature resulted in a gradual increase of catalyst from 4.88 g to 5.22 g (7.5 min). This value later decreased to 4.82 g when activation time was increased to 10 min.

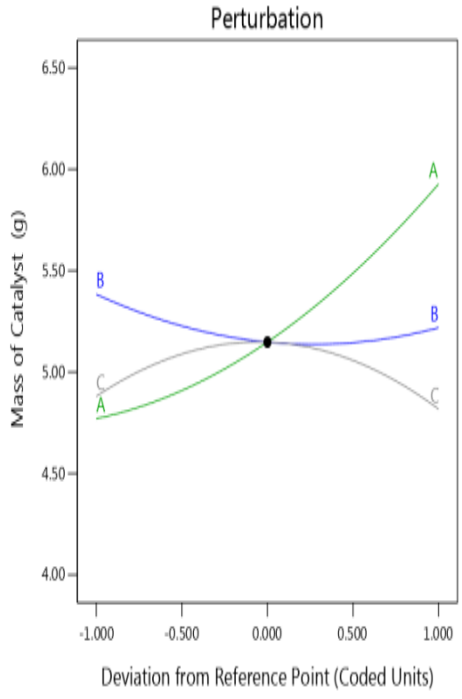


Figure 2: Perturbation plot of HI yield

To determine the optimum values of parameters such as the acid concentration, activation temperature and activation time in HI, BBD of RSM of design expert software v13 was employed. The optimal conditions are shown in the desirability plot Figure 3 and presented in Table 4. Furthermore, the accuracy of the model was validated by activating Itu clay with H_2SO_4 using the optimal process parameters. An optimal HI yield value of 6.16 g was obtained at optimized conditions of 5.95 M H_2SO_4 concentration, 63.43 ^oC activation temperature and 6.61 min activation time. The result of the validation of the optimal conditions for the activation process is depicted in Table 4. From the table, the percentage error of the response was less than 2%. This signifies that the model was adequate in predicting the response.

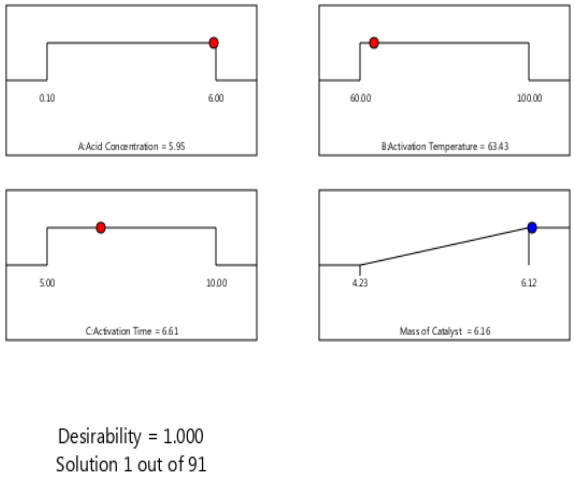


Figure 3: Composite desirability plots for HI

Chemical composition of the samples

The chemical composition of raw (RI) and H_2SO_4 modified Itu clay (HI) in weight percentages (w %) was determined using XRF and presented in Table 5. From the Table, the silica (SiO_2) content of RI and HI samples are 43.01 wt% and 55.87 wt% respectively. These values are similar to those reported by Kgabi *et al*., (2023), Okorie *et al*., (2015), Ahmed *et al*., (2012) and Dewu *et al*.,

(2011) where 2:1 clay such as smectite showed a higher silica content and lower alumina content.

Table 4: Validation of optimal values for HI yield

S/N	Responses (unit)	Values
1	H_2SO_4 concentration (M)	5.95
2	Activation temperature (^oC)	63.43
3	Activation time (min)	6.61
4	Actual catalyst yield (g)	6.16
5	Predicted catalyst yield (g)	6.17
6	% error of yield	0.16

The increase in silica content of HI can be attributed to the presence of quartz which further reveals the sample's crystalline nature. Calcium oxide (CaO) was present in moderate concentrations typical of Ca-bentonite while low concentrations of manganese oxide (MnO) were recorded for both samples. The SiO_2/Al_2O_3 ratio values obtained for RI and HI were 3.20 and 5.48 respectively. A ratio above 2 indicates the presence of a 2:1 clay mineral (Kgabi *et al*., 2023). As such, the clay used in this study can be referred to as montmorillonite. There were high concentrations of Fe_2O_3 in the samples. This explains the brownish colour of the raw and modified clays (Ahmed *et al*., 2012). The Fe_2O_3 concentration may also indicate higher surface acidities and bleaching capacities in the samples (Anumata *et al*., 2021). The RI contains more water and organic matter. This is a reflection of their LOI values; RI (21.20 wt%) and HI (19.19 wt%) respectively.

Comparison of the chemical composition of the catalyst produced with previous investigations

The chemical composition of raw Itu clay (RI) and Itu/H_2SO_4 catalyst (HI) was compared with those of some existing modified clays in literature and presented in Table 6. The major oxides observed in RI and HI are SiO_2, Al_2O_3 and Fe_2O_3. This was also observed in all of the clay samples listed in Table 9. The SiO_2 content of RI is 43.01%.

Table 5: Chemical composition of Raw and Modified Itu clay

Parameters	**Raw Itu Clay (RI) (wt%)**	**Acid Modified Itu Clay (HI) (wt%)**
SiO_2	43.01	55.87
Al_2O_3	13.46	10.20
Fe_2O_3	13.91	9.43
TiO_2	2.67	1.48
CaO	2.95	1.35
P_2O_5	0.01	0.01
K_2O	1.92	0.90
MnO	0.01	0.01
MgO	0.09	0.45
Na_2O	0.08	0.28
LOI	21.20	19.19

This value increased to 55.87% after modification with H_2SO_4. The observed Al_2O_3 content was 13.46% and 10.20% for RI and HI respectively. The decrease in Al_2O_3 content is a result of dealumination that occurs when clay samples are treated with acids. Similar observations were reported by Gandhi *et al*., (2022) and Ahmed *et al*., (2012) when Raw Kachch clay (RK) and Raw Pindiga bentonite (RP) were modified with H_2SO_4, respectively. The SiO_2/Al_2O_3 ratio values obtained for RI and HI were 3.20 and 5.48 respectively. A ratio above 2 indicates the presence of a 2:1 clay mineral (Kgabi *et al*., 2023). This is similar to the values obtained and reported by other researchers that are listed in Table 9. Thus, the clay used in this study can be referred to as montmorillonite. The difference between this study and the previous research is the modeling and optimization of the

Table 6: Comparison of RI and HI with relevant literatures

Material	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**TiO_2**	**CaO**	**P_2O_5**	**K_2O**	**MnO**	**MgO**	**Na2O**	**SiO_2/Al_2O_3**	**Reference**
Raw Itu clay (RI)	43.01	13.46	13.91	2.67	2.95	0.01	1.92	0.01	0.09	0.08	3.20	Current study
Raw Pindiga bentonite (RP)	43.60	14.00	26.54	2.06	2.46	-		0.38			3.11	Ahmed *et al*., (2012)
Raw Kachch clay (RK)	51.38	22.77	17.46	1.581	2.11	-	0.17	0.182	2.30	1.58	2.26	Gandhi *et al*., (2022)
Raw Heidelberg bentonite (RH)	58.19	13.67	2.43	0.16	0.97	0.06	1.03	0.07	2.32	2.34	2.26	Kgabi *et al*., (2023)
Raw Ashaka clay (RA)	48.16	14.86	4.80	0.94	1.16	1.06	1.60	-	2.08	1.66	3.24	Abdullahi *et al*., (2017)
Raw Tango clay (RT)	49.87	14.98	5.12	0.87	1.81	1.01	1.76	-	2.08	1.43	3.33	
Itu/H_2SO_4	55.87	10.20	9.43	1.48	1.35	0.01	0.90	0.01	0.45	0.28	5.48	Current study
RK/H_2SO_4	70.62	17.33	6.91	2.20	0.46	-	0.14	0.01	0.94	0.09	4.08	Gandhi *et al*., (2022)
RP/ H_2SO_4	52.40	11.00	15.34	2.29	1.55			0.07			4.76	Ahmed *et al*., (2012)

modification process and the use of indigenous Itu clay.

CONCLUSION

In the present study, raw Itu clay was modified with H2SO4. The modification process was optimized using BBD of RSM in DOE (v13) and the chemical composition of the samples was studied using XRF analysis. The following deductions were drawn after the research:

i. Run 7 gave the highest HI yield of 6.12 g when H2SO4 concentration, activation temperature and activation time of 6.0 M, 60 oC, and 7.5 mins respectively were considered for the activation of Itu clay. The lowest HI yield was recorded at run 17 (4.23 g) using 0.1 M H2SO4

concentration, 80 oC activation temperature and 5 mins activation time.

ii. The XRF analysis of both RI and HI shows that the clay minerals are calcium montmorillonite with dominating SiO_2:Al_2O_3:CaO (43.01:13.46:2.95 for RI and 55.87:10.20:1.35 for HI) in both RI and HI.

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DISCLOSURE OF ANY CONFLICT OF INTEREST

The authors declared that there is no conflict of interest.

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