Synthesis and Characterization of Amine Impregnated Zeolite from Enugu Clay for CO_2 Adsorption

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ABSTRACT

Synthesis and characterization of zeolite from Enugu kaolinite clay was investigated. Clay from Thinkers corner, Emene Enugu was converted to zeolite and the zeolite was subsequently impregnated with monoethanolamine (MEA) using appropriate methods. The raw clay, zeolite produced and the amine impregnated zeolite were then characterized using x-ray fluorescence (XRF), x-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), and scanning electron Microscopy (SEM) analysis. Also, post-combustion adsorption of CO_2 using the amine-impregnated zeolite was carried out to investigate the effectiveness of the adsorbent for the capture of carbondioxide. The effect of temperature on the adsorption capacity of the adsorbent was investigated. Results of the XRF show that the amount of SiO_2-Al_2O_3 present in the raw clay gave the ratio of SiO_2/Al_2O_3 as 1.57, which is greater than 1, invariably implying that Thinkers Corner clay can be used for zeolite production. For the XRD analysis, the intensity of the diffraction peak did not vary after impregnation with amine, implying that the pore structure order was not affected by the amine. The IR spectra and the observed functional groups present in the amine impregnated zeolite confirmed the integration of amine inside the channels of the zeolite, while for the SEM analysis, the morphology of the zeolite synthesized from kaolinite clay are found to be similar to that of zeolite prepared from other sources. Adsorption studies showed that adsorption capacity of the adsorbents decreased with an increase in temperature. Therefore, Enugu Thinkers Corner clay has proven to be effectively converted to zeolite and utilized for CO_2 adsorption.

Keyword: *Clay, Kaolinite, Zeolite, Amine, Adsorption.*

1. Introduction

Globally, serious attention is been given to the capture of CO_2. Carbon capture and storage (CCS) is a promising technology for alleviating climate change and meeting CO_2 emission reduction targets [1]. Anthropogenic CO_2 emitted into the atmosphere must be reduced to the barest minimum in order to mitigate the unrestrained release of greenhouse gases into the atmosphere [2][3]. The Capture of CO_2 from flue gas emitted from power plants by post combustion capture is very useful in addressing the problem of its emission into the atmosphere. Post-combustion CO_2 capture using adsorption technology guarantees that the adsorbent is in direct contact with the CO_2 gas in an adsorption column. Recently, several materials like zeolites, chitosan, activated carbon, has been synthesized from varying sources for CO_2 capture. Zeolites are micro-porous alumina-silicate minerals used for numerous commercial and domestic applications. These include applications in petroleum and petrochemical industries as catalysts, adsorbents and ion exchangers, nuclear industries for nuclear reprocessing, heating, and refrigeration, detergents, construction as material additives, medicine, agriculture as a soil treatment, gemstones, as ion-exchange beds in domestic and commercial water purification and softening [4]. This study concentrated on synthesizing zeolite from Enugu clay and examining the adsorption performance of the prepared zeolite and amine impregnated zeolite as an adsorbent during post combustion CO_2 capture.

## 2. Materials and Methods

2.1 Material

Raw clay was sourced from Thinkers Corner in Enugu North L.G.A of Enugu state. Analar grade reagents were used for the production and for impregnating the zeolite with amine.

2.2 METHODS

2.2.1 Production of Zeolite from Clay
Procedure for zeolite powder preparation

The clay was first converted to metakaolin using the method as proposed by [5], by exposing to high temperature of about 550°C for about 1.5 hours where its structure was destroyed and any undesired volatile matter was removed according to the following reaction equation:

$$2Al_2Si_2O_5(OH)_4 \longrightarrow 2Al_2Si_2O_7 + 4H_2O$$
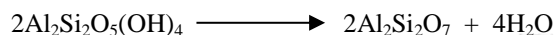
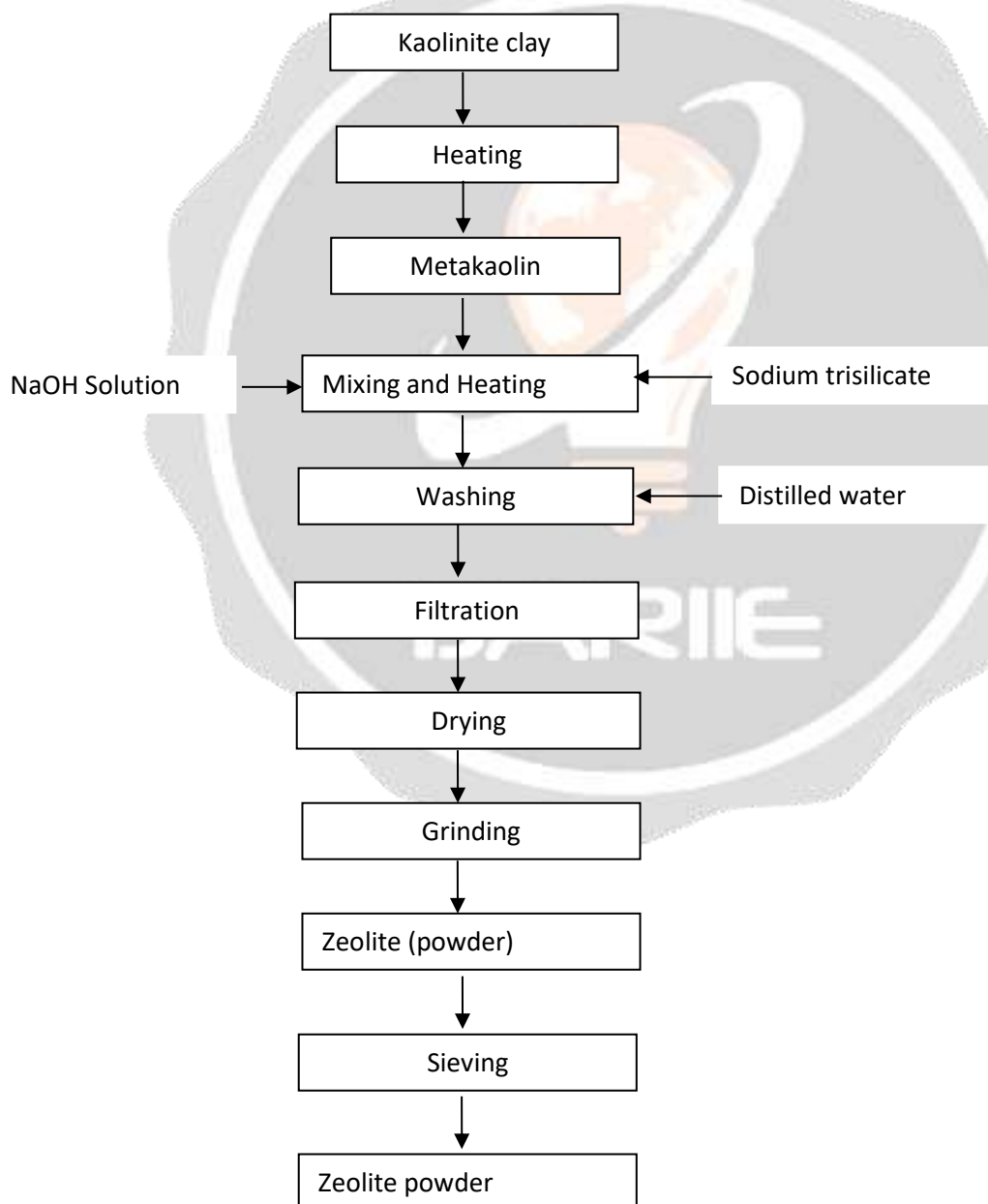The flow chart for the process is given below:

Figure 1: The Schematic diagram for the preparation of zeolite X powder.

2.2.2 Amine Impregnation of the Zeolite

Amine impregnation of the zeolite using monoethanolamine (MEA) was done using the method as described by [6].

2.2.3. Characterization of the prepared zeolite and amine Impregnated Zeolite

2.2.3.1 X-ray Fluorescence (XRF)

X-ray Fluorescence (XRF) spectroscopy was used to carry out a qualitative and quantitative elemental analysis of the clay sample and the produced zeolite.

2.2.3.2 X-ray diffraction (XRD)

The X-ray diffraction (XRD) patterns of the clay sample, zeolite X and amine impregnated zeolite X were done using CuKα (λ=1.54Å) radiation. X-ray diffractometer (XRD) provides the most comprehensive description of members of zeolite groups.

2.2.3.3 Scanning Electron Microscopy

The Scanning Electron Microscopy (SEM) was performed to examine the physical structure change of the adsorbents using SEM model Phenom ProX by PhenomWorld Einhoven, The Netherlands. Samples were placed on double adhesive which was on a sample stub, was coated sputter coater by quorum technologies model Q150R, with 5nm of gold. Thereafter, it was taken to the chamber of SEM machine where it was viewed via NaVcaM for focusing and little adjustment, it was then transferred to SEM mode, was focused and brightness contrasting was automatically adjusted to give the sample's morphology at different magnifications.

2.2.3.4 Fourier Transform Infrared Spectral Analysis

The FT-IR spectra of the raw clay, prepared zeolite and amine-impregnated zeolite were recorded on a Shimatzu Fourier Transform Infrared Spectrometer (FT-IR). Scans were collected for each measurement over the spectral range of 4000-400cm^{-1} with a resolution of 4cm^{-1}. All spectra were presented without baseline correction or normalization.

2.2.3.5 Adsorption CO_2

Adsorption of CO_2 was carried out using established methods. The dynamic adsorption capacity of the adsorbents (Qads) was calculated according equation (1),

$$Q_{ads} = \frac{FC_o t_q}{M} \tag{1}$$

where **F** (mol/min) is the total molar flow of feed gas, **Co** is the CO_2 concentration of the inlet stream, **M** (g) is the mass of the solid adsorbent loaded in the column, and **tq** (min) is the stoichiometric time which was determined from the breakthrough curve according to Equation (2) [7];

$$t_q = \int_0^\infty \left(1 - \frac{C_A}{C_o}\right) dt \tag{2}$$

where **C$_o$** and **C$_A$** are the CO_2 concentrations of inflow and outflow gas stream of the column.

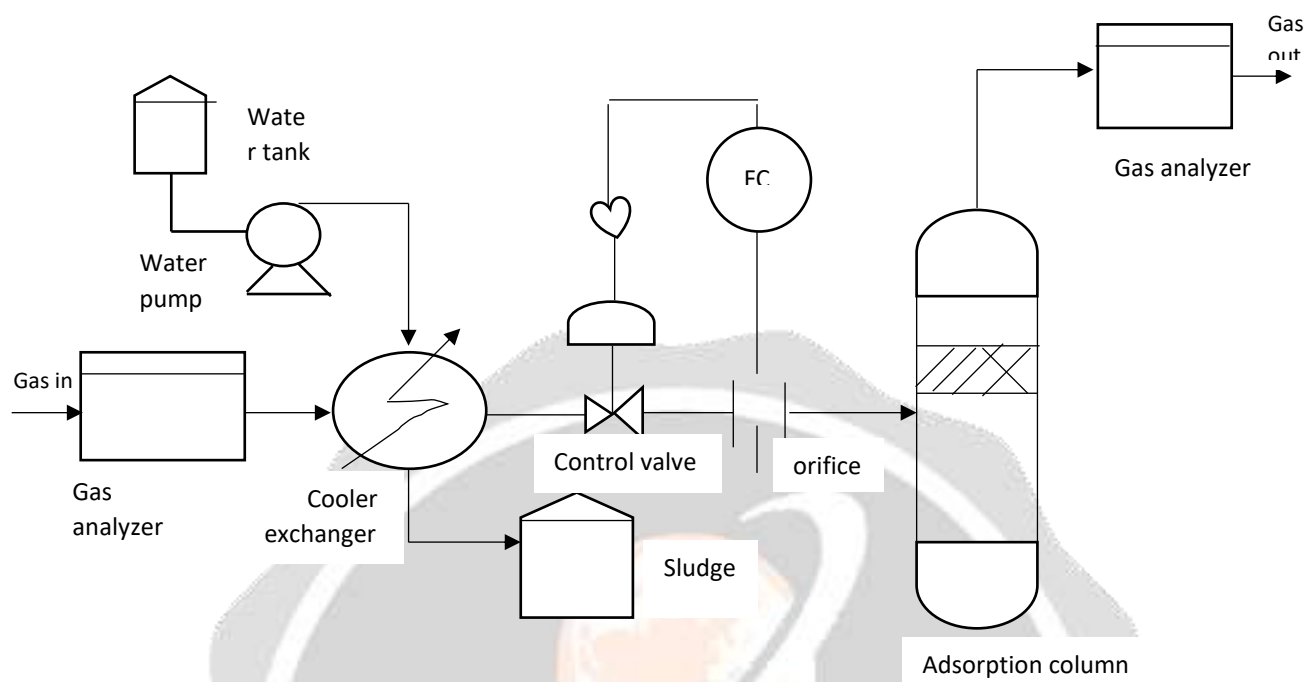The flow diagram of the process is presented below:

Figure 2: Flow diagram of CO_2 Adsorption on the zeolite

3.   Results and Discussion

3.1 Characterization of the raw clay, zeolite and amine impregnated zeolite.

3.1.1 Chemical Analysis by X-Ray Fluorescence (XRF)

Table 1 show the chemical analysis conducted on the raw clay, zeolite and amine impregnated zeolite using X-Ray Fluorescence (XRF). The results show that Enugu North kaolin is rich in oxides of potassium, iron, titanium and magnesium. The amount of SiO_2-Al_2O_3 present in the raw clay gave a ratio of SiO_2/Al_2O_3 as 1.57, which is greater than 1. This is in accordance with the specification for clays that can be used for zeolite synthesis given by [8]. This conformity to Breck's specification invariably implies that Thinkers Corner clay can be used for zeolite formation. Notably also, the value of SiO_2 reduced from 53.789% to 49.553% due to the removal of free silica (quartz) from the raw kaolin. Table 1 also indicated that Enugu North clay is ferric in nature due to its high content of iron oxide as compared with that of potassium.

Table 1: Chemical Composition of the raw clay, prepared zeolite and amine impregnated zeolite

Chemical Constituent	Raw Clay (wt %)	Zeolite (wt %)	Amine impregnated zeolite (wt %)
SiO_2	51.860	49.553	47.298
Al_2O_3	33.010	23.130	22.827
Na_2O	0.051	13.965	--
CaO	0.1148	0.662	0.902
P_2O_5	0.334	0.000	0.000
MgO	0.508	0.234	0.000
TiO_2	2.139	1.566	2.823
K_2O	0.337	0.172	0.918
SO_3	0.327	0.221	0.115

Cl	0.017	0.035	--
SrO	0.021	0.017	--
Fe_2O_3	14.026	3.18	23.213
Cr_2O_3	0.020	0.022	0.077
ZnO	0.019	0.007	0.039
Mn_2O_3	0.045	0.014	--

3.1.2 X ray Diffraction

Figures 3 to 5 below shows the XRD spectra of the raw clay, zeolite produced and amine impregnated zeolite, respectively. X-Ray diffraction was used to study the crystalline and framework structure of the materials. As can be seen, the clay's consistent diffraction pattern was modified by the amine. The sample of the diffraction peaks located at $2\theta = 12^0$, 17^0, 22^0 and 26^0 associated with the crystal structure of zeolite Y can be clearly observed in figures 4 and 5. The intensity of the diffraction peak did not vary after impregnation with amine, implying that the pore structure order was not affected by the amine. These changes were caused by the pores being filled in the clay channels and the amine coating on the outer surface of the clay crystals. These results are consistent with [9].
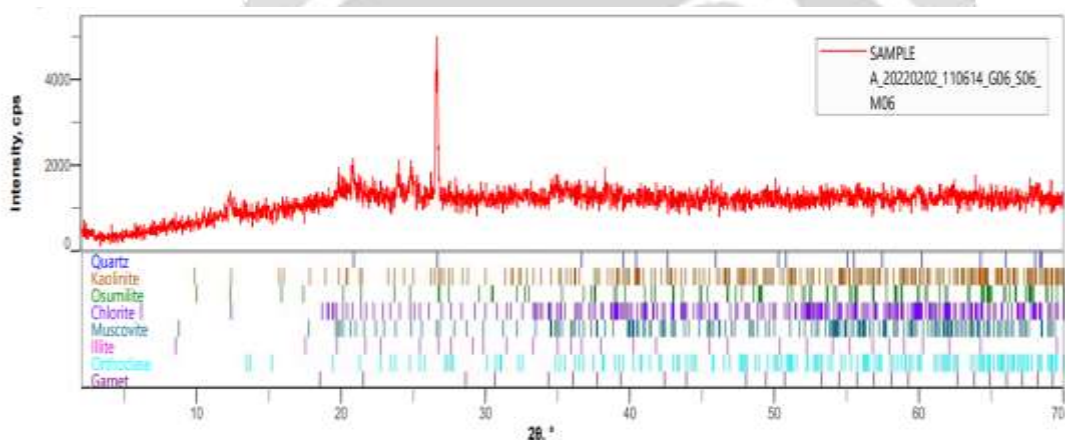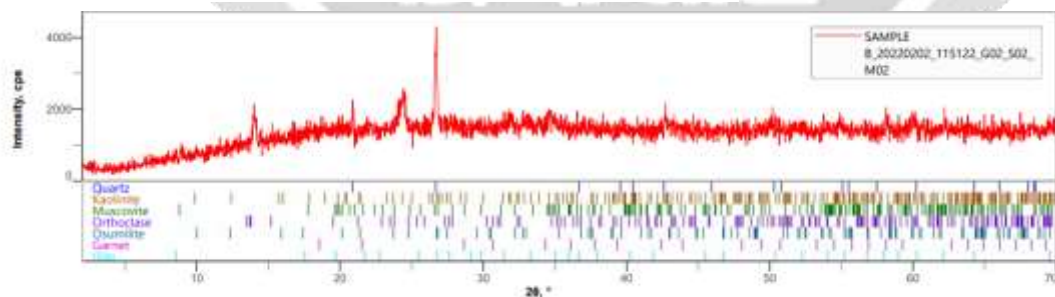

Figure 3: X-ray Diffractogram of the raw clay

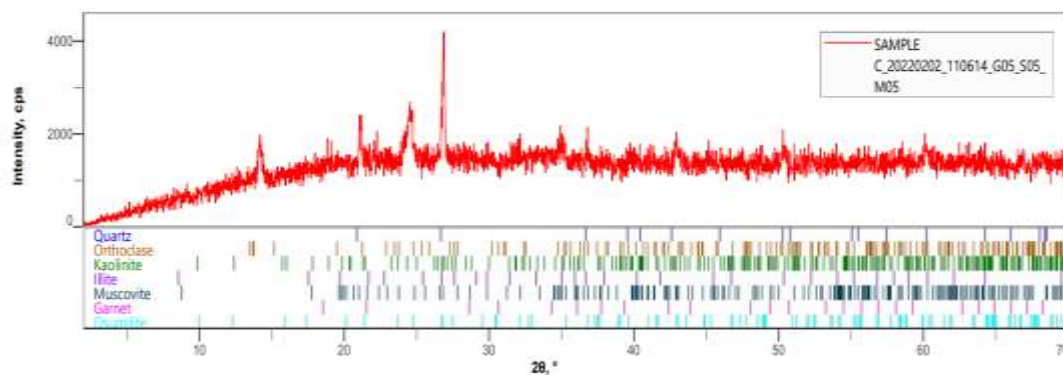**Figure 4**: X-ray Diffractogram of the synthesized zeolite

Figure 5: X-ray Diffractogram of amine-impregnated zeolite

3.1.3: Scanning Electron Microscopic (SEM) Analysis

The result of the SEM analysis of amine impregnated zeolite presented in figure 6 (a, b) Confirmed that there was successful amine impregnation. The zeolite, after being modified with MEA, still has many available pores. Notably also, the morphology of the zeolite synthesized from kaolinite clay (figure 6), are found to be similar to that of zeolite prepared from other sources. These SEM images further confirm the successful synthesis of zeolite from kaolin clay.
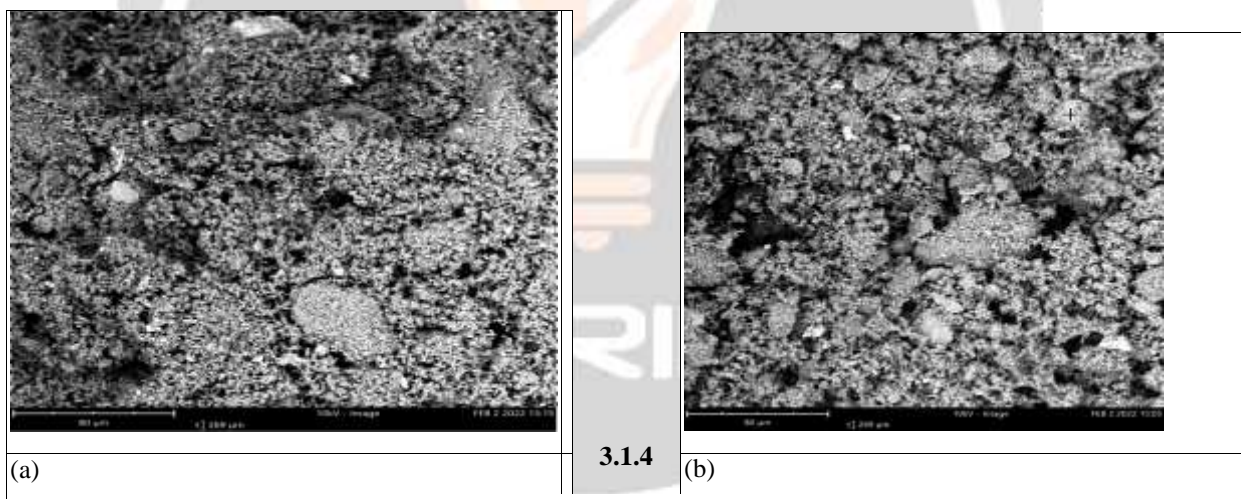

(a)

3.1.4

(b)

Figure 6: SEM Micrograph of (a) zeolite produced from kaolinite clay (b) amine impregnated zeolite

3.1.4   Fourier Transform Infra-Red Spectroscopy

Figures 7 and 8 shows the FTIR spectrograph of zeolite from kaolinite clay and amine impregnated zeolite, respectively. The IR spectra was used to study nitrogen surface functional groups showing alteration in amine-impregnated zeolite. The IR spectra of the amine-impregnated zeolite was different from pure amine because it exhibited several peaks. After the modification of the zeolite, the adsorption peaks at 1453-1654cm^{-1} and 2765-2881cm^{-1} were associated with the stretching vibration of -NH$_2$. The peak at 1640cm^{-1} corresponds to -NH$_3$ +O-Si/-NH$_2$ + O-Si. Hence, the IR spectra of amine impregnated zeolite confirmed the incorporation of amine inside the networks of the zeolite.
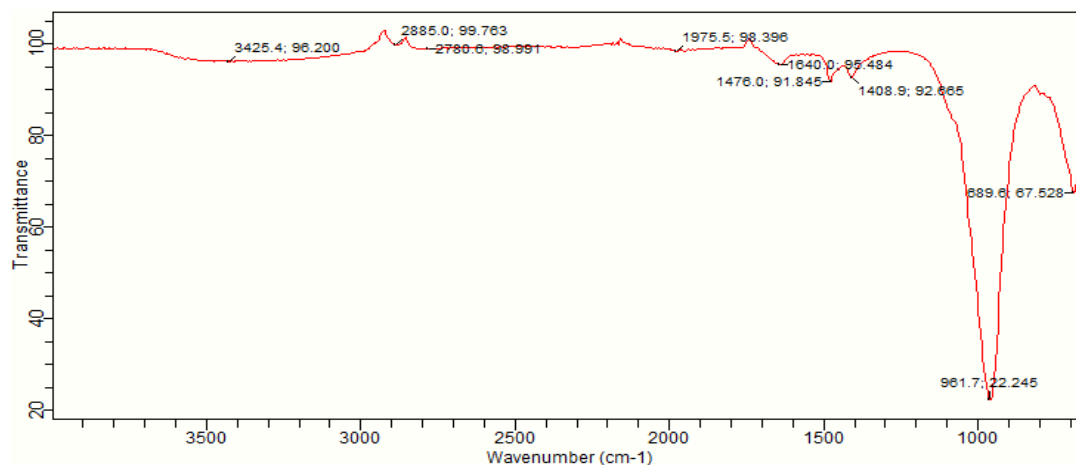
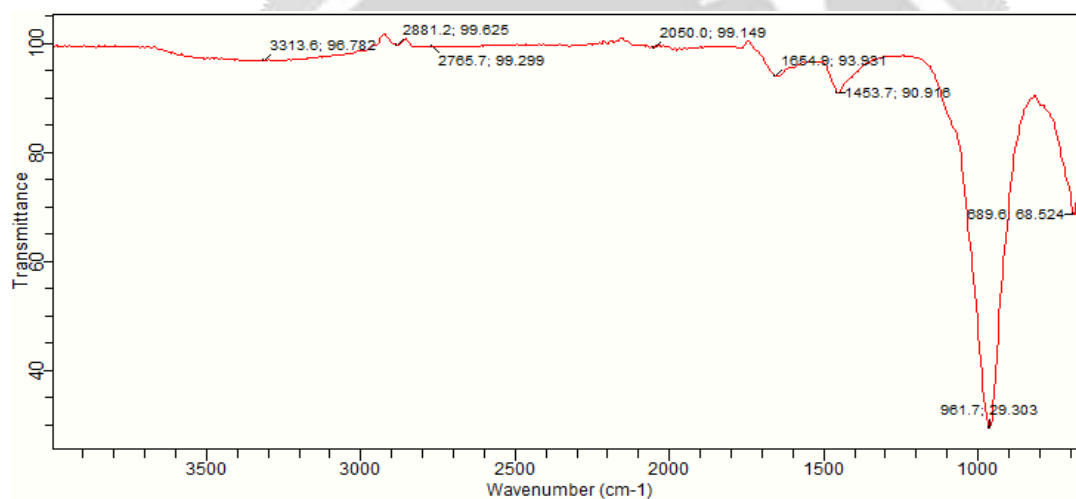**Figure 7:** FTIR spectrograph of zeolite synthesized from kaolinite clay

Figure 8: FTIR spectrograph of amine impregnated zeolite.

3.1.5   Result of the Adsorption studies

Effect of Temperature on the Adsorption Capacity of the Sorbents

Figure 9 illustrates the effect of temperature on the adsorption capacity of the as-prepared zeolite and amine impregnated zeolite (AIZ). As can be clearly seen, adsorption capacity decreased as temperature increases from 40^0C to 60^0C for the zeolite prepared. Once the temperature is raised, more internal energy is provided for the CO_2 molecules in the gas phase. Similar result was obtained with AIZ at 40^0C and 45^0C. However, adsorption capacity increased as temperature increased from 50^0C to 60^0C for AIZ. This is due to the onset of chemisorption as elevated temperatures as a result of the incorporation of amine in the zeolite. Generally, adsorption capacity of the amine impregnated zeolites was higher than the unmodified zeolite. This is due to the high hydrophilic nature of unmodified zeolite which causes its adsorption capacity to decline greatly in the presence of water in the flue gas. It has also been reported that there is a detrimental effect of water on CO_2 adsorption, because it gets preferentially adsorbed from the gas mixture [10][11]. Small amounts of water could significantly decrease the CO_2 adsorption capacity, because it gets competitively adsorbed on the zeolite surface and blocks the access for CO_2 [10]. In another study, CO_2 and water vapor adsorption on zeolite 13X has also indicated that the adsorption of CO_2 is considerably inhibited by H_2O [11].

This decrease in adsorption capacity as temperature rises is also an indication of the existence of physical adsorption between the zeolite and CO_2 molecules. According to [12], physisorption process involves high surface adsorption

energy and molecule diffusion at elevated temperatures, which results in instability of the adsorbed gas on the surface of the zeolite and consequently, desorption process will occur.
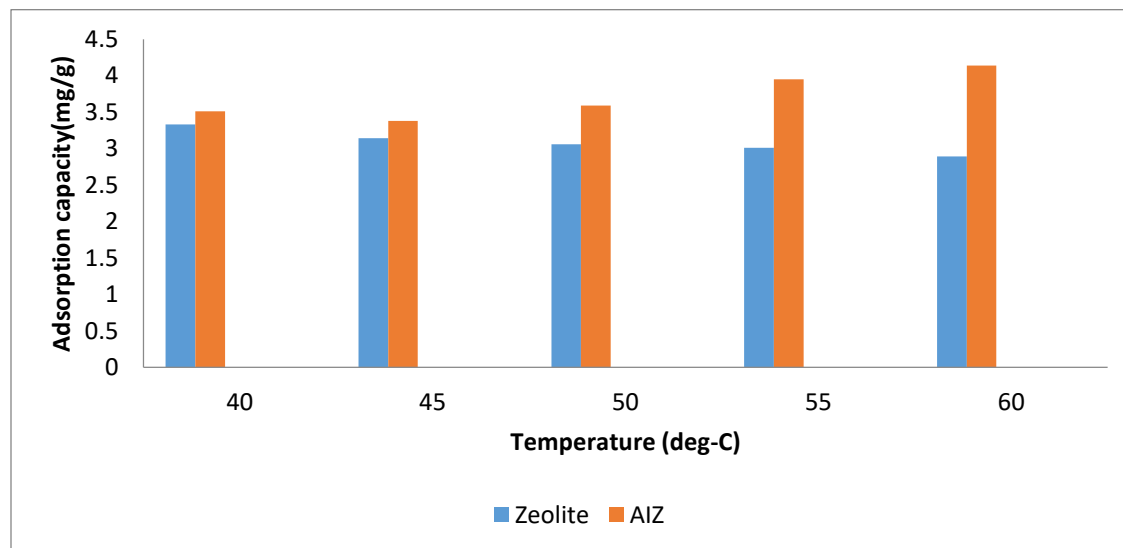

Figure 9: Effect of temperature on the adsorption capacity of the prepared zeolite and amine impregnated zeolite

4.   Conclusion

The possibility of synthesizing zeolite from Enugu Thinkers Corner Clay and impregnating it with amine was investigated. The adsorption was carried out in a purpose-built adsorption column. The CO_2 sorption capacity was found to be dependent on variables such as temperature, pressure and time. Amine-impregnation of zeolites has proved to be a successful method of obtaining adsorbents with high adsorption capacities under mild reaction conditions. Successful amine-impregnation was also proven by the FT-IR spectra of the amine-impregnated zeolite X. It is therefore possible for highly substituted aluminosilicates to be gotten under mild conditions.

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