

CHARACTERIZATION OF MIXED AMINE FUNCTIONALIZED CARBON NANOTUBE FROM NIGERIAN SUB BITUMINOUS COAL

ABSTRACT

It is a known fact that the behaviour and performance of any sorbent material such as functionalized CNTs is dependent on its inherent or modified micro structural property. Carbon nanotubes (CNTs) adsorbent was produced and characterized from Nigerian Sub-bituminous coal obtained in Udi, Enugu state. A mixture of two amines (Mono ethanol Amine (MEA) and Tri ethanol amine (TEA)) of different proportion was immobilized into the pores of the Carbon nanotube by wet impregnation method. The prepared adsorbent was characterized before and after amine modification with X-ray Diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), Brunauer-Emmett-Teller (BET), Transition Electron Microspore (TEM) Scanned Electron Microscope (SEM), and thermogravimetric analysis (TGA) technique. Results from the XRD analysis shows that there is a drastic decrease in the height of the peaks at $2\theta = 27$, which correspond to 100 for CNT-MEA x-TEA y composites. This can be attributed to the filling of the pores by the amine in the Carbon nanotube. Similarly, there is a dominating appearance of amine functional group at different peaks of the FTIR spectrum. Furthermore, the internal morphology of the adsorbent as revealed by the TEM image shows that the dominant product is a twisted multi-walled CNT, which is partly filled with metal-like particles from the catalyst. The SEM image depicts a clear variation in the surface chemistry of the various CNTs initiated by differences in the mixed amine formulation. Finally, observation from the BET analysis shows a decrease in the surface area, total pore volume and pore size of the CNTs adsorbent after it was modified with Amine. All of these result shows that combination of the two different amines, can further improve the adsorption capacity of functionalized CNT sorbents for CO₂ adsorption, in mitigating global warming.

Key Word: Coal gas, Carbon capture, Mixed amines, Carbon Nanotube, adsorbent.

INTRODUCTION

Greenhouse gases (GHG) emission especially carbon dioxide (CO₂) is the main contributor to global climate change, the world is facing today. Anthropogenic emission stemming from predominantly existing point sources, such as fossil-fuel power plant and blast furnace, has caused the sharp increase in CO₂ concentration in the earth's atmosphere (Rochelle, 2009). Modern climate

scientists project that the accumulation of greenhouse gases in the atmosphere will contribute to an increase in the earth's surface air temperature, thereby leading to global warming (Sun *et al.*, 2011). Global warming is caused by enhancement of the greenhouse effect, a phenomenon that is due to the thick layer of mixed gases which surrounds the earth, trapping some of the solar radiation. The gases present in the atmosphere convert radiation energy to thermal energy by absorption (Clausse *et al.*, 2011). Carbon dioxide from fossil fuel-fired combustion can be removed from flue gas through pre and post combustion, oxy-fuel and chemical-looping combustion (Metz *et al.*, 2005). In recent years, Carbon Capture and Storage (Sequestration) CCS, has been proposed as a potential method to the continual use of fossil fuel for power generation, whilst preventing emission of CO₂ from reaching the atmosphere (Zang *et al.*, 2008, 2009). This achieved through various means, such as the use of Amines in CO₂ capture from flue gases.

Amines compound have a high affinity for CO₂ and are well known for their reversible reaction with carbon dioxide, which makes them ideal for carbon dioxide capture from several streams, including flue gas. The reaction of carbon dioxide with amine occurs via a Zwitterion mechanism to form Carbamates (Chen *et al.*, 2009). The high heat of formation associated with carbamate formation leads to considerable energy penalty for regeneration. Amine scrubbing using aqueous amine is currently the most mature technology for CO₂ capture through absorption. However, the approach has some challenges, such as high heat of regeneration, toxicity, corrosiveness of equipment during the solvent regeneration and solvent degradation. (Aroonwilas and Veawab, 2004; Filburn *et al.*, 2005). Solid amine sorbents are an alternative to overcoming the problems associated with absorption. Solid amine adsorbents have the advantage of high adsorption capacity, low heat for regeneration, low corrosion of adsorption devices and a rapid adsorption rate.

Amine functionalized solid sorbents can be prepared by covalent grafting of amines on porous surface using silane coupling agents or wet impregnation of liquid organic amines into porous supports (Wang *et al.*, 2015, Samanta *et al.*, 2012).

Carbon nanotube (CNT): Carbon nanotubes (CNTs) have gained popularity as potential gas carriers due to their high surface area, enhanced porosity, superior thermal conductivity, and mechanical, and electrical properties (Chen *et al.*, 2000; Cinke *et al.*, 2003). CNTs are categorized as single-walled nanotubes (SWNTs), multi-walled nanotubes (MWNTs) and branched walled nanotube with single and multiple rolled layers of graphene respectively. However, due to the hydrophobic and inert nature of the surface of CNTs, modification of the surface is necessary in order to improve the interaction of

CNTs and foreign molecules (Hsu *et al.*, 2010). The predominant methods currently used for the synthesis of CNTs are arc discharge, laser ablation and chemical vapor deposition (CVD). The functionalization of CNTs includes covalent functionalization and non-covalent functionalization. In the covalent functionalization the chemical reaction forms bonds on the nanotube sidewalls, resulting sometimes in a change in structure (Cinke *et al.*, 2003). The non-covalent dispersion of CNTs in a solution allows preservation of their aromatic structure and thus their electronic characteristics (Bilalis *et al.*, 2014).

2. EXPERIMENT

2.1 Materials

Cobalt nitrate $\text{Co}(\text{NO}_3)_2$ Analytical grade, Sigma- Aldrich), Aluminum oxide ($\gamma\text{-Al}_2\text{O}_3$) Analytical grade, Sigma- Aldrich, $\text{Fe}(\text{NO}_3)_3$ Iron nitrate. Analytical grade, Sigma- Aldrich Nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) HNO_3 Analytical grade, Sigma- Aldrich. Coal gas, Mono Ethanol Amine (MEA Analytical grade, Sigma- Aldrich), Tri Ethanol Amine (TEA Analytical grade, Sigma- Aldrich.) and Anhydrous Ethanol (EtOH 98 vol.%) were purchased from United surgical Co. Ltd. Deionized water was used in all experiment. Coal Gas. 99 vol.% CO_2 gas for adsorption was purchased from Nigerian Bottling Company. Nitrogen N_2 gas for simulating gas adsorption was purchased from Air Liquid Nigeria.

2.2 Preparation

2.2.2 Preparation of catalyst in a horizontal CVD reactor.

The preparation of catalyst for the synthesis of CNT was adopted from the works of Aliyu *et al.*, (2017). For each catalyst, 6g of Aluminium hydroxide, 2.0 g of $\text{Co}(\text{NO}_3)_2$ plus 3.0g $\text{Fe}(\text{NO}_3)_2$ from Panlac Plc, was dissolved in 300cm^3 of distilled water. The solution was then added to 15 g $\gamma\text{-Al}_2\text{O}_3$, stirred and aged for 90 minutes, after which it was dried in an oven at a temperature of 120°C for 12 hours. This was then calcined at a temperature range of 300°C - 400°C , to give Fe-Co catalyst on $\gamma\text{-Al}_2\text{O}_3$.

2.2.3 Synthesis of Carbon Nanotube

The synthesis of carbon nanotube is similar to the method applied in the works of Ahmed Aliyu et al, (2017). The carbon source gas is the coal gas at a flowrate of 150 mL/min, while the carrier gas (Nitrogen gas) is of 98% purity at a flow rate of 230mL/min. Pyrolysis temperature of 800°C - 900°C was used for the synthesis of carbon nanotube (Moothi et al., 2015) . The catalyst used for the synthesis is the prepared Fe-Co on γ -Al₂O₃ precursor. A reaction time of 1 hour was observed. For each run, 100 mg of Fe-Co/ γ -Al₂O₃ catalyst was placed inside the quartz boat at the middle of quartz tube. The furnace temperature was ramped to 900°C at a heating rate of 20°C/minute in flowing nitrogen. Once the temperature reaches 900°C, coal gas was introduced at a flow rate of 60 mL/min into the horizontal CVD reactor. The experiment lasted for 60 minutes, after which, the furnace was allowed cool down to room temperature. The deposited carbon nanotube was collected and further purified in nitric acid of 30% wt. It was then washed in distilled water until a pH of 7.0 is achieved. The CNT was dried in an oven at 120°C for 12 hours. Amine functionalization of the carbon nanotube was done by immobilizing a mixture of MEA and TEA in different proportion in the carbon nanotube by means of wet impregnation technique using Ethanol, (Plaza et al., 2010). The MEA and TEA are in the ratio of 25vol.% MEA 75vol.% TEA; 50 vol.% MEA 50vol.% TEA and 75vol.% MEA 25vol.% TEA respectively.

2.3 Characterization of Sample

The carbon nanotube and the amine modified carbon nanotube was characterized using Brunauer-Emmett-Teller (BET) model to analyze the specific surface area and pore volume for adsorbent in relative pressure (P/P_0) range of 0.05-0.03. Thermal stability of adsorbent was carried out using thermalgravimetric analysis (TGA, NETZSCH TG Model: STA449F3). The test was performed using pure Nitrogen at a flow rate of 50mL/min. For each run, 20mg of sample was ground and placed in a platinum pan. The temperature was increased from 25°C to 650°C at a heating rate of 10°C/min. X-ray Diffraction (XRD) was used to determine the crystallinity index of the adsorbent. The structures and fingerprint characterization of blank and modified carbon nanotube were derived from XRD. Rigaku D/max 2500 PC X-ray diffractometer with Cu K α radiation ($\lambda=0.154\text{nm}$) in angle range of $2\theta = 10-70^\circ$. Coal gas composition was determined using GCMS. Scanning Electron Microscope (SEM) was used to determine the surface morphology of the carbon nanotube. Transition Electron Microscope (TEM) was used to study the internal morphology of the Carbon nanotube. Thermogravimetric Analyzer (TGA) was also used to carry out the adsorption-desorption test of the adsorbents. Fourier Transform Infrared Spectroscopy (FTIR) was used to determine the functional group present in the samples.

3. RESULT AND DISCUSSION

3.1 XRD analysis of CNTs adsorbents.

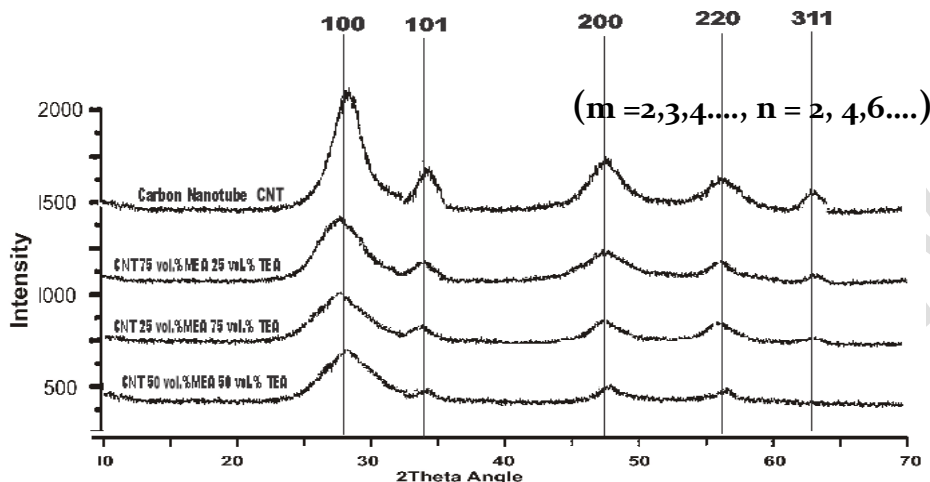


Figure 1: XRD Analysis result of adsorbent

The crystallinity of the carbon nanotube and amine modified Carbon nanotube was carried out using a X-ray Diffractometer. From Figure 2, the XRD patterns of Carbon nanotube shows a sharp peak at $2\theta = 27$, which correspond to 100, $2\theta = 39$, which correspond to 101, $2\theta = 48$, which correspond to 200, $2\theta = 56$, which correspond to 220 and $2\theta = 64$, which correspond to 311 respectively. Following the amine functionalization of the Carbon nanotube, there is a drastic decrease in the height of the peaks at $2\theta = 27$, which correspond to 100 for CNT-MEA x-TEA y composites. The decrease in the peaks can be attributed to the filling of the pores by the amine in the Carbon nanotube (Pevida et al., 2008). This indicates that the amines were successfully impregnated unto the carbon nanotube.

3.2 Functional Group of the CNTs Sorbent

The functional group of the pure CNTs adsorbent and functionalized adsorbent is presented in the FTIR spectra of Figure 2.

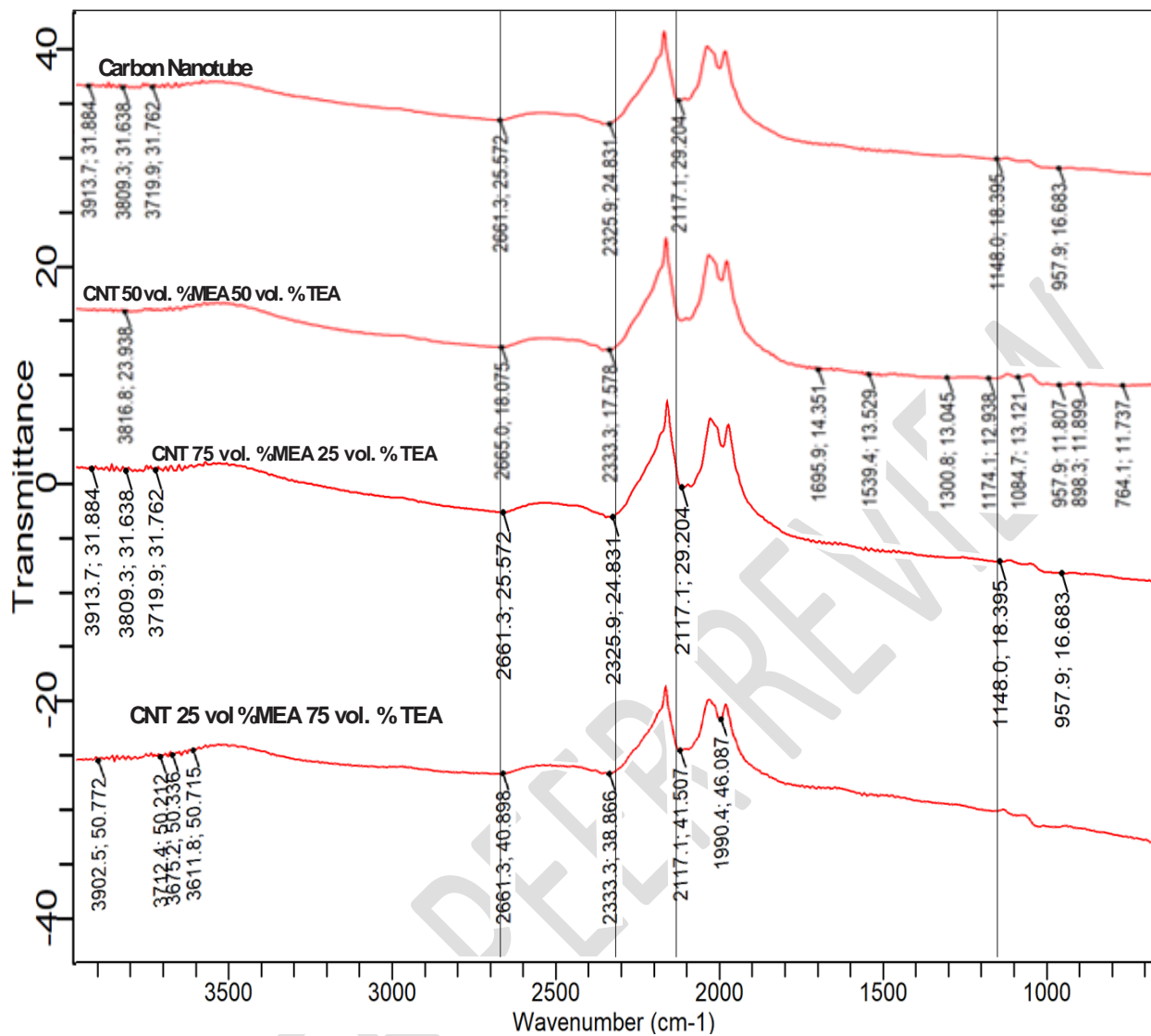


Figure 2: FTIR Analysis of the adsorbents

Table 1: FTIR Spectra of sorbent

Wavenumber (cm ⁻¹)	Intensity	Class	Assignment
764.1	11.737	Aromatics	C-H out of plane
898.3	11.89	Amine	NH ₂
957.9	16.68	Carboxylic acids	RCOOH OH bend
1084.7	13.121	Amine	C-N Stretch
1148.0	18.395	Ethers	C-O Stretch
1174.1	12.938	Misc.	S=O Sulfonxy chloride
1300.8	13.045	Amine	Ar-N stretch
1539.4	13.529	Amine	NH out of plane

1695.9	14.351	Amine	C=O Stretch
1990.4	46.087	Misc.	R-N=C
2117.1	41.507	Misc.	Si-silane OH
2333.3	38.866	Misc.	Si-silane OH
2325.9	24.831	Alkane	-CH ₂ -
2661.3	40.898	Amine	C-N Stretch
2665.0	18.075	Amine	NH stretch
3611.8	50.715	Alcohol	O-H Stretch
3816.8	23.938	Misc.	Si-OH
3902.5	50.772	Misc.	Si-OH

3.3 Transition Electron Microscope (TEM) of Carbon Nanotube.

The Image of the produced Carbon Nanotube was analysed using a Transition Electron Microscope.

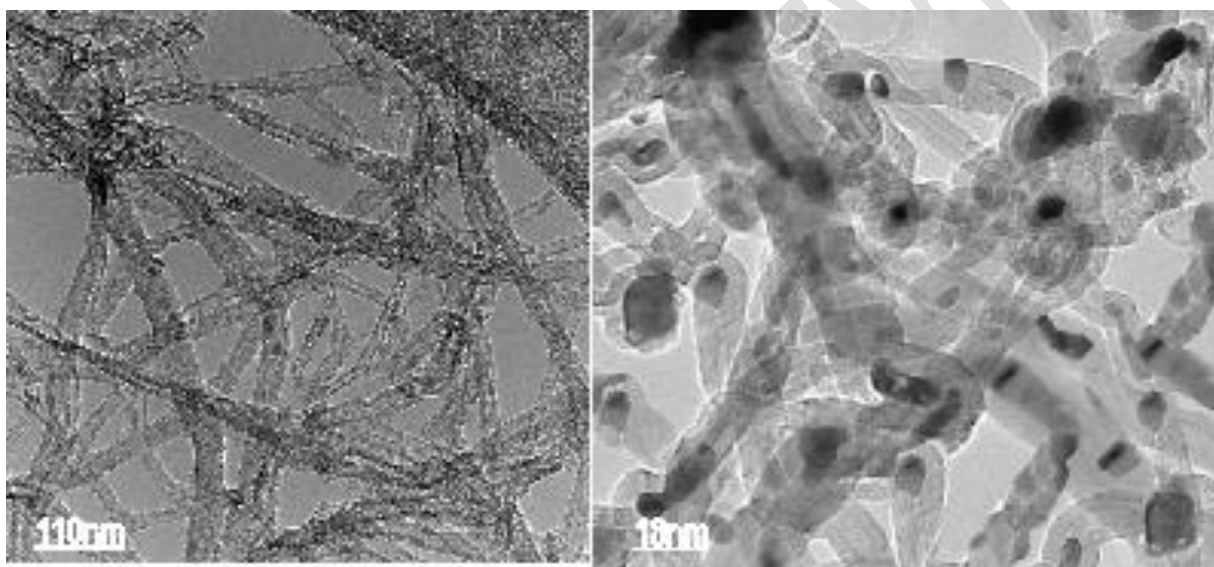


Figure 3: TEM Image of Carbon Nanotube (CNT)

Figure 3 which present the internal morphology of adsorbent shows that the dominant product is a twisted multiwalled CNTs that are partly filled with metal-like particles. These are the catalyst particles as seen in the image. The outer diameter of the tube varies in range of 30 – 50nm.

The result indicates that CNTs filled catalyst can be made in large quantity with coal gas as carbon source. A comparison of CNTs from coal gas and the ones produced from CH₄ or C₂H₄ gas shows that the quality of CNT from coal gas is higher than those from pure CH₄, CO or C₂H₄. This according to literature (Kumurim and Adndo V., 2010) result strongly suggest that the complex composition of coal gas is beneficial to the production of high quality CNTs. It is reasonable to assume that the carbon containing species in the coal-gas directly get involved in the formation and growth of CNTs structures

as the precursors of active basic structure unit, while non-carbon gases may play a role in the formation of filled nanostructures through a kind of synergic effect.

3.4 Surface Morphology of the CNTs Sorbent

The figure below presents the surface chemistry of the pure and differentiated CNTs.

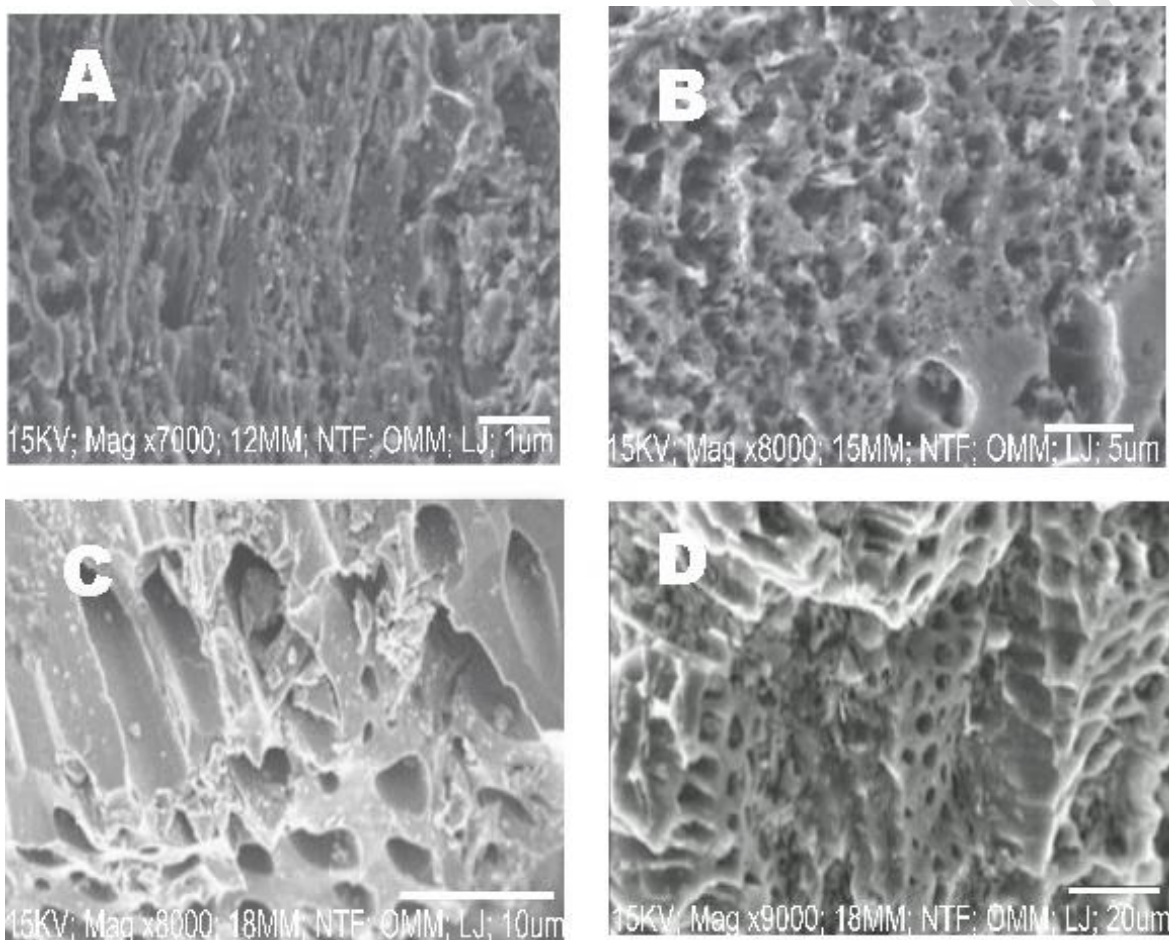


Figure 4: SEM Image of CNT sorbent

Figure 4 shows the surface geometry/structure of CNTs. The pores structure and distributions of the Unmodified CNTs and Modified CNTs. Picture B,C and D depicts the mixed amine modified CNTs.

3.5 BET analysis of the CNTs Sorbent

Table 2: BET Analysis Showing Surface area, Pore size and Pore volume of Sorbent

Sample ID	Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Pore Size (nm)
Carbon Nanotube CNT	946.53	1.8315	18.61
CNT 25% MEA 75% TEA	607.89	0.5207	9.29
CNT 50% MEA 50% TEA	589.72	0.0612	10.62
CNT 75% MEA 25% TEA	512.39	0.7003	8.94

Table 2 shows the BET result of the pore size distribution of the CNTs adsorbents. It was observed that a decrease in the surface area, total pore volume and pore size of the CNTs adsorbent after it was modified with Amine. Previous research shows that there is significant decrease in pore size of an amine functionalized adsorbent. The pore size are mesopores. That is (2nm-50nm) IUPAC standard.

4.0 Conclusion

This work presents the micro structural properties of mixed amine functionalized CNTs sorbent, produced from a mixture of two amine of Mono ethanol amine (MEA) and Tri ethanol amine (TEA), immobilized onto the surface of the CNT through wet impregnation method. Characterization of the CNTs was carried out using XRD, FTIR, TEM, SEM and BET analysis. General observation from the characterization result reveals that the mixed amine have a positive modifying effect on the CNTs for further adsorption studies. The results show that combination of the two different amines, can further improve the adsorption capacity of functionalized CNT sorbents for CO₂ adsorption, in mitigating global warming.

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