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## PREPARATION OF ACTIVATED CARBON FROM RICE HUSK AND COMPARITIVE CO<sub>2</sub> ADSORPTION STUDIES OF DIFFERENT AMINE GROUP FUNCTIONALIZED RICE HUSK ACTIVATED CARBON SAMPLES

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**Abstract:** Preparation of activated carbon from local available rice husk with simple methods. The activated carbon impregnated with different amine functional groups like Mono Ethyl Amine (MEA), Di Ethyl Amine (DEA) and Poly Ethylene Imine (PEI) with different weight percentage ratio for studies of CO<sub>2</sub> adsorption. Nowadays carbon dioxide is regarded as one of the main greenhouse gases and its causes Global warming resulting from the emission of greenhouse gases, mainly CO<sub>2</sub>, has become a widespread concern in the recent years. In this context, adsorption is one of the best processes for the capture of CO<sub>2</sub> and it can be carried out by the either physical adsorption or chemical adsorption. 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. But the selectivity is poor and has an opportunity for surface modification. Surface modifications with amine functionalized materials have greater ability for the capture of CO<sub>2</sub>. In general, porous materials are widely applicable for CO<sub>2</sub> 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 an activated carbon from rice husk which can serve as a best adsorbent for CO<sub>2</sub> [1-10]. Rice husk ash samples prepared at different temperatures under N<sub>2</sub>+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 BET, FTIR and CO<sub>2</sub> adsorption studies.

**KEYWORDS:** Rice husk activated carbon (RHAC) samples, Amines-MEA, DEA, PEI, Break through curve (BTC), Impregnation, and Adsorption

### 1. Introduction

Improving the efficiency of strength utilization and growing the use of low carbon power sources are considered to be manageable strategies to reduce

carbon dioxide emissions. Recently, carbon catch and sequestration are receiving large interest and being identified as a 1/3 option. Also, enriched CO<sub>2</sub> streams can be an quintessential

beginning fabric for artificial convenient fuels and chemicals. For carbon sequestration, the prices of seize and separation are estimated to make up about three-fourths of the total fees of ocean or geologic sequestration. It is therefore important to find out new methods for CO<sub>2</sub> separation [11, 12]. Adsorption is one of the promising strategies that need to be relevant for setting aside CO<sub>2</sub> from gasoline mixtures, and several lookups have been performed on separation of CO<sub>2</sub> with the useful resource of adsorption in the final 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 nice materials for CO<sub>2</sub>adsorption in modern-day times. However, it is challenging to avoid the shortage of the activated carbon raw fabric due to the fact of the dwindling of the world's forests and coal resources. Therefore, it has step by step emerge as a hot research to discover special raw substances for activated carbon preparation. Biomass is an ample and renewable electricity source. It contains much less Sulphur and ash however extra hydrogen than coal. Because of zero CO<sub>2</sub> emission characteristics, biomass therefore is possibly to be an alluring smooth enchancement mechanism choice for decreasing greenhouse gas emission. Rice husk is one of the most essential agro- based totally absolutely biomass

produced in large quantities in developing international locations like India and China. Rice husk useful resource is significant in India, but the rice husk utilization and conversion price are low and the environmental pollution is serious. Rice husk has excessive content material of constant carbon and can be used as a unique uncooked material for the training of activated carbon [18-19]. As a area of our persevering with effort in the development of the floor change on activated carbon to expand CO<sub>2</sub> adsorption functionality at excessive temperatures, consequences of the usage of Mono Ethyl Amine (MEA), Di Ethyl Amine (DEA) and Poly Ethylene Imine (PEI) as modification retailers had been investigated. In this discover out about ash was as soon as organized at 600<sup>0</sup>C temperature beneath nitrogen+steam ecosystem from rice husk named as RHNS-6, which used to be 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 suitable polymer with its affinity in the path of fuel molecules, broadly speaking CO<sub>2</sub>molecule due to the truth there are many nitrogen atoms in the molecule to react with CO<sub>2</sub> [20]. All these samples are subjected to characterization research and CO<sub>2</sub> adsorption research

## 2. Materials and methods :

### Preparation of Activated Carbons from rice husk:

A tubular furnace for carbonization provided with temperature programmer was used to prepare activated carbons. 10 g of dried rice husk was heated in the furnace under nitrogen atmosphere at 10<sup>0</sup>C/min.

from room temperature to a 600<sup>0</sup>C and maintained for an hour. After carbonization, the furnace was cooled to room temperature under continuous flow of nitrogen

to avoid post-oxidation process. Thus produced solids

were washed with hydrochloric acid (1M) followed by thorough washing with hot distilled water to remove chloride ions and other residues until the pH became neutral. The purified solids were dried at 110<sup>0</sup>C for 10 hr. Thus produced biochar is activated by using H<sub>3</sub>PO<sub>4</sub> reagent to modify surface properties. 5 gr. of this bio char is first impregnated with 30 wt. % H<sub>3</sub>PO<sub>4</sub> and then heated at 250<sup>0</sup>C under air for 2 hr. Then the same

sample is subjected to heating at 600<sup>0</sup>C under nitrogen atmosphere for activation. This sample is named as RHAC.

### *Amine incorporated Rice Husk Ash (RHA)*

Amine incorporated rice husk activated carbon (RHAC) was prepared by wet

impregnation method. Briefly, desired quantity of MEA was dissolved in anhydrous methanol then rice husk activated carbon prepared at different temperatures under N<sub>2</sub> atmosphere was added with vigorous stirring for 30 mins followed by drying at room temperature in nitrogen protection and vacuum drying at 110<sup>0</sup>C 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/RHAC-T, where x represents the weight percentage of MEA and T represents the temperature in multiples of hundred (<sup>0</sup>C). In similar procedure DEA and PEI were also impregnated on rice husk ash samples.

### **Characterization and activity studies**

All the Rice Husk activated carbon samples organized in extraordinary atmospheres at special temperature stipulations had been characterised for BET Surface area, Pore extent and FTIR techniques. The activities for these samples are evaluated with the aid of using a metallic reactor interlaced with a fuel chromatograph (Nukon-GC) at 40 ml/min. drift free at distinct temperatures 50<sup>0</sup>C, 70<sup>0</sup>C and 90<sup>0</sup>C. Different temperatures had been implied to study the effect of temperature on CO<sub>2</sub> adsorption capacity. Carbon dioxide adsorption experiment was carried out on a lab made apparatus. 1 gram of the sample was once loaded in steel reactor between the two quartz plugs and pretreated at 473K for 1 hr. in downstream of nitrogen at a glide price of forty ml/min. observed by means of cooling to favored adsorption temperature.



Then a mixture of 10% CO<sub>2</sub> balanced helium used to be exceeded at a flow rate of 40 ml/min. until the adsorbent was saturated. The gas flows were controlled through mass flow controllers and temperature used to be controlled by way of PID controllers. The effluent gases have been analyzed via gas chromatography equipped with a thermal conductivity detector and having poropack Q column (3 meters size and 3 mm ID). The adsorption potential used to be calculated from the breakthrough curve (BTC).

### 3. Results and Discussion

Rice husk activated carbon (RHAC) 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 activated carbon prepared in nitrogen and steam atmosphere at 600°C (RHAC-6) [22]. The surface area, average pore diameters of MEA/RHAC-6, DEA/RHAC-6 and PEI/RHAC-6 loaded with different wt. percentages are measured and listed in Table-1 and displayed in Fig.1. The actual surface area of RHAC-6 is 311.5 m<sup>2</sup>g<sup>-1</sup> 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 suggest that the amount of amines on the rice husk ash does not affect much of the surface

properties

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/RHAC-6	305.5	3.2	300.8	3.2	280.2	3.01	270.1	3.0	250.6	2.91
DEA/RHAC-6	300.2	3.0	295.8	2.81	275.1	2.83	269.6	2.76	245.8	2.39
PEI/RHAC-6	298.5	2.7	280.3	2.69	275.1	2.52	260.6	2.70	230.8	2.62

- Wt.% indicates the amineloadings

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

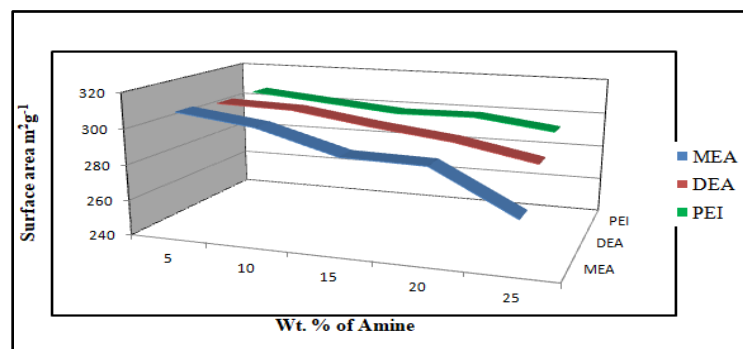


Fig.1 Surface area of modified RHAC samples with amines

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<sup>-1</sup> 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 contain NH<sub>3</sub> group [23]. The band at 2000 cm<sup>-1</sup> 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  $2000\text{ cm}^{-1}$  is due to the presence of aliphatic groups of the adsorbed long chained PEI [24]. Other bands  $2833, 2960\text{ cm}^{-1}$  correspond 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  $4000\text{ cm}^{-1}$  are possibly due to the presence of surface hydroxylic groups and chemisorbed water [25]. These results confirm that PEI was successfully loaded when compared to MEA and DEA

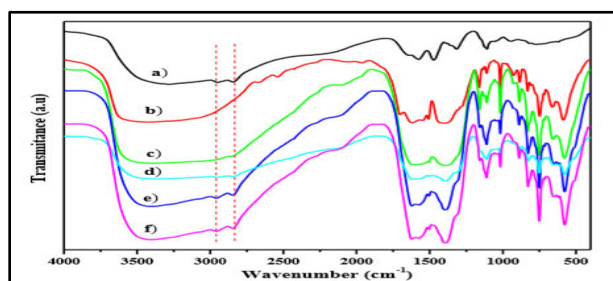


Fig.2. FT-IR patterns of a) 15 MEA/RHAC-6 b) 20 MEA/RHAC-6 c) 15 DEA/RHAC-6 d) DEA/RHAC-6 e) 15 PEI/RHAC-6 f) 20 PEI/RHAC-6

### Effect of amine loading on CO<sub>2</sub> 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<sub>2</sub> on modified RHAC-6 samples at 50°C and 0 to 1 atm pressure. It can be seen that the amounts of CO<sub>2</sub> adsorbed on all modified RHAC-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<sub>2</sub> adsorption. This may also be 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<sub>2</sub> to diffuse in to the pores. More importantly it is observed that the pure RHAC-6 has higher CO<sub>2</sub> adsorption capacity [26] than the PEI modified RHAC-6.

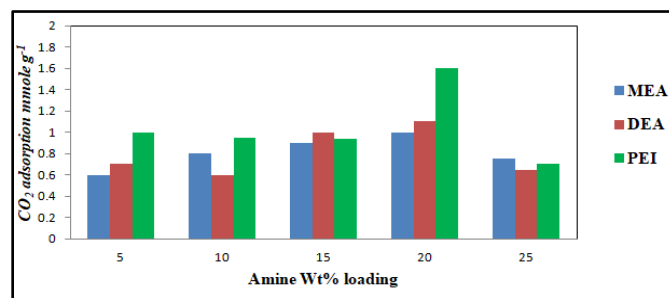


Fig.3 CO<sub>2</sub> adsorption (BTC) on modified RHAC-6 samples with MEA, DEA, PEI amine groups

### Effect of Temperature on carbon dioxide adsorption:

At 50°C pure RHAC-6 sample shows more CO<sub>2</sub> adsorption than PEI modified a sample which is shown in Fig.4. As temperature increases the PEI modified RHAC-6 shows higher adsorption capacities that the pure support at the same temperature. The Fig.5 & 6 shows the

isotherms of CO<sub>2</sub> on pure RHAC-6 and 20 wt. % PEI loaded on RHAC-6 at 70<sup>0</sup>C & 90<sup>0</sup>C and 0 to 1 atm pressure. It can be clearly observed that the amounts of CO<sub>2</sub> adsorbed on 20 wt. % PEI modified sample is more than pure RHAC-6 sample. In the beginning, the adsorption capacities of all samples are very close.

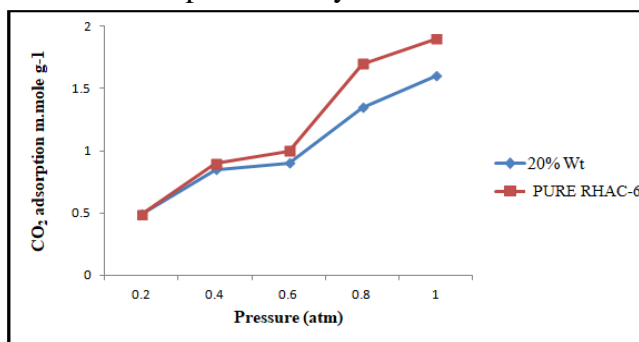


Fig.4.CO<sub>2</sub> adsorption isotherms of pure RHAC-6 & PEI modified RHAC-6 in different wt. % loadings at 50<sup>0</sup>C

When the pressures are increased, the adsorption capacities of the RHAC-6 modified with PEI up to 20 wt. % is significantly higher though the surface area and pore volume are lower than the pure RHAC-6. It implies that chemical adsorption dominates the CO<sub>2</sub> adsorption on the modified RHAC-6. The results confirm that the increase in the temperature facilitates the transfer of the adsorbed CO<sub>2</sub> molecules from the surface in to the bulk of PEI by overcoming physical adsorption. On the other hand, further increase in temperature above 90<sup>0</sup>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 RHAC-6 at 90<sup>0</sup>C and are close to the adsorption capacities at 70<sup>0</sup>C. The notable point is that the modified PEI 20 wt. % sample at 50<sup>0</sup>C has higher CO<sub>2</sub> adsorption capacity than that at 70 and 90<sup>0</sup>C.

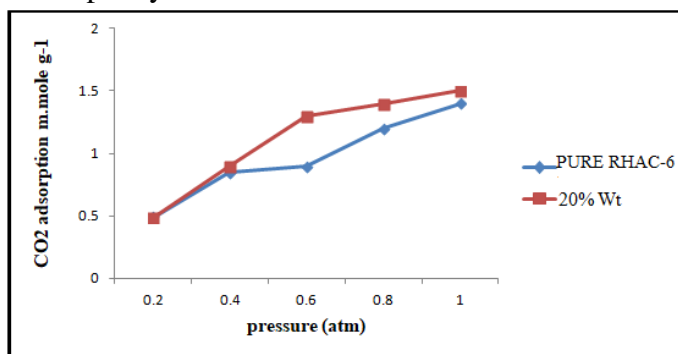


Fig.5 CO<sub>2</sub> adsorption isotherms of pure RHAC-6 & PEI modified RHAC-6 in different wt. % loadings at 70<sup>0</sup>C

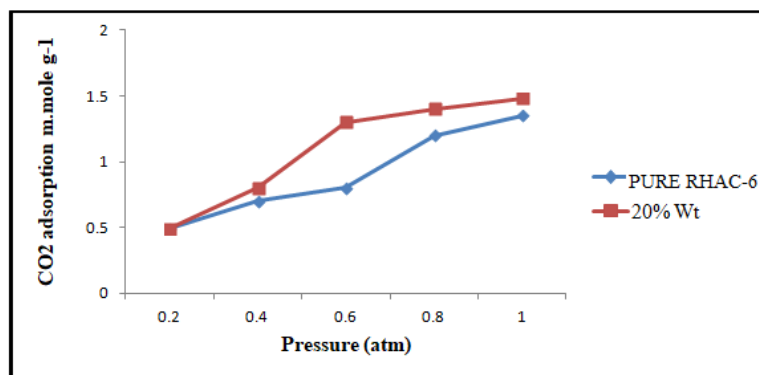


Fig.6 .CO<sub>2</sub> adsorption isotherms of pure RHAC-6 & PEI modified RHAC-6 in different wt. % loadings at 90<sup>0</sup>C.

#### 4. CONCLUSION

The amine modified RHAC-6 has been synthesized in laboratory for carbon dioxide adsorption studies with low cost



methods. CO<sub>2</sub> 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<sup>0</sup>C pure RHAC-6 shows more adsorption than modified samples. But the 20 PEI/RHAC-6 samples show higher CO<sub>2</sub> adsorption capacity than pure RHAC-6 at 70<sup>0</sup>C and 90<sup>0</sup>C temperature. From this it can be concluded that the adsorption capacities of PEI modified samples can be enhanced at higher temperatures.

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## 6. REFERENCES

- [1] W. Jianwen, L. Lei, X. Yu, Z. Pei, S. Yao, Capture of carbon dioxide by amine-impregnated as-synthesized MCM-41, *J. Environ. Sciences*, 22(10):1558-63, 2010.
- [2] E. S. Kikkinides, R. T. Yang, S. H. Cho, Concentration and recovery of carbon dioxide from flue gas by pressure swing adsorption *Ind. Eng. Chem. Res.* 32 (11), 2714–2720, 1993
- [3] K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R.A. Pierotti, J. Rouquerol, T. Siemieniewska, Reporting Physisorption Data For Gas/Solid Systems With Special Reference To The Determination Of Surface Area and Porosity *J. Pure. Appl. Chem.* 57(4), 603-619, 1985.
- [4] F. Su, C. Lu, S. C. Kuo, W. Zeng, Adsorption of CO<sub>2</sub> on Amine-Functionalized Y-Type Zeolites *Energy Fuels* 24(2), 1441–1448, 2010.
- [5] O. Leal, C. Bolivar, C. Ovalles, J. J. Carcia, Y. Espide, Reversible adsorption of carbon dioxide on amine surface-bonded silica gel *Inorg. Chim. Acta.* 240(1-2), 183-189, 1995.
- [6] F. Junpei, Y. Katsunori, Carbon Dioxide Adsorption onto Polyethylenimine-Functionalized Porous Chitosan Beads, *Energy Fuels* 28, 6467-6474, 2014.
- [7] H. G. Aliakbar, B. Youssef, S. Abdelhamid, Polyethylenimine-impregnated mesoporous silica: effect of amine loading and surface alkyl chains on CO<sub>2</sub> adsorption, *Langmuir*, 27(20), 12411-12416, 2011.
- [8] W. J. Son, J. S. Choi, W. S. Ahn, Adsorptive removal of carbon dioxide using polyethyleneimine-loaded mesoporous silica materials, *Micro. Mesopor. Mater.* 113, 31-



- 40,2008.
- [9] C. C. Chen, W. J. Son, K. S. You, J. W. Ahn, W. S. Ahn, *Chem. Eng. Jour.* 161 (2010)46.
- [10] X. Yan, L. Zhang, Y. Zhang, K. Qiao, Z. Yan, S.Komarneni, Amine-modified mesocellular silica foams for CO<sub>2</sub> capture, *Chem. Eng. Jour.* 168(2),918-924,2011.
- [11] Song.C., Gaffney, A.M., Fujimoto, K., Eds: CO<sub>2</sub> conversion and utilization: ACS symposium series, American Chemical Society (ACS): Washington, DC.: Vol.809, 448 pp,2002.
- [12] Maroto-Valer, M.M., Song.C., Song, Y., Eds. Environmental Challenges and Greenhouse Gas Control for Fossil Fuel Utilization in the 21<sup>st</sup> Century, Kluwer Academic/Plenum Publishers: New York,447 pp 2002.
- [13] Ma, Y.H.:Mancel.C. Diffusion Studies of CO<sub>2</sub>, NO, NO<sub>2</sub> and SO<sub>2</sub> on Molecular Sieve Zeolites by Gas Chromatography, *AIChE J.* 18(6),1148-1153,1972
- [14] Ma.Y.H.:Roux.A.J. *AIChE J.* 1973. 19.105-109.Hayhurst, D.T. *Chem.Eng.Commun.* 1980, 4,729-735
- [15] Han.C.: Harrison, D.P. Simultaneous shift reaction and carbon dioxide separation for the direct production of hydrogen, *ChemEng.Sci.* 49, 5875-5883,1994.
- [16] Kapoor.A.:Yang.R.T. Kinetic Separation of Methane-Carbon Dioxide Mixture by Adsorption on Molecular Sieve Carbon, *Chem.Eng.Sci.* 44 (8),1723-1733,1989.
- [17] DimitriosKalderis, Sophia Bethanis, PanagiotaParaskeva, Production of activated carbon from bagasse and rice husk by a single-stage chemical activation method at low retention times [J], *Bioresource Technology*, 99:6809-6816,2008.
- [18] K.Y. Foo, B.H. Hameed, Utilization of rice husks as a feedstock for preparation of activated carbon by microwave induced KOH and K<sub>2</sub>CO<sub>3</sub> activation [J], *Bioresource Technology*, 102: 9814-9817,2011
- [19] Aroua, M.K., Daud, W.M., TA.W., Yin.C.Y, and Adinata, D. Adsorption capacities of carbon dioxide, oxygen, nitrogen and methane on carbon molecular basket derived from polyethyleneimine impregnation on microporous palm shell activated carbon. *Separation and Purification Technology*, 62,609-613,2008.
- [20] Y. Lin, H. Lin, H. Wang, Y. Suo, B. Li, C. Kong, L. Chen, J. Mater. Chem. A 2 (2014)14658.
- [21] B.N.Srinivas et al. Study of physical properties of Bio-Waste materials like rice husk ash prepared in different atmospheres and temperatures, *International Journal of Recent Innovation in Engg. and*



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