Modification of Activated Carbon from Biomass Nypa and Amine Functional Groups as Carbon Dioxide Adsorbent

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ABSTRACT: *The increase in carbon dioxide (CO_2) has been a major cause for global warming and climate change. Therefore, a study of CO_2 adsorption by using activated carbon (AC), which has sorption capacity, surface area, and pore structure, is introduced. AC is produced by using sulfuric acid by dehydration method with biomass nypa. Then, to enhance the selectivity of AC to adsorb CO_2, characterisation and modification of AC are performed by using amine functional groups, diethanolamine (DEA) with 10%, 20% and 30%. The samples were characterised using BET, FTIR, XRD, and SEM. FTIR analysis found that peak areas of the 10%, 20%, and 30% DEA/AC samples are associated with stretching of the functional group OH. The presence of functional groups grows with the increase in the mass of the DEA. Meanwhile, XRD analysis indicated that the chemical composition of the results is carbon, and salts such as sodium sulfate were produced from the dehydration reaction. The AC samples have more surface pores than the DEA/AC samples; SEM analysis shows that the pore area of the DEA/AC samples is covered with amine compounds that accumulate in the pores of AC. Physical adsorption for the AC samples is higher in the BET surface area of 339.09 m^2/g with average pores size of 1.1 nm. The DEA/AC samples showed a significant decrease in the surface area because DEA compounds dispersed and covered the surface and pores of AC. The performance of the adsorbent increases when the functional group increases after CO_2 flow, as indicated by FTIR analysis. An analysis of CO_2 adsorption showed that the AC samples have a higher CO_2 adsorption of 38.37 cm^3/g compared with the DEA/AC samples. Hence, the presence*

of AC with an amine functional group can increase the capacity for physical adsorption on the basis of the characterisation that was performed.

1.   INTRODUCTION

Carbon dioxide (CO_2) is an essential gas to life on earth as it is a main product of human respiration. It is also the main greenhouse gas emitted by human activities; one such activity is the burning of fossil fuels, such as oil, natural gas and coal, for energy production and transportation. Approximately 2 to 3 million tons of CO_2 are released every year through coal-fired power plant activities throughout the world.[1] The increase in CO_2 has led to global warming and climate change. Therefore, green technologies that may reduce emissions, such as CO_2 capture and storage are being developed. Adsorption is one of the most promising CO_2 capture and storage technologies in commercial and industrial applications.[2]

Adsorption can be divided into two methods, namely, physical and chemical adsorption. This process involves the adhesion of atoms, ions or molecules of a liquid, gas or solid solutions that are adsorbed on the surface of an adsorbent. Physical and chemical adsorptions have differences. Physical adsorption causes the desired molecules to be attracted to the high surface area of pore walls through van der Waals forces and have a weak bond. In chemisorption, certain adsorbent sites with a higher adsorption heat will bind with gas, thereby forming a new covalent bond.[3]

Physical adsorption can be analysed based on adsorption and desorption isotherms of nitrogen. This analysis is known as Brunauer-Emmett-Teller (BET) analysis (Emmett 1936). Physical adsorption can be carried out to identify a porous material on the basis of pore size, surface area and pore volume. Porous materials such as activated carbon (AC) can be characterised based on the obtained data. The resulting isotherm can be classified according to the type of existing isotherms, which consist of six classes.[4,5] Adsorption isotherm is available based on the volume of nitrogen adsorption, and desorption isotherms were obtained from the quantity of gas removed from the sample because of the relatively low pressure.

Usually, the adsorbents that are used in CO_2 adsorption are AC, mesoporous silica, zeolite, metal oxides, carbon nanotube, and mesoporous molecular sieve.[6,7] AC is always selected as the main adsorbent in the adsorption process

to remove contaminants from gases and liquids because of its advantages in terms of adsorption capacity, surface area, pore structure, adsorption kinetics and mechanical properties.[8,9]

Studies on AC are increasing because of such advantages. The development of AC research has led to a new discovery with regard to the reuse of disposable materials or biomaterial as an alternative to AC sources. AC is commonly produced from carbon-rich organic material.[10] Thus, the biomass of nypa was introduced to obtain the source of AC. *Nypa fruticans* is a monoecious palm with special characteristics, and it grows throughout pond estuaries in brackish water. Nypa is selected to synthesise AC because its characteristics will create potential raw material for fuels and chemicals.[11] Each part of nypa can be characterised to lignin, starch, protein, inorganic constituents, cellulose and hemicellulose. Moreover, the ash content of nypa is high; thus, it will produce good AC that consists of major inorganic elements, such as Cl, K, and Na, and minor inorganic elements such as Ca, Mg, P, Si, Al and S.

However, AC is less selective on CO_2 adsorption. Thus, in this work, the surface properties of nypa AC are modified to enhance CO_2 adsorption selectivity; this modification was conducted jointly with the amine functional group to examine the ability and effectiveness of AC as adsorbent. The amine functional group is selected in the modification of AC because of its high adsorption capacity and selectivity for CO_2.[12] Then, the prepared modified AC and amine groups are characterised using various methods.

2. EXPERIMENTAL

2.1 Preparation of Activated Carbon

The sample of dehydrated nypa biomass was prepared in advance to obtain AC before it is characterised by analysis. First, the raw nypa biomass were washed and dried. Then, they were ground and sieved by using a blender to obtain an ultra-particle size of 0.2 mm. Afterwards, 25 g of dried biomass samples were dehydrated by using 15 ml concentrated sulfuric acid. Finally, the samples were washed repeatedly with distilled water before dried in an oven at 75°C for 24 h.

These dried dehydrated nypa biomass were then washed again with 1 M sodium hydroxide (NaOH) to obtain more pores. Calcine combustion with nitrogen gas was carried out at 600°C for 30 min to yield and forming AC. The formed AC then were cooled and weighed. These AC next were characterised by using BET, Fourier

transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and X-ray diffraction (XRD). After characterisation, the modification continued with AC by using different mass percentages of the amine functional group (diethanolamine (DEA)) to determine the effects of the use of amine functional groups with AC. Finally, the adsorption test was conducted by using BET method and FTIR to study the effect after CO_2 gas adsorption.

2.2 Characterisation Method

2.2.1 Functional group

The surface functional groups of AC were analysed by using FTIR with Perkin Elmer Model GX through attenuated total reflectance. The characterisation of AC samples with amine functional groups was also assessed by using the same method. 30% of DEA impregnated with AC was flow with CO_2 gas and been analysed using this analysis. This FTIR instrument is useful for identifying the chemicals found in samples from which data were collected and converted to the spectrum by using the interference pattern.

2.2.2 Material crystallinity

Analysis of material crystallinity through XRD analysis is a unique way of identifying the shape and type of crystal that results in AC. XRD characterisation is conducted to identify and characterise the structure and size of crystals. This method allows the analysis and determination of the distribution of the orientation of the crystal in the sample. In this study, XRD was performed by using Bruker AXS D8 Advance with a radiation source of X-rays of Cu Kα (40 kV, 40 mA) to record the diffraction angle of 2θ.

2.2.3 Surface morphology

The structures of the pores were examined by using SEM type ZEISS Supra VP55. SEM is an electron microscope that produces an image of a sample by using a scanning electron to examine the structure, topography, and the composition of the sample.

2.2.4 Physical adsorption and porosity

To characterise AC by using a physical adsorption analyser, BET was used to analyse the BET surface area, pore volume, and pore diameter after CO_2 adsorption. BET analysis was performed by using Micromeritics ASAP 2020. The analysis

was performed by activating the nitrogen adsorption isotherms on the AC samples. Normally, this method is more focused on identifying the porosity and surface area of the sample.

2.3   CO$_2$ Adsorption

The physical adsorption of CO$_2$ was measured using BET method by using CO$_2$ as carrier gas at 30°C. The CO$_2$ adsorption capacity was determined by volume of adsorbed gas per gram of adsorbents. The possible chemical adsorption of CO$_2$ was studied by continuous flow of CO$_2$ gas at 50 mL/min into the adsorbent in closed bottle for 30 min at 30°C. The chemical change during CO$_2$ adsorption was determined using FTIR analysis to monitor new bond and functional groups form due to chemical interaction of CO$_2$ and amines group.

3.   RESULTS AND DISCUSSION

From this study, the activated carbon yielded was of 8.07 g or 31%. Then, the complete characterisations were carried out by using FTIR, BET, SEM and XRD on AC obtained from nypa biomass resources to study the presence functional groups, surface properties, porosity, morphology, and phase crystallinity of the adsorbent.

3.1   Functional Group (FTIR)

Figure 1 shows the infrared spectrum of AC for different percentages of AC/DEA, namely, 10%, 20% and 30%. The peak area of the AC sample is 1112.34 cm^{-1}, which refers to a functional group of CO stretching. The peak areas for 10%, 20%, and 30% DEA/AC were each located at 3278.91, 3288.29 and 3283.29 cm^{-1}. All three samples were associated with the functional group OH, and this strain showed the presence of hydroxides bound in the AC biomass commander. Moreover, the presence of an amine functional group and nitro compounds can be seen in every sample for each percentage of DEA on AC. This means that the presence of functional groups grows with the increase in the mass of the DEA.

The presence of nitrogen functional groups in amine functional groups on the carbon surface will increase the adsorption capacity.[13] As the percentage of DEA increase, the intensity of presented amine tends to increase in each sample adsorbent. The presence of amine functional groups will also increase the chemical bonds on the surface of AC.[14]
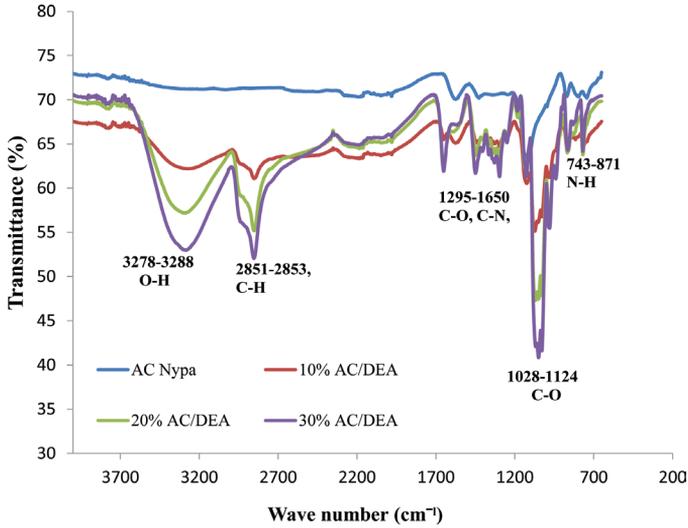
Figure 1. Spectrum of AC and AC supported DEA.

3.2 Crystallinity (XRD)

The shape and type of crystal that results in AC is identified through XRD analysis. Figure 2 shows that the chemical composition of the resulting sample is mostly carbon, and no significant change is observed in the diffraction for all samples. However, the presence of salts such as sodium sulphate compounds can be seen in the sample. These salts result from the reaction of sodium hydroxide and sulfuric acid (dehydration) during the production of AC.
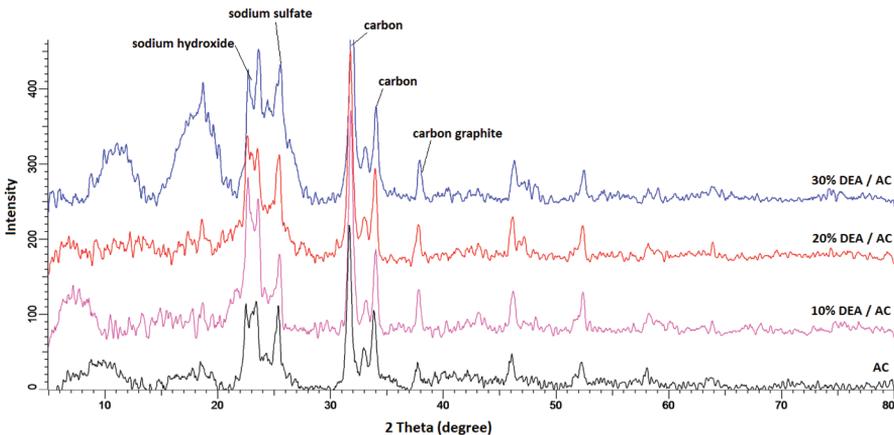
Figure 2. Analysis of XRD spectrum on AC nypa and different DEA loadings on AC.

3.3   Surface Morphology (SEM)

SEM analysis found that the resulting surface pores on the surface of the sample vary according to the type of AC. Figure 3 shows the morphology of AC at a magnification scale of 30 KX. Apart from the presence of pores in the percentage of the mass of DEA, the existence of such salts can also be seen in the physical morphology of AC in white compound form. The presence of salts such as sulphates may be due to the use of concentrated sulfuric acid in carrying out the chemical activation of AC.
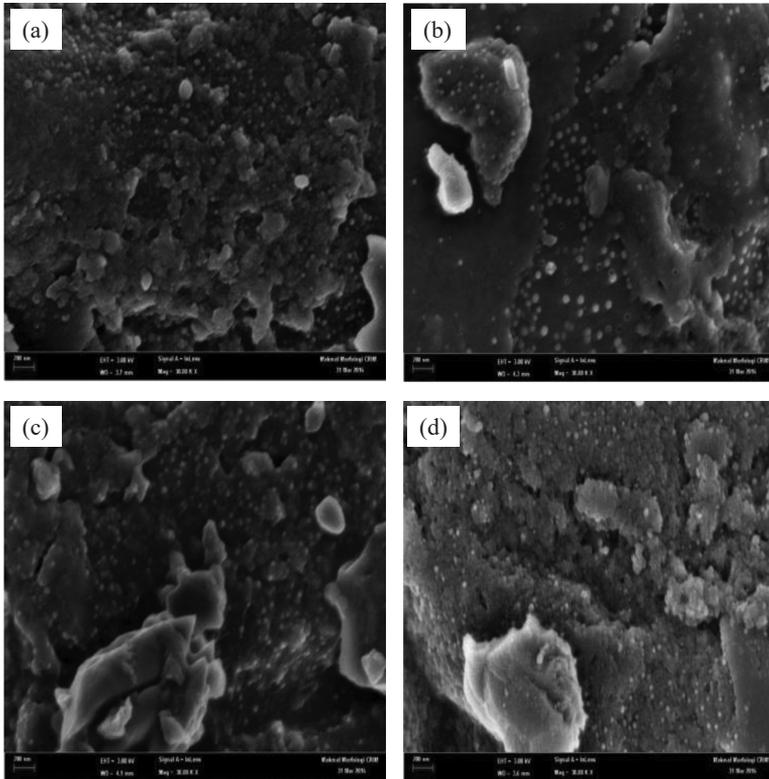
Figure 3:   Morphology of SEM for a) AC, b) 10% DEA/AC, c) 20% DEA/AC, d) 30% DEA/AC.

3.4   Physisorption Properties

Physical adsorption analysis was performed by using BET to review the BET surface area, pore volume, pore size, and pore size distribution (Emmett 1936). The analysis was performed by the flow of the nitrogen on the AC samples.

Table 1 shows that the BET surface area of the AC sample represents the surface area of 339.09 m^2/g and contains more pores compared to the DEA/AC samples. The process of hydration with concentrated sulfuric acid clearly yielded a high surface area and porosity. AC samples that were modified with amine compounds showed a significant decrease in surface area. This finding shows that these compounds were dispersed and covered the surface and pores of AC.[15] However, the BET surface area of the 30% DEA/AC sample was higher than that of the other DEA samples at 0.96 m^2/g. The average pore size of 7.0 nm is found in the 10% DEA/AC sample. According to the International Union of Pure and Applied Chemistry (IUPAC), AC and 30% DEA/AC are classified as micropores given that their pore size is <2 nm, while the 10% and 20% DEA/AC samples are classified as mesopores given that the width of the mesopores ranges between 2 and 50 nm.

Table 1: Summary analysis of physical properties of material.

Sample	BET surface area (m²/g)	Micro pore area (m²/g)	Pore size (nm)	Pore volume (cm³/g)
AC	339.09	278.76	1.11	0.19
10% DEA/AC	0.75	−0.06	7.00	2.63×10^{-3}
20% DEA/AC	0.93	−0.38	3.07	1.43×10^{-3}
30% DEA/AC	0.96	−0.65	1.11	0.53×10^{-3}

Figures 4(a) to 4(d) show the adsorption and desorption of nitrogen in each sample. Nitrogen adsorption and desorption isotherms of AC samples refer to the isotherm type I, which is present because of the interaction between the adsorbent adsorbed in micropores of molecular dimensions. DEA/AC samples can be classified as type II isotherm group, which is usually associated with the intermediate flat region that corresponds to monolayer formation. The isotherm resulting from analysis BET-N_2 is an isotherm of type I for sample AC and the isotherm for sample DEA/AC is type II.

3.5   Effect of Performance of CO_2 Adsorption and Porosity

Adsorption of CO_2 was done by flowing CO_2 gas for 30 min, and this adsorption effect was analysed using FTIR analysis. Based on Figure 5, it was indicated that the 30% AC spectrum with DEA shows the decreases of wavelength after CO_2 adsorption. These decreases occurred because the adsorption column was successfully filled with CO_2. Therefore, prior to CO_2 adsorption, the entrance was covered with DEA. However, the resulting functional group increased because of the resulting chemical bond between CO_2. The reaction of CO_2 and amine can produce new compounds, such as carbamates. However, the formation of
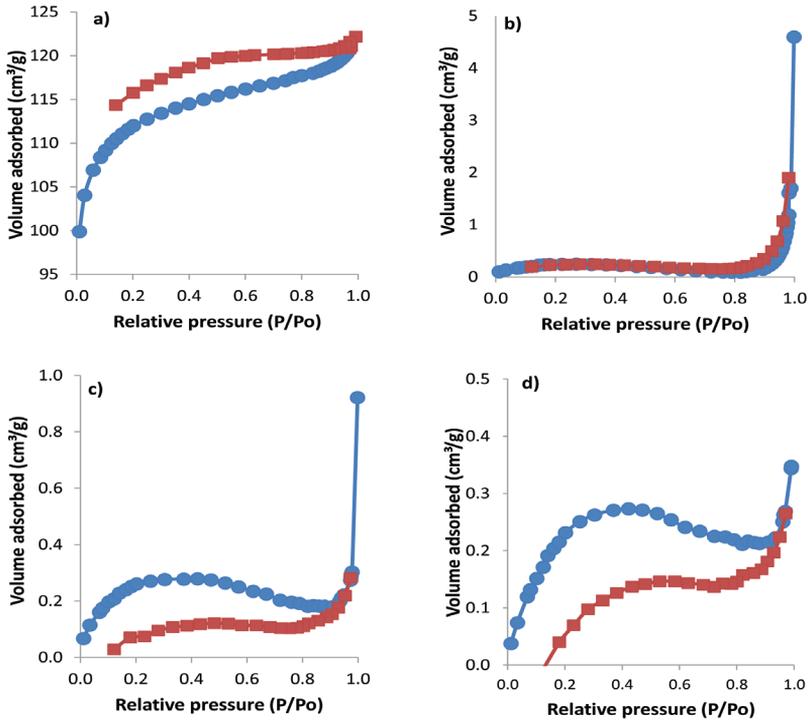
Figure 4:　Adsorption-desorption isotherm of BET for a) AC, b) 10% DEA/AC, c) 20% DEA/AC, and d) 30% DEA/AC (blue: adsorption, red: desorption).

carbamate compounds will deactivate the amine material during CO_2 adsorption.[16] In this study, a secondary amine of DEA did not provide any new chemical bonds after exposure to CO_2.

Physical adsorption of CO_2 was analysed for each sample to determine if the adsorption capacity was successful. Table 2 shows that the AC sample has a CO_2 volume adsorption of 38.37 cm^3/g, which is higher than that of the other samples by 7.03%. The BET surface area of the AC sample is high, thereby proving that CO_2 adsorption was successful, as indicated by the number of active sites on the surface of the sample. Then, this physical adsorption of CO_2 proved that the surface of adsorbent was fully covered by the DEA. However, the volume of the adsorbent is uneven; the 20% DEA/AC sample adsorbs less than the 10% DEA/AC sample does with 17.86 cm^3/g < 22.36 cm^3/g, but the volume increased to 23.50 cm^3/g when the mass percentage increased. Therefore, the 10% DEA/AC sample is applicable because its adsorption rate is the same as that of the 30% DEA/AC sample.
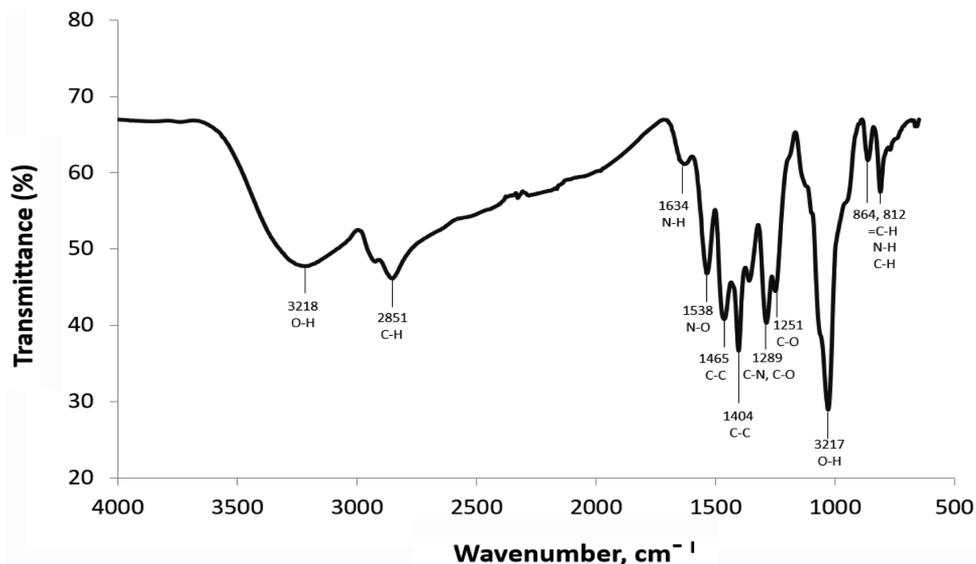
Figure 5: FTIR spectrum of 30% DEA/AC after adsorption by flow CO_2 gas.

Table 2: Volume of CO_2 adsorption.

Samples	Volume of adsorption (cm^3/g)	Total adsorption capacity (wt.%)	Quantity CO_2 adsorbed per unit surface area (g/m^2)
AC	38.36	7.54	0.02×10^{-2}
10% DEA/AC	22.36	4.39	5.85×10^{-2}
20% DEA/AC	17.86	3.51	3.77×10^{-2}
30 % DEA/AC	23.50	4.62	4.81×10^{-2}

The CO_2 physical adsorption volume of the DEA/AC adsorbents is less than that of the AC. It was maybe due to less surface area of AC-supported amine. However, the physical adsorption occurred on adsorbent surface and was closely related to the surface area. The results showed that AC-supported amine have higher quantity of CO_2 adsorbed per unit surface area. 10% DEA/AC showed a higher quantity of CO_2 physically adsorbed per unit surface area, compared to higher DEA loadings. The presence of higher loadings of amine functional group causes the actual pore size to decrease during amine functionalisation which also reduces the volume of the resulting pore.[17] Subsequently, the pore volume decreasing proportionally with amine loadings gives a significant effect to the CO_2 adsorption capacity. However, it was clearly shown that AC adsorption capacity and selectivity for CO_2 can greatly improve when the surface area increases with amine functionalisation.[18]

Figure 6 shows that the adsorption isotherm that results from CO_2 is a type I isotherm, which exists due to improvement of interaction between the adsorbent and adsorbate species in the pores. This pore is formed when hydration is carried out with acid because activation is considered to have resulted in more active pore sites, which later evolved into mesopores.[19] CO_2 adsorption will proportionally increase by pore size of the adsorbent due to better gas diffusion on the surface of adsorbent. The presence of nitrogen compound on the AC surface can assist the interaction of Lewis acid CO_2 gas on modified adsorbent surfaces.
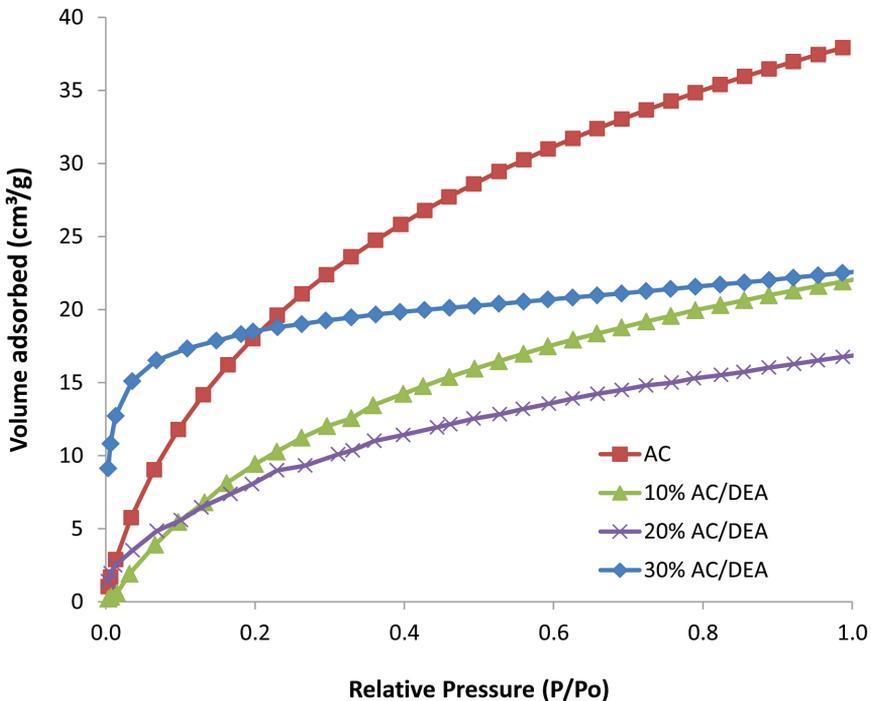
Figure 6: Combination of adsorption of CO_2 isotherm.

4. CONCLUSION

In this study, a total amount of 8.07 g of AC was successfully yielded with the percentage of 31% for further modification with amine functionalisation. Then, the effectiveness of the addition of amine functional groups, namely diethanolamine (DEA) on nypa AC was performed using different mass loading of 10%, 20% and 30%. FTIR analysis showed that the functional groups increased with the increase in the percentage of the mass of DEA. XRD analysis shows that the resulting

diffraction was more focused on elements, such as carbon and sodium sulphate, per sample. The morphology of the pores visible in the AC samples with DEA was analysed through SEM analysis. The BET analysis found that the surface area of the AC samples was greater than that of the DEA/AC samples. However, the pore size of the 10% DEA/AC adsorption material was larger because the DEA was adsorbed and fully covered the AC micropores. The modified adsorbents DEA/AC are classified as mesopores, having a pore size > 2 nm, and these pores formed when dehydration is carried out with acid because activation is considered to have resulted in more active pore sites. From BET-CO_2 method, it was shown the AC with amine functionalisation has higher physical adsorption capacity per unit surface area (g/m^2). However, there was no significant difference for higher loadings of amine to the adsorption capacity. FTIR results showed no chemical change of AC-supported amines after CO_2 adsorption and contribute ease CO_2 desorption.

5.   ACKNOWLEDGEMENT

6.   REFERENCES

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