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COMPARITIVE CO_2 ADSORPTION STUDIES OFDIFFERENT AMINE FUNCTIONALIZED RICE HUSK ASH SAMPLES

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ABSTRACT

Nowadays carbon dioxide is regarded as one of the main greenhouse gases in the environment and is produced by burning of fossil fuels and automobiles exhaust [1-2]. Global warming resulting from the emission of greenhouse gases, especially CO2, has become a widespread concern in the recent years.Various technologies were developed to capture the atmospheric CO2. In this context, adsorption is one of the best processes for the capture of CO2 and it can be carried out by the either physical adsorption or chemical adsorption [3]. For adsorption, in addition to physical adsorbents, various mesoporous solid adsorbents impregnated with polyamines are reviewed in this work. These materials are nontoxic, inexpensive and mesoporous with reasonably good surface area [4-5]. But the selectivity is poor and have an opportunity for surface modification. Surface modifications with amine functionalized materials have greater ability for the capture of CO2. In general, porous materials are widely applicable for CO2 adsorption due to their high surface area and easily susceptible nature for the surface modification by amine functional groups [6-10]. The main objective of this workpresented 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 N2+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

I. INTRODUCTION

Improving the efficiency of energy utilization and increasing the use of low carbon energy sources are considered to be potential ways to reduce carbon dioxide emissions. Recently, carbon capture and sequestration are receiving significant attention and being recognized as a third option. Also, enriched CO_2 streams can be an important starting material for synthetic clean fuels and chemicals. For carbon sequestration, the costs of capture and separation are estimated to make up about three-fourths of the total costs of ocean or geologic sequestration. It is therefore important to explore new approaches for CO_2 separation [11, 12]. Adsorption is one of the promising methods that could be applicable for separating CO_2 from gas mixtures, and numerous studies have been conducted on separation of CO_2 by adsorption in the last two decades. Various adsorbents, such as activated carbons, pillared clays, metal oxides and zeolites have been investigated [13-17]. Activated carbons are proved to be one of the best materials for CO_2 adsorption in recent times. However, it is difficult to avoid the shortage of the activated carbon raw material because of the dwindling of the world's forests and coal resources. Therefore, it has gradually become a hot research to find other raw materials for activated carbon preparation. Biomass is an abundant and renewable energy source. It contains less Sulphur and ash but more hydrogen than coal. Because of zero CO_2 emission characteristics, biomass therefore is likely to be an attractive clean development mechanism option for reducing greenhouse gas emission. Rice husk is one of the major agro-based biomass produced in large quantities in developing countries like India and China. Rice husk resource is abundant in India, but the rice husk utilization and conversion rate are low and the environmental pollution is serious. Rice husk has high content of fixed carbon and can be used as a good raw material for the preparation of activated carbon[18-19]. As a part of our continuing effort in the development of the surface modification on activated carbon to increase CO_2 adsorption capacity at high temperatures, effects of using Mono Ethyl Amine

(MEA), Di Ethyl Amine (DEA) and Poly Ethylene Imine (PEI) as modification agents were investigated. In this study ash was prepared at 600^0C temperature under nitrogen+steam atmosphere from rice husk named as RHNS-6, which was impregnated with Mono Ethyl Amine (MEA), Di Ethyl Amine (DEA) and Poly Ethylene Imine (PEI) in 5, 10, 15, 20 and 25 wt.%.PEI is a good polymer with its affinity towards gas molecules, especially CO_2 molecule because there are many nitrogen atoms in the molecule to react with CO_2 [20]. All these samples are subjected to characterization studies and CO_2 adsorption studies.

II. MATERIALS AND METHODS

Preparation of Adsorbents

Amine incorporated Rice Husk Ash (RHA)

Amine incorporated rice husk ash was prepared by wet impregnation method. Briefly, desired quantity of MEA was dissolved in anhydrous methanol then rice husk ash prepared at different temperatures under N_2 atmosphere was added with vigorous stirring for 30 mints followed by drying at room temperature in nitrogen protection and vacuum drying at 110^0C for 12 h [21]. A series of catalysts with 5, 10, 15, 20 and 25 wt.% loadings of MEA were prepared and denoted as x MEA/RHNS-T, where x represents the weight percentage of MEA and T represents the temperature in multiples of hundred (^{0}C). In similar procedure DEA and PEI were also impregnated on rice husk ash samples.

Table: 1 Surface area (S.A) and Pore size distribution (PSD) of modified RHNS-6 samples

Sample	**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

Characterization and activity studies

All the Rice Husk Ash samples prepared in different atmospheres at different temperature conditions were characterized for BET Surface area, Pore volume and FTIR techniques. 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 50^0C, 70^0C and 90^0C. 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. 1 gram of the sample was loaded in metal reactor between the two quartz plugs and pretreated at 473K for 1 hr. 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 flows were controlled by mass flow controllers and temperature was controlled by PID controllers. The effluent gases were analyzed by gas chromatography (GC, Nucon Technologies, India) equipped with a thermal conductivity detector and having poropack Q column (3 meters length and 3 mm ID). The adsorption capacity was calculated from the break through curve (BTC).

III. RESULTS AND DISCUSSION

Rice husk ash samples and modified rice husk ash samples were characterized by BET surface area, Pore volume and FTIR studies. Surface area, pore volume, and pore diameter of the adsorbents are shown in Table-1. The surface area of pure rice husk ash prepared in nitrogen and steam atmosphere at 600^0C (RHNS-6) is maximum when compared with other samples which was discussed by Srinivas et al [22]. 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

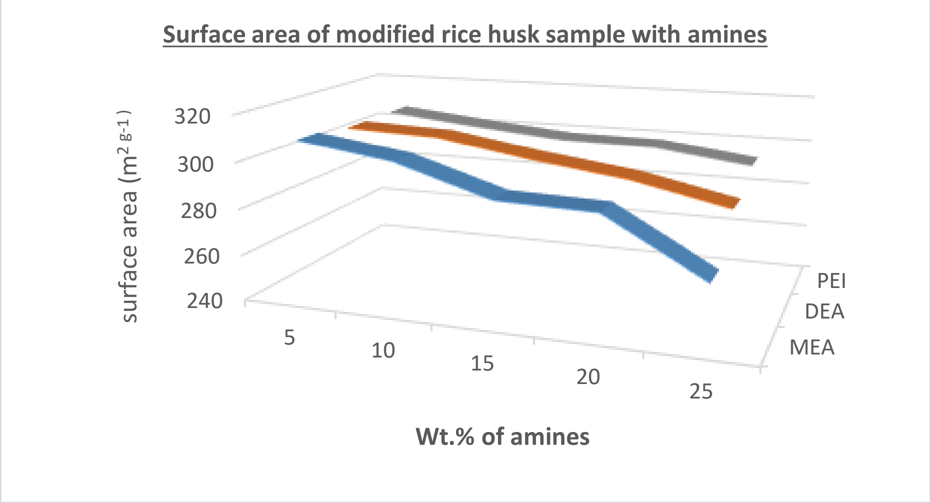

Fig.1 Surface area of modified RHA samples with amines

Table-1 and displayed in Fig.1. The actual surface area of RHNS-6 is 311.5 m^{2}g$^-$ and the average pore diameter is 3.3 nm. After loading different wt. percentages of amines, in all these samples there is marginal decrease in surface area and pore volume is observed which might be due to blockage of the micro pores present on the texture of the support. These results suggests that the amount of amines on the rice husk ash does not affect much of the surface properties.

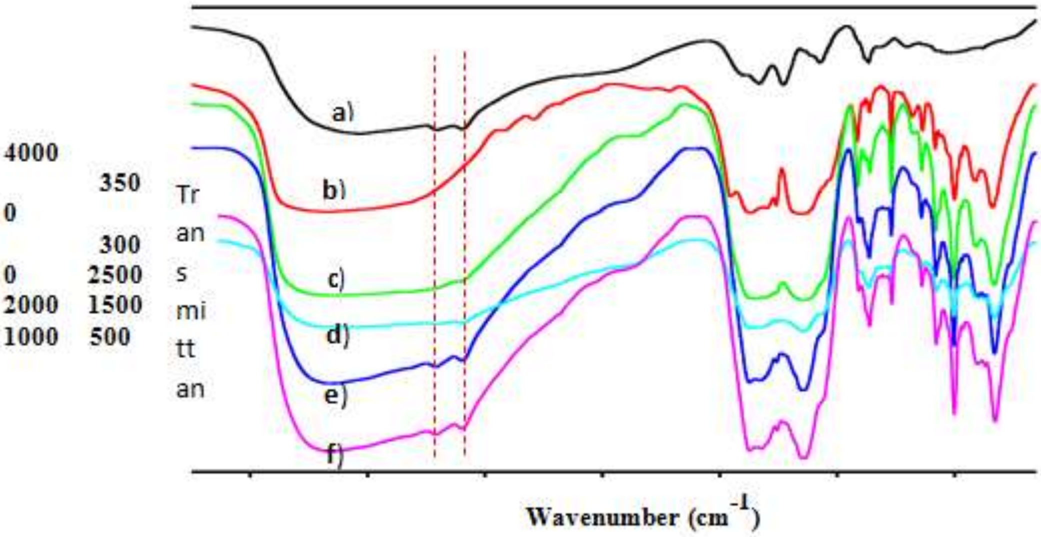

Figure-2: FT-IR patterns of a) 15 MEA/RHNS-6 b) 20 MEA/RHNS-6 C) 15 DEA/RHNS-6 d) 20 DEA/RHNS-6 e)15 PEI/RHNS-6 f)20 PEI/RHNS-6

The FTIR transmission spectra of modified rice husk ash samples, 15 wt.% and 20 wt.% of MEA, DEA and PEI are shown in Fig.2. The band at 1470cm^{-1} represents the N-H bond, in which its slight increase in the transmittance for the amine impregnated samples compared to pure rice husk ash sample as they contains NH$_3$ group [23]. The band at 2000 cm^{-1} is usually ascribed to the single C-H bond, which decreases in the transmittance for MEA when compared to PEI samples. From this observation it is assumed that PEI impregnation decreases the ratio of C-H bonds. The reduction of the C-H bond indicates the relative reduction in the presence of these generally hydrophobic bonds, which enables the more hydrophilic N-H bonds to be attached on the support surface. The broad bands beyond 2000 cm^{-1} is due to the presence of aliphatic groups of the adsorbed long chained PEI [24]. Other bands 2833, 2960 cm^{-1} correspondstothesymmetricandasymmetricstretchingof(C-H)group,whichindicates that the amine groups especially PEIgrouphasbeenattachedtocoordinatedunsaturatedsites of the support. The stretching vibrations from approximately 3,250 to 4000 cm^{-1} are possibly due to the presence of surface hydroxylicgroups and chemisorbed water [25]. These results confirm that PEI was successfully loaded when compared to MEA and DEA.

Effect of amine loading on CO_2 adsorption

Pore volume and average pore diameter will play an important role in adsorption capacity of adsorbents. Fig.3 shows separately the isotherms of CO_2 on modified RHNS-6 samples.at 50^0C and 0 to 1 atm pressure. It can be seen that the amounts of CO_2 adsorbed on all modified RHNS-6 samples increase with increase in the amount of MEA, DEA and PEI from 5 to 20 wt.%. This trend is due to increase in nitrogen containing group, in turn, increases the CO_2 adsorption. This may also attributed that upto 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 capacity 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 [26] than the PEI modified RHNS-6.

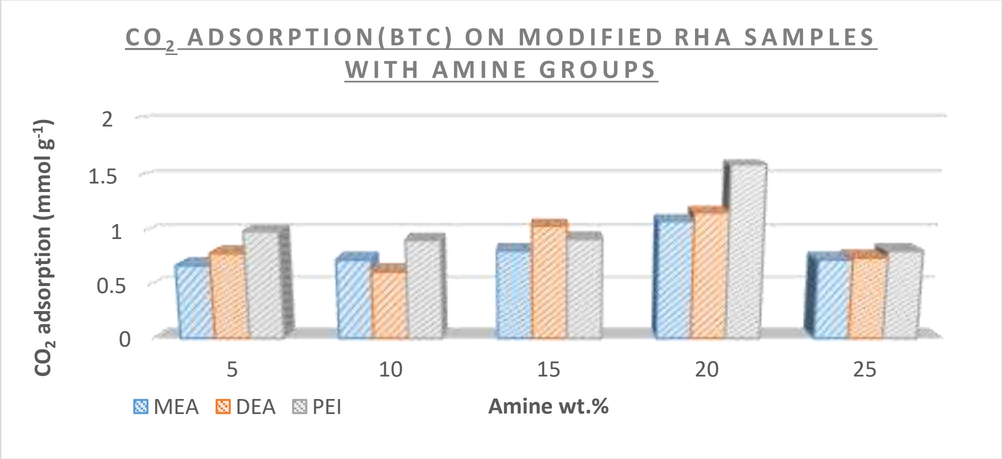

Fig.3 CO_2 adsorption (BTC) on modified RHNS-6 samples with MEA, DEA, PEI amine groups

Effect of Temperature on carbon dioxide adsorption

At 50^0C pure RHNS-6 sample shows more CO_2 adsorption than PEI modified samples which is shown in Fig.4. As temperature increases the PEI modified RHNS-6 shows higher adsorption capacities that the pure support at the same temperature. TheFig.5 and 6 shows the isotherms of CO_2 on pure RHNS-6 and 20 wt. %PEI loaded on RHNS-6 at 70^0C& 90^0C and 0 to 1 atm pressure. It can be clearly observed that the amounts of CO_2 adsorbed on 20 wt. % PEI modified sampleis more than pure RHNS-6 sample. In the beginning, the adsorption capacities of all samples are very close.

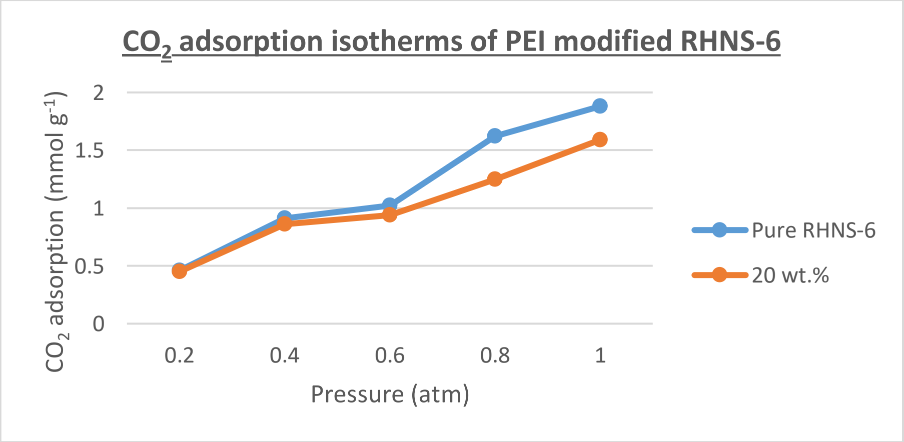

Fig.4 CO_2 adsorption isotherms of pure RHNS-6 & PEI modified RHNS-6 in different wt.% loadings at 50^0C

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 90^0C 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 90^0C and are close to the adsorption capacities at 70^0C. The notable point is that the modified PEI 20 wt. % samples at 50^0C has higher CO_2 adsorption capacity than that at 70 and 90^0C.

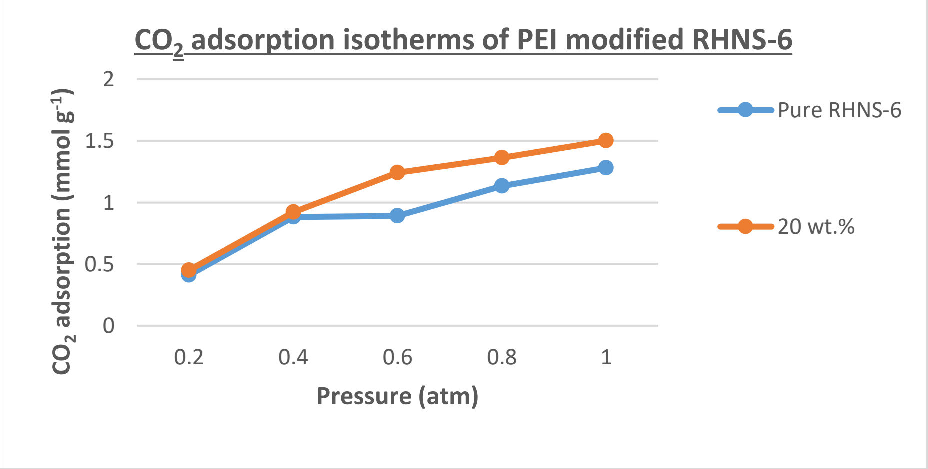

Fig.5 CO_2 adsorption isotherms of pure RHNS-6 & PEI modified RHNS-6 in different wt.% loadings at 70^0C

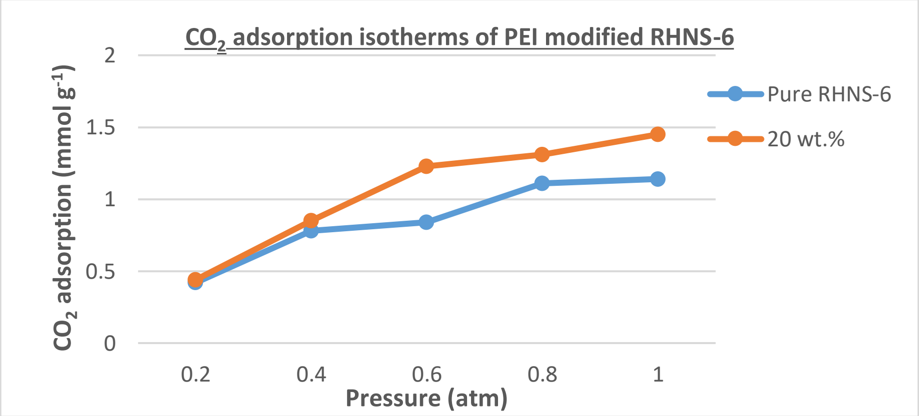

Fig.6 CO_2 adsorption isotherms of pure RHNS-6 & PEI modified RHNS-6 in different wt.% loadings at 90^0C

IV. 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 50^0C pure RHNS-6 shows more adsorption than modified samples. But the 20 PEI/RHNS-6 samples shows higher CO_2 adsorption capacity than pure RHNS-6 at 70^0C and 90^0C temperature. From this it can be concluded that the adsorption capacities of PEI modified samples can be enhanced at higher temperatures. However, this has to be optimized under different atmospheres and calcination conditions which is our future plan of action.

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