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Impact of Amine Functional Group on Rice Husk Ash Samples Derived From Rice Husk: A Comparative Co_2 Adsortion Studies

Anil Kumar Turaka*[1], P.Geetha[2], Ch.Bhargavathi[3], G.Sirisha[4] , G. Hima Bindu Sri[5]
[1,2,3,4,5] Department of Chemistry, Ramachandra College of Engineering, ELURU, AP ,
534007

ABSTRACT:

Surface modifications with amine functionalized materials have greater ability for the capture of CO_2. In general, porous materials are widely applicable for CO_2 adsorption due to their high surface area and easily susceptible nature for the surface modification by amine functional groups. The main objective of this work presented is to develop a Nano porous solid adsorbent which can serve as a best adsorbent for CO2. Rice husk ash samples prepared at different temperatures under N_2+steam atmospheres are impregnated with Mono Ethyl Amine (MEA), Di Ethyl Amine (DEA) and Poly Ethylene Imine (PEI) in 5, 10, 15, 20 and 25 wt.%. All these samples are subjected to Characterization studies and CO2 adsorption studies.

KEYWORDS: Rice husk ash (RHA) samples, Amines-MEA, DEA, PEI, Break through curve (BTC), Impregnation, and Adsorption

INTRODUCTION:

Improving the proficiency of vitality usage and expanding the utilization of low carbon vitality sources are viewed as potential approaches to diminish carbon dioxide outflows. As of late, carbon catch and sequestration are getting noteworthy consideration and being perceived as a third choice. Additionally, improved CO_2 streams can be a significant beginning material for engineered clean powers and synthetic substances. For carbon sequestration, the expenses of catch and division are assessed to make up around three-fourths of the absolute expenses of sea or geologic sequestration. It is consequently critical to investigate new methodologies for CO_2 partition [1]. Adsorption is one of the promising techniques that could be material for isolating CO_2 from gas blends, and various investigations have been led on detachment of CO_2 by adsorption over the most recent two decades. Different adsorbents, for example, initiated carbons, pillared dirts, metal oxides and Zeolites have been examined [2]. Actuated carbons are end up being perhaps the best material for CO_2 adsorption as of late. In any case, it is hard to maintain a strategic distance from the lack of the actuated carbon crude material in light of the decreasing of the world's woodlands and coal assets. Subsequently, it has step by step become a hot research to discover other crude materials for actuated carbon planning. Biomass is a copious and sustainable power source. It contains less Sulfur and debris yet more hydrogen than coal. In view of zero CO_2 outflow qualities, biomass along these lines is probably going to be an alluring clean improvement component choice for lessening ozone depleting substance discharge.

Rice husk is one of the major agro-based biomass delivered in huge amounts in creating nations like India and China. Rice husk asset is bottomless in India, however the rice husk usage and transformation rate are low and the ecological contamination is not kidding. Rice husk has high substance of fixed carbon and can be utilized as a decent crude material for the planning of actuated carbon [3]. As a piece of our proceeding with exertion in the advancement of the surface adjustment on enacted carbon to build CO_2 adsorption limit at high temperatures, impacts of utilizing Monoethylamine (MEA), Diethylamine (DEA) and Polyethyleneamine (PEI)as change operators were explored. Right now was set up at 600^oC temperature under nitrogen and steam climate from rice husk named as RHNS-6, which was impregnated with Monoethylamine (MEA), Diethylamine (DEA) and Polyethyleneamine (PEI) in 5, 10, 15, 20 and 25 wt.%. PEI is a decent polymer with its fondness towards gas particles, particularly CO_2 atom on the grounds that there are numerous nitrogen in the particle to respond with CO_2 [4].

MATERIALS AND EXPERIMENTAL METHODS:

Preparation of Amine Incorporated Rice Husk Ash (RHA) Adsorbent:

Amine incorporated Rice husk ash (RHA) was prepared by wet impregnation method. Briefly, required quantity of Monoethylamine (MEA), Diethylamine (DEA) and Polyethyleneamine (PEI) was dissolved in anhydrous methanol then rice husk ash geared up at different temperatures below N_2 atmosphere was added with vigorous stirring for 30 mints followed by drying at room temperature in nitrogen protection and vacuum drying at 110^oC for 12 h [21]. A series of Rice husk ash with 5, 10, 15, 20 and 25 wt.% loadings of Monoethylamine (MEA), Diethylamine (DEA) and Polyethyleneamine (PEI) were prepared and denoted example like as x MEA/RHNS-T, where x represents the weight percentage of MEA and T represents the temperature in multiples of hundred (^oC).

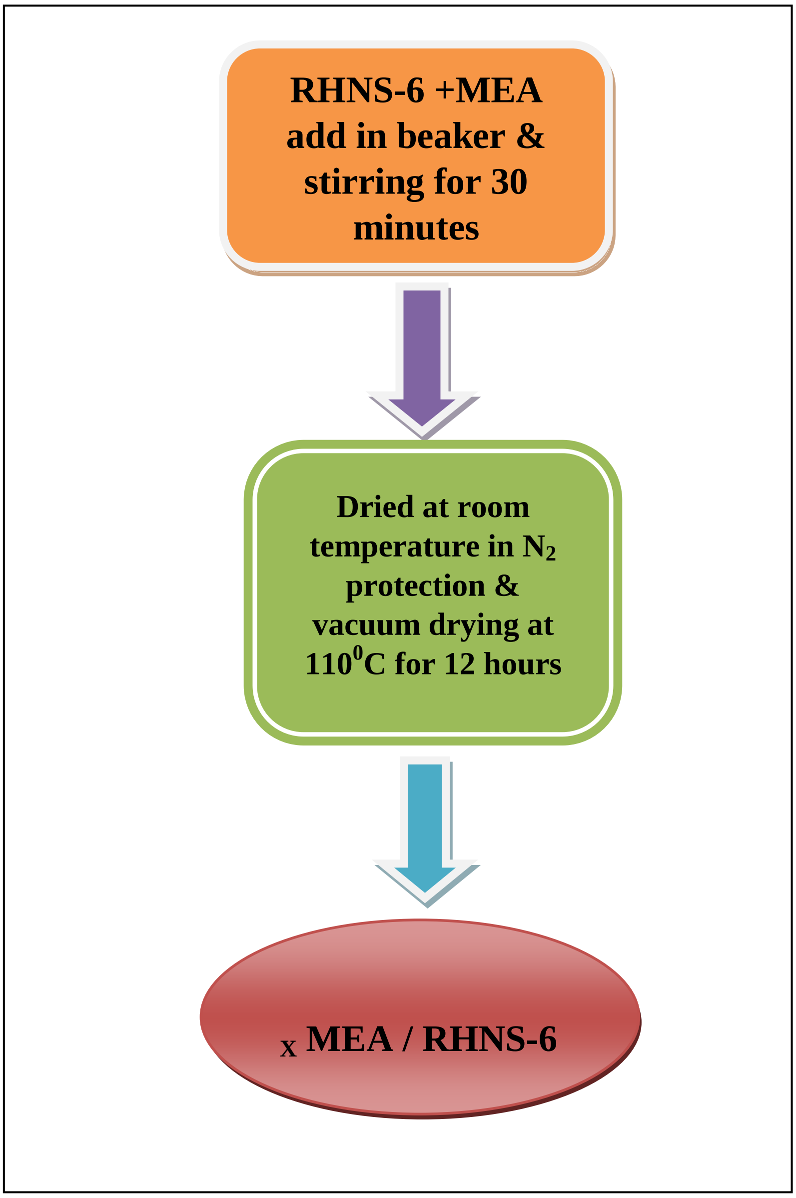

Fig: 1. Flow chart of Amine incorporated Rice Husk Ash samples

CHARACTERIZATION OF PREPARED ADSORBENT:

All the Rice husk ash (RHA) samples prepared subjected to characterized by BET Surface area, Pore volume and FTIR techniques.

RESULTS AND DISCUSSION:

BET surface and Pore Volumes of Adsorbents:

Rice husk ash samples and modified rice husk ash samples were characterized by BET surface area, Pore volume. Surface area (SA), pore volume, and pore diameter of the adsorbents are given in Table:1 surface area of pure rice husk ash prepared in N_2 and steam atmosphere at 600^oC (RHNS-6) is maximum when compared with other samples which was discussed by **Srinivas et al** []. The surface area, average pore diameters of MEA/RHNS-6, DEA/RHNS-6 and PEI/RHNS-6 loaded with different wt. percentages are measured and listed in Table: 4.1 and displayed in Fig:4.2. The actual surface area of RHNS-6 is $311.5m^2g^{-1}$

and the average pore diameter is 3.3 nm. In the wake of stacking diverse wt. rates of amines, in every one of these examples there is negligible decline in surface territory and pore volume is seen which may be because of blockage of the miniaturized scale pores present on the surface of the help. This outcome recommends that the measure of amines on the rice husk debris doesn't influence a great part of the surface properties.

Sample Name	**5 wt.%**		**10 wt.%**		**15 wt.%**		**20 wt.%**		**25 wt.%**	
	S.A	**PSD**	**S.A**	**PSD**	**S.A**	**PSD**	**S.A**	**PSD**	**S.A**	**PSD**
MEA/RHNS-6	308.5	3.2	302.8	3.2	290.2	3.01	289.1	3.0	265.6	2.91
DEA/RHNS-6	306.2	3.0	304.8	2.81	298.1	2.83	292.6	2.76	283.8	2.39
PEI/RHNS-6	306.5	2.7	302.3	2.69	298.1	2.52	298.6	2.70	292.8	2.62

- Wt.% indicates the Amine loadings

Table: 1. Surface area (S.A) & Pore Size Distribution (PSD) of Modified RHNS-6 Samples

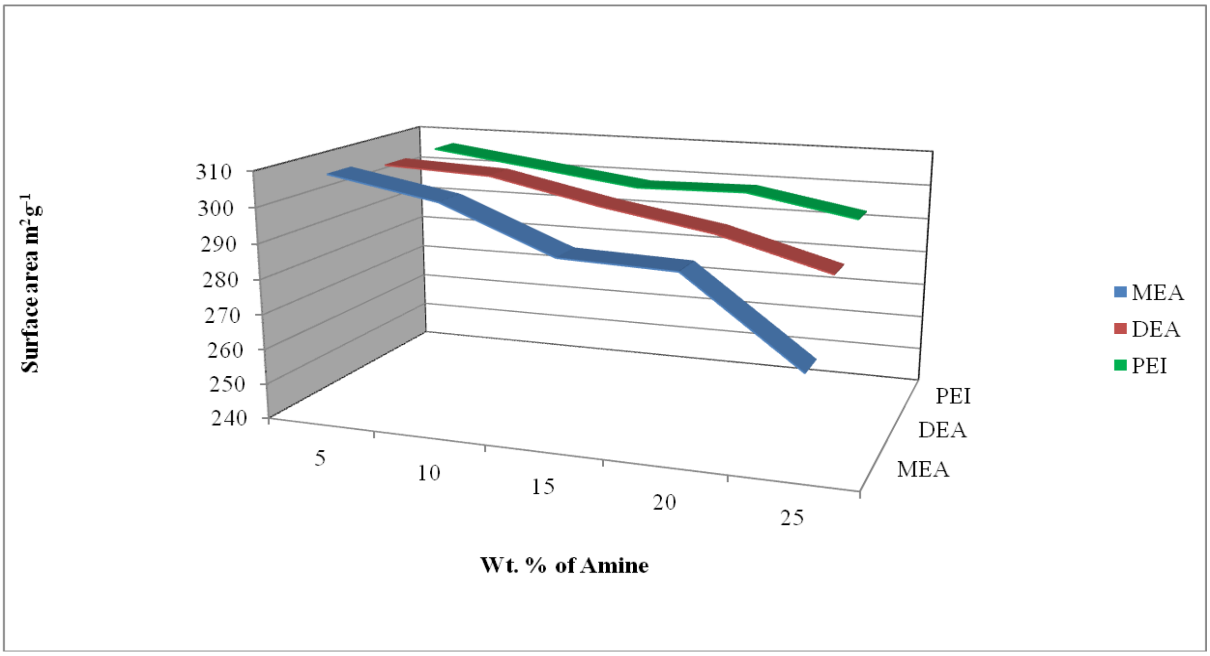

Fig: 2 Surface Area of modified RHA samples with amines

FTIR transmission spectra of Adsorbents:

The FTIR transmission spectra of modified rice husk ash samples, 15 wt. % and 20 wt. % of Monoethylamine (MEA), Diethyl amine (DEA) and Polyethylene amine (PEI) are given in Fig.4.3. The band at 1470cm^{-1} denotes the NH bond, in which its minor increase in the transmittance for the amine incorporated samples compared to pure rice husk ash sample as they contains NH_3 group [271]. The band at 2000 cm^{-1} is usually noted as single CH bond, which decreases in the transmittance for MEA when compared to PEI samples. From this observation it is assumed that PEI decreases the ratio of C-H bonds. The reduction of the C-H bond indicates the relative reduction in the presence of these usually hydrophobic bonds, which enables the more hydrophilic N-H bonds to be attached on the support surface. The broad band beyond 2000 cm^{-1} is due to the presence of aliphatic groups of the adsorbed long chained PEI [272]. Other bands 2833, 2960 cm^{-1} corresponds to the symmetric and asymmetric stretching of (C-H) group, which indicates that the amine groups especially PEI group has been attached to coordinated unsaturated sites of the support. The stretching vibrations from approximately 3,250 to 4000 cm^{-1} are possibly due to the presence of surface hydroxyl groups and chemisorbed water [273]. These results confirm that PEI was successfully loaded when compared to MEA and DEA.

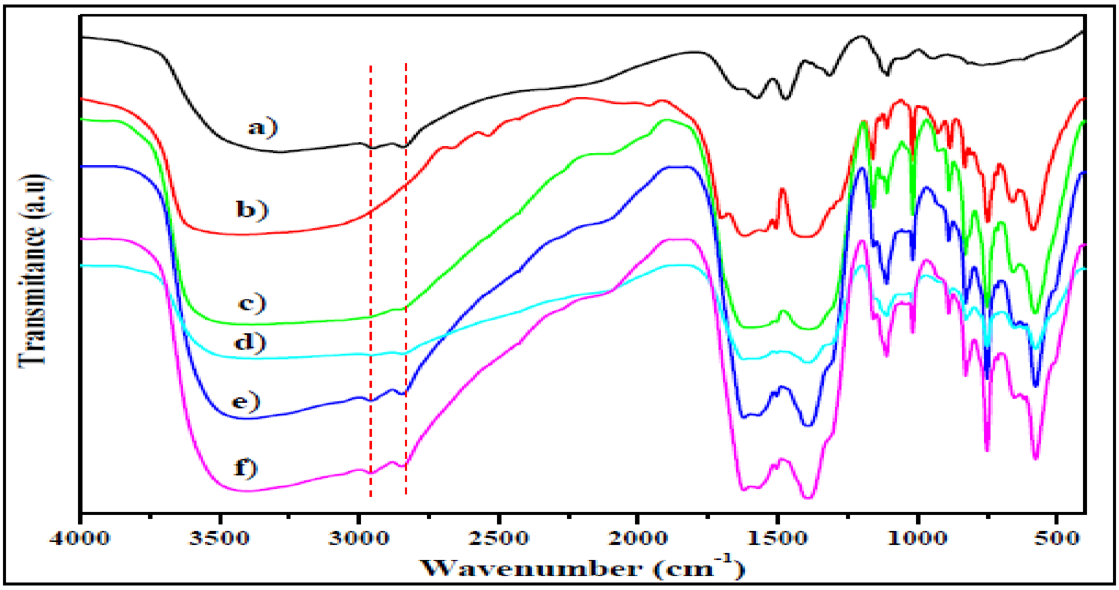

Fig: 3 FT-IR patterns of a) 15wt. % MEA/RHNS-6 b) 20wt. % MEA/RHNS-6 C) 15 wt. % DEA/RHNS-6 d) 20wt.% DEA/RHNS-6 e) 15wt.% PEI/RHNS-6 f) 20wt% PEI/RHNS-6

4.5 ADSORBENT ACTIVATION:

The activities for these samples are evaluated by using a metal reactor interlaced with a gas chromatograph (Nukon-GC) at 40mL/min. flow rate at different temperatures 50°C, 70°C and 90°C. Different temperatures were implied to study the effect of temperature on CO_2 adsorption capacity. Carbon dioxide adsorption experiment was carried out on a lab made apparatus. 1g of the sample was loaded in metal reactor between the two quartz plugs and pretreated at 473K for one hour in downstream of nitrogen at a flow rate of 40 mL/min.

followed by cooling to desired adsorption temperature. Then a mixture of 10% CO_2 balanced helium was passed at a flow rate of 40 mL/min. until the adsorbent was saturated. The gas streams were constrained by mass stream controllers and temperature was constrained by PID controllers. The emanating gases were examined by gas chromatography (GC, Nucon Technologies, India) furnished with a warm conductivity identifier and having Poropack Q section (3 meters length and 3 mm ID). The adsorption limit was determined from the achievement bend (BTC)

MODIFIED ADSORBENT ACTIVITY STUDIES:

Effect of Amine loading on CO_2 Adsorption:

Pore volume and normal pore width will assume a significant job in adsorption limit of adsorbents. Fig.4.3 shows separately the isotherms of CO_2 on modified RHNS-6 samples at 50^oC and zero to one atmospheric pressure. The amounts of CO_2 adsorbed on all modified RHNS-6 samples increase with increase in the amount of Monoethylamine (MEA), Diethyl amine (DEA) and Polyethylene amine (PEI)from 5 to 20 wt.%. This trend is due to increase in N_2 containing group, in turn, increases the CO_2 adsorption. This may also attributed that up to 20 wt. % loading monolayer of amines might be formed and after that amine multilayer formation might have taken place, which reduces the exposure of more number of active sites like basic groups. This leads to decrease in adsorption capability when the amount of amines is increased to 25 wt. % and higher. This may also be attributed to the pore filling effect that blocks the pores of adsorbent preventing CO_2 to diffuse in to the pores. More importantly it is observed that the pure RHNS-6 has higher CO_2 adsorption capacity [274] than the PEI modified RHNS-6.

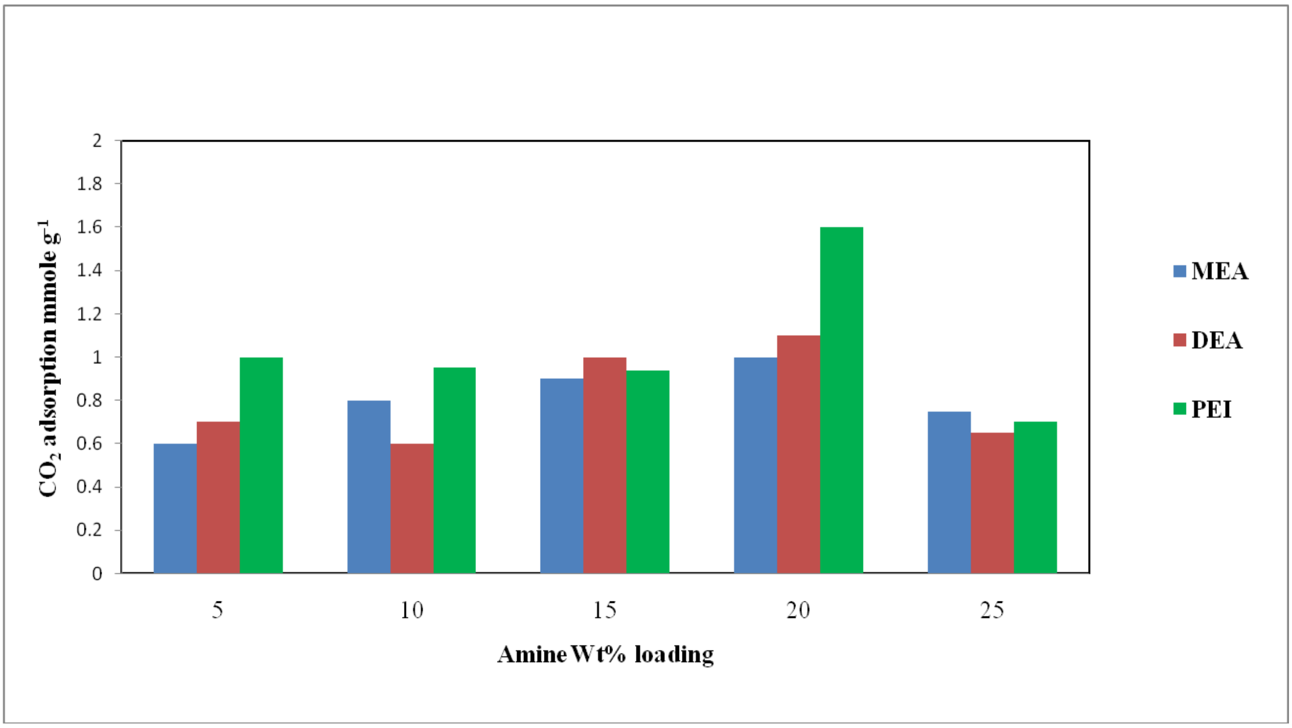

Fig: 4. CO_2 adsorption (BTC) on modified RHNS-6 samples with MEA, DEA, PEI amine groups

Effect of Temperature on carbon dioxide adsorption:

At 50°C pure RHNS-6 sample shows more CO_2 adsorption than PEI modified a sample which is shown in Fig.4.4. As temperature increases the PEI modified RHNS-6 exhibits higher adsorption capacity that the pure support at the same temperature. The Fig.4.5 & 4.6 shows the isotherms of CO_2 on pure RHNS-6 and 20 wt. % PEI loaded on RHNS-6 at 70°C & 90°C and 0 to 1 atm pressure. It can be clearly observed that the amounts of CO_2 adsorbed on 20 wt. % PEI modified sample is more than pure RHNS-6 sample. At first stage the adsorption capacities of all samples are very close.

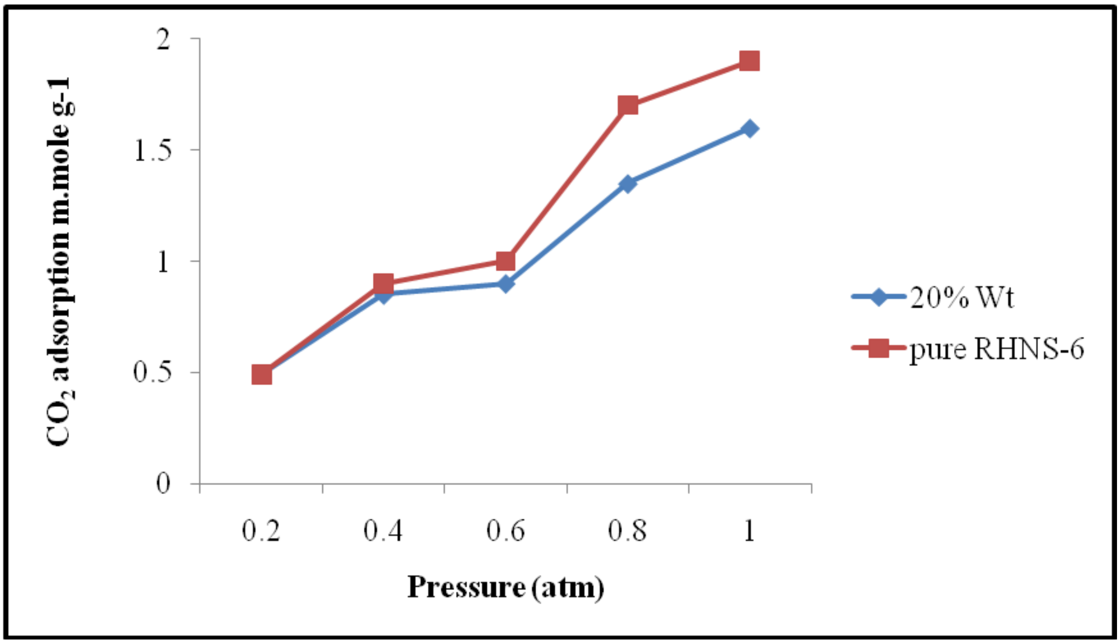

Fig: 5 CO_2 adsorption isotherms of pure RHNS-6 & PEI modified RHNS-6 in different wt. % loadings at 50°C

When the pressures are increased, the adsorption capacities of the RHNS-6 modified with PEI up to 20 wt. % is significantly higher though the surface area and pore volume are lower than the pure RHNS-6. It implies that chemical adsorption dominates the CO_2 adsorption on the modified RHNS-6. The results confirm that the increase in the temperature facilitates the transfer of the adsorbed CO_2 molecules from the surface in to the bulk of PEI by overcoming physical adsorption. On the other hand, further increase in temperature above 90°C slightly reduces the carbon dioxide adsorption capacity, as the forces of attraction between adsorbent and adsorbate starts breaking at higher temperature. The adsorption capacities have same trend of RHNS-6 at 90°C and are close to the adsorption capacities at 70°C. The notable point is that the modified PEI 20 wt. % sample at 50°C has higher CO_2 adsorption capacity than that at 70°C and 90°C.

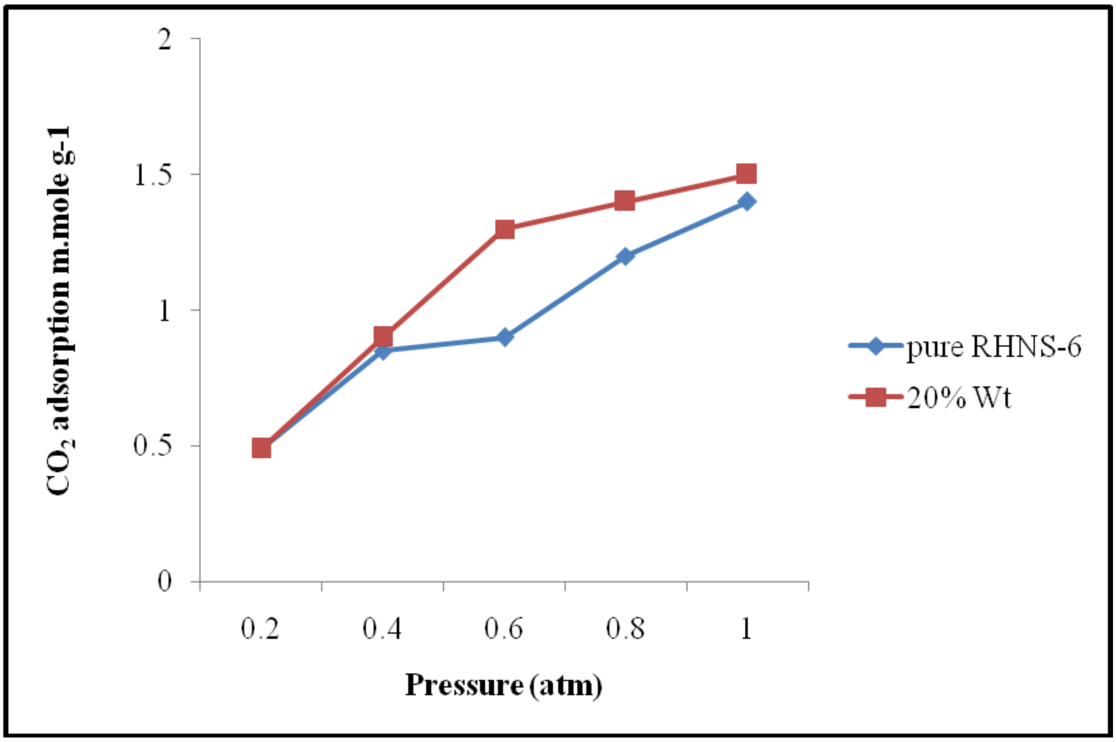

Fig: 6 CO_2 adsorption isotherms of pure RHNS-6 & PEI modified RHNS-6 in Different wt. % loadings at 70°C

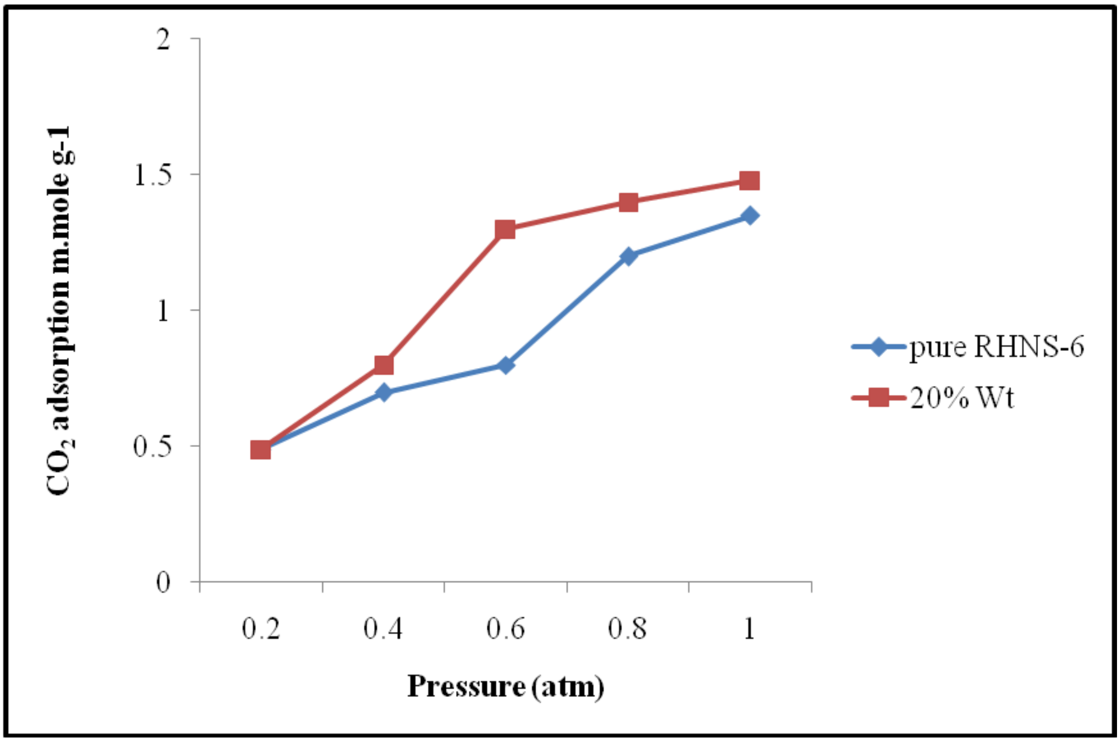

Fig: 7 CO_2 adsorption isotherms of pure RHNS-6 & PEI modified RHNS-6 In Different wt. % loadings at 90°C

CONCLUSION

- The amine modified RHNS-6 have been synthesized in laboratory for carbon dioxide adsorption studies. CO_2 adsorption capacities are increased with increase in wt. % of amines like MEA, DEA and PEI.
- However PEI shows more adsorption capacities as it contains more number of basic or nitrogen containing groups on the surface matrix.
- Adsorption capacity on all the samples gradually increases from 5 wt. % to 20 wt. % of amines and then shows decreasing trend.
- This may be due to amine multilayer formation and pore blocking. At low temperature around 50^{o}C pure RHNS-6 shows more adsorption than modified samples.
- But the 20wt%. PEI/RHNS-6 samples show higher CO_2 adsorption capacity than pure RHNS-6 at 70^{o}C and 90^{o}C temperature.
- From this it tends to be reasoned that the adsorption limits of PEI altered examples can be upgraded at higher temperatures. Be that as it may, this must be upgraded under various climates and calcinations conditions which are our tentative arrangement of activity.

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