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Preparation of Surface Modified Activated Carbons from Rice Husk and CO_2 Adsorption Studies

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Abstract:*Rice husk is an agricultural biomass used to produce low-cost activated carbon using chemical activating reagents. The aim of this study is to find out the surface changes occurring in rice husk during activation with phosphoric acid (H_3PO_4) and ammonium hydrogen phosphate $(NH_4)_2HPO_4$. The surface area and pore volumes of the formed phosphoric acid treated rice husk activated carbon (RHPAC) and ammonium hydrogen phosphate treated rice husk activated carbon (RHAAC) were determined by BET method. Fourier transform infrared (FT-IR) spectroscopic analysis identified the presence of carbonyls, alkenes and hydroxyl groups. Powder X-ray diffraction (XRD) analysis indicated the appearance of broad diffraction background revealed predominantly amorphous structure. Amine impregnations were carried out on RHPAC and RHAAC activated carbons by using tetra ethylene penta amine (TEPA) for CO_2 adsorption studies. Effect of temperature on adsorption of CO_2 was carried out on all modified activated carbons. With increase in temperature the extent of adsorption increased up to 70^0C and beyond that temperature adsorption decreases. The stability of best catalyst TEPA-RHACC was also studied by carrying adsorption-desorption studies on same catalyst up to 5 cycles, which has shown a decrease in adsorption by 10%.*

Keywords:*Rice husk, Activated carbons (AC), CO_2 adsorption, TEPA*

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I. Introduction

It is well known that carbon dioxide is strongly adsorbed at room temperature on microporous solids having pores with diameters close to the diameter of adsorbate by a factor of 2-5, such as activated carbons and zeolites [1, 2]. The physical and surface chemical properties of activated carbons can be modified by several different heat treatments and impregnation procedures [3-5].Activated carbons (AC) are made from materials rich in carbon through carbonization and an activation process. A porous structure and its adsorption properties can be obtained in carbonaceous materials via either chemical or physical [6] activation. Physical activation involves pyrolysis of the source material at 800ºC -1000ºC to produce charcoal. This is then followed by activation using steam, carbon dioxide (CO_2) or oxygen (O_2). Chemical activation involves the impregnation of the precursor material with a chemical activating agent followed by activation at temperatures of 400ºC-700ºC under nitrogen atmosphere [7]. Zinc chloride ($ZnCl_2$), potassium hydroxide (KOH) and phosphoric acid (H_3PO_4) are widely used as chemical activating agents. The activating chemical agents influence the pyrolytic decomposition and inhibiting formation of tar and volatile matter, thus enhancing the yield of activated carbon [8]. The dehydration and oxidation characteristics of chemical activation agent require much lower activation temperature compared to physical activation [9]. A comparative study of chemical (H_3PO_4) and physical activation using biomass fiber as AC has been reported [10]. The research found that the surface area recorded by physical activation was slightly higher than chemical activation but lower in terms of yield. The carbonization of biomass at high temperature would trigger the emission of higher greenhouse gaseous (GHG) such as carbon monoxide and methane [11] which leads to drastic damage to environment.There has been remarkable interest in the production of AC due to its adsorptive, environmental, thermal, electrical and mechanical characteristics [12-13]. It is proof from previous study that AC is one of the leading industrial materials due to its well developed pore structure and adsorption properties [14-16]. Recent developments in modern technologies have resulted in various novel applications of AC. Coal-based AC is the most common adsorbent used, however, it is costly and not sustainable. Abundant low cost agriculture biomass, which contain high amounts of natural polymers such as cellulose, hemicellulose, and lignin, are suitable alternative materials to produce low-cost and green adsorbents with necessary modification to enhance its efficiency[17]. Various studies on the production of AC have been done by applying different agricultural biomass including rice husk [18-23]. This study is focused on preparing activated carbons from rice husk by using reagents like phosphoric acid and ammonium hydrogen phosphate to improve textural properties. These activated carbons are then functionalized with tetra ethylene penta amine for amine incorporation to increase basic sites on the surface. Later amine incorporated activated carbons were used for CO_2 adsorption studies.

II. Experimental methodology

2.1. Raw materials

The rice husk sample was obtained from Krishna district, Andhra Pradesh, India. Phosphoric acid (H_3PO_4), Ammonium hydrogen phosphate $(NH_4)_2HPO_4$ and Sodium Hydroxide (NaOH) were analytical grade obtained from Merck (M) India.

2.2. Sample preparation

Preliminary washing of the raw materials with hot distilled water was carried out and dried in an oven at 110°C for 24 h to remove all moisture. The dried samples were cut into small pieces, sieved to 40 mesh size particles and stored in air-tight containers. Chemical activation was carried out by initially carbonizing the precursor in a tubular furnace under inert atmosphere from room temperature to carbonization temperature of 400°C for 1 hour. The resulting char was labelled as RHAC.

2.2.1 Preparation of RHPAC

RHAC was subsequently impregnated with 30% ortho-phosphoric acid (H_3PO_4) with impregnation ratios of 1:5 (w/w) and soaked for 24 h. Then the sample was filtered using a vacuum pump and dehydrated overnight in an oven at 110°C. The dried sample was then pyrolysed for activation at temperatures of 600°C. After the activation period of 1 hour the sample was allowed to cool down to the room temperature. The resultant activated carbon was labelled as RHPAC, washed with 1.0 M NaOH and successively rinsed with hot distilled water followed by cold distilled water until the filtrate reached a stable pH of 6.5-7. The samples were then dried in an oven at 110ºC for 24 h.

2.2.2 Preparation of RHAAC

5 gr of RHAC is impregnated with 30 wt. % of $(NH_4)_2HPO_4$ and then heated at 250^0C under air for 2 hr. Then the same sample is subjected to heating at 600^0C under nitrogen atmosphere for activation. This sample is named as RHAAC.

2.2.3 Preparation of catalysts

1 mmol of tetraethylenepentamine (TEPA) was dissolved in 20 ml of dry toluene, stirred for 30 min then 1 gm of RHPAC was added to the reaction mixture followed by refluxing for 12 h. The resulting material was filtered, washed with dry toluene, ethanol and dried at 373 K overnight. During this process, the unsaturated sites of RHPAC were functionalized with tetraethylenepentamine and this material has been denoted as TEPA-RHPAC. In similar method TEPA-RHAAC was also prepared by using RHAAC activated carbon.

III. Results and discussions

3.1 BET Surface area and Pore volume

The textural parameters of all activated carbons prepared from rice husk are shown in Table-1 and variation of surface area after chemical treatment of activated carbons is shown in Fig.1. The BET surface area of RHAC 863.2 m^2g^{-1} and its average pore size is 2.9 nm. After phosphoric acid treatment the surface area is drastically increased to 1408 m^2g^{-1} which indicates the opening of micropores during acid treatment and expelling of organic volatile matter. But the increase in surface area is slightly less when treated with ammonium hydrogen phosphate. After amine modification of activated carbons with TEPA the surface area is decreased due to occupation of part of surface by amine groups and also due to pore blockage.

3.2 X-ray diffraction patterns

Fig.2 shows the XRD patterns of RHAAC, RHPAC, TEPA-RHPAC, and TEPA-RHAAC. As the rice husk samples are activated in air and nitrogen atmosphere, there is no clear evidence for SiO_2 peaks. The diffraction patterns of RHAC are in line with previous report [24].The XRD pattern of TEPA-RHPAC, TEPA-RHAAC is same as that of RHAAC, RHPAC which indicates the structure is intact after amine modification. The intensity of peaks was decreased due to attachment of amine group [25].

3.3 FT-IR analysis

The qualitative characterization of surface functional groups of activated carbon samples was performed by FTIR technique. Fig.3 shows FT-IR spectra of TEPA, TEPA-RHPAC, and TEPA-RHAAC have shown similar shapes with most of the bands located on the same wave number range. The bands at 2968 and 2854 are attributed to C-H stretching of aliphatic carbon which indicates that RHPAC and RHAAC are functionalized with TEPA. The band at 1523 corresponds to the C=O group vibration of carboxyl or anhydride groups [26]. The bands at 1412 are assigned to vibration in aromatic skeleton generally found in carbonaceous material, such as activated carbons [27].

3.4 Thermogravimetric analysis

Fig.4 shows thermo gravimetric analysis of TEPA, TEPA-RHPAC and TEPA- RHAAC. Figure-4 (a) indicates the decomposition of TEPA below 250^0C. Whereas TEPA-RHPAC and TEPA- RHAAC decomposes in the temperature range of 550-650^0C due to the decomposition of volatile organic matter.

IV. CO_2 adsorption analysis

Carbon dioxide adsorption experiments were carried out under dynamic conditions using 10% CO_2 balance helium. The typical procedure was as follows. 0.5 gm of adsorbent was packed between the two quartz plugs in a tubular reactor with an inner diameter of 10 m.m and length 200 m.m and the catalyst was pretreated at 200 °C for 1 hr. in a downstream of N_2 flow at a rate of 40 ml/min followed by cooling to the desired adsorption temperature. Then N_2 flow was replaced with binary mixture (CO_2 + He) at a rate of 10 ml/min until the adsorbent was saturated. The CO_2 concentrations in the influent and effluent gas streams was analyzed at regular intervals using gas chromatograph (Nucon, India) equipped with a packed porapak Q column (2 m length and 3 mm ID) and TCD detector. The adsorption capacity of the adsorbent was calculated by the integration of the area of breakthrough curve, CO_2 concentration in the inlet gas, flow rate, saturation time and mass of the adsorbent. After adsorption, the sorbent was heated to 200 °C for 1 hr. for regeneration. Several CO_2 adsorption – desorption cycles were conducted on the adsorbent for testing of stability of the material.

4.1 Effect of Tetra Ethylene Penta Amine (TEPA) functionalized activated carbons on CO_2 adsorption

CO_2 adsorption studies were carried out by following above described method on all activated carbon samples. Break through adsorption capacity of all the samples at different temperatures (40, 70, 90^0C) were shown inFig.5.At 40^0C, the least CO_2 adsorption capacity is observed for RHAC is 0.42mmol/g as it was a pure activated carbon with low surface area and without any basic sites incorporation. At same temperature, highest activity 0.86 mmol/gr was shown by TEPA-RHAAC sample, though the surface area of TEPA-RHAAC is lesser than TEPA-RHPAC. This can be attributed to more number of basic sites incorporated and better functionalization of TEPA on the surface ofTEPA-RHAACsample. Thehighest adsorption capacities are shown by TEPA-RHAAC sample which are recorded as 0.86mmol/gm at 40^0C, 1.56 mmol/gm at 70^0C and0.94 mmol/gm at 90^0C respectively. The adsorption capacity increases with increase in temperature up to 70^0C due to high mobility of amine groups in the interior of the adsorbent which are responsible for showing higher adsorption of CO_2. Further increase of temperature decreases the CO_2 adsorption due to weak interaction between the CO_2 and amine group and promotes desorption of captured CO_2. Therefore, 70^0C is the optimum temperature for amine functionalized adsorbents. Primary and secondary amines are readily react with$CO_2$to form stable carbamate shown in equation 1 and 2[28-29].

$$\mathrm{CO_2 + 2RNH_2 \rightarrow NH_4^+ + R_2NCOO^-}\text{……… (1)}$$

$$\mathrm{CO_2 + 2R_2NH \rightarrow R_2NH_2^+ + R_2NCOO^-}\text{…… (2)}$$

4.2Effect of moisture

Moisture plays an importantcomponent role in the flue gas and water is proton transfer agent in the reaction of CO_2 and amine group. Therefore, influence of moisture in the adsorption of CO_2 has been studied. The sorption break through with 10% CO_2 balanced helium along with moisture and without moisture has been studied over TEPA-RHAAC at 70^0C. The adsorption capacity of TEPA-RHAAC in the presence of moisture is 1.89 mmol/gm, whereas in dry condition it shows a value of 1.56 mmol/gm. The results indicate that moisture plays an important role in the adsorption of CO_2. Generally two moles of amine group of TEPA-RHAAC react with one mole of CO_2 to form carbamate in anhydrous condition. But in case of water one mole of amine reacts with one mole of $CO_2$to form ammonium carbonate and carbonate species shown in equation-3 [30-31].

$$\mathrm{CO_2 + RNH_2 + H_2O \leftrightarrow RNH_3^+ + HCOO^-}\text{…….. (3)}$$

4.3 Recyclability

Recyclability of adsorbent is an important factor in capture of CO_2. The initial adsorption capacity of TEPA-RHAAC is 1.56 mmol/g. Recyclability has been carried out up to 5 cycles, there is 10.2% drop of adsorption capacity and the uptakes are shown in Fig.6.

IV. Figures and tables

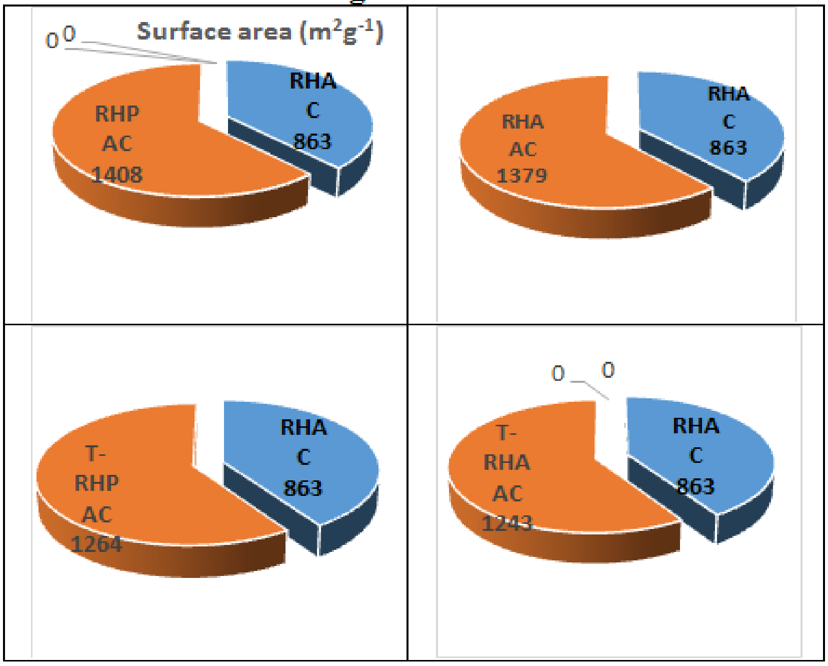

Fig.1 Variation of surface area of activated carbon after chemical treatment

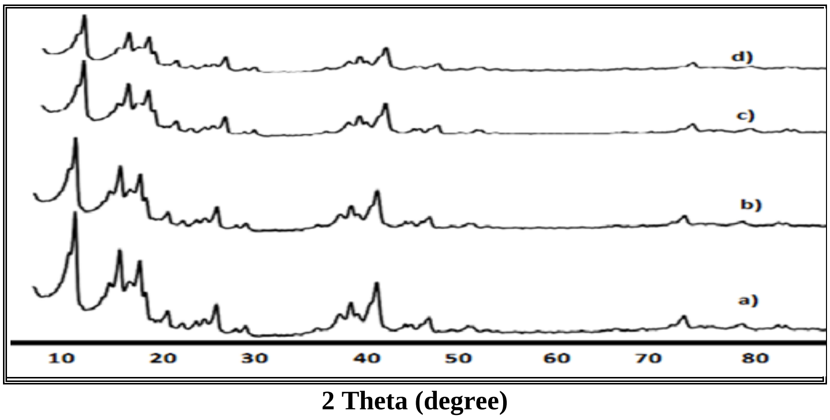

Fig.2: XRD Patterns Of A) RHAAC B) RHPAC C) TEPA-RHPAC D) TEPA-RHAAC

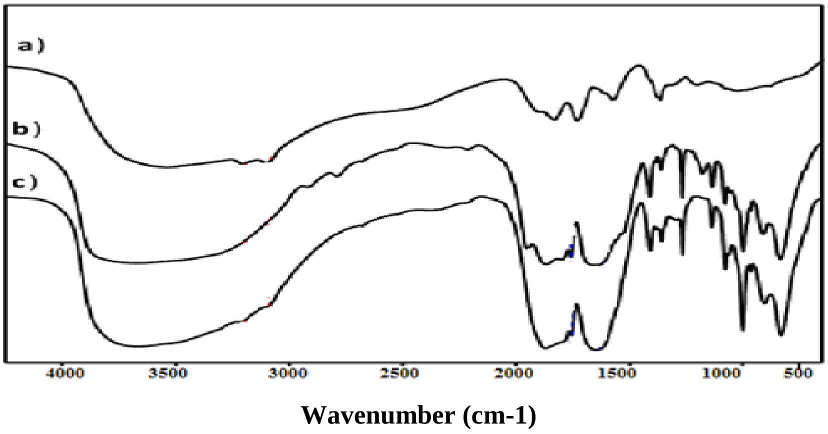

Fig.3:FT-IR Patterns of A) TEPA, B) TEPA-RHPAC C) TEPA- RHAAC

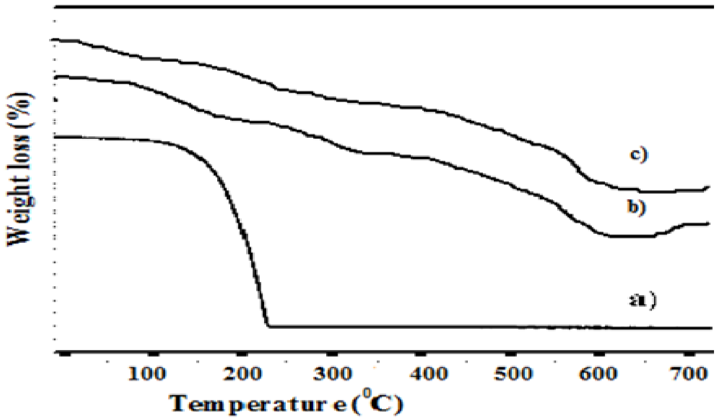

Fig.4: Thermo gravimetric analysis of a) TEPA b) TEPA-RHPAC c) TEPA- RHAAC

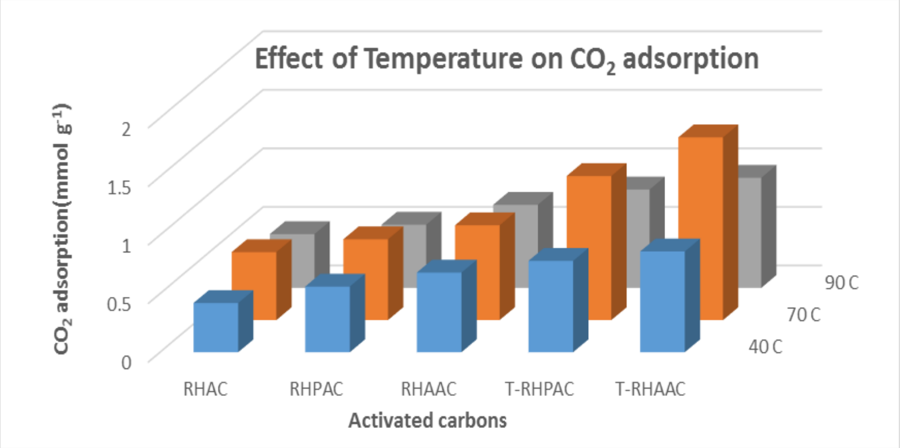

Fig.5 Effect of temperature on CO_2 adsorption

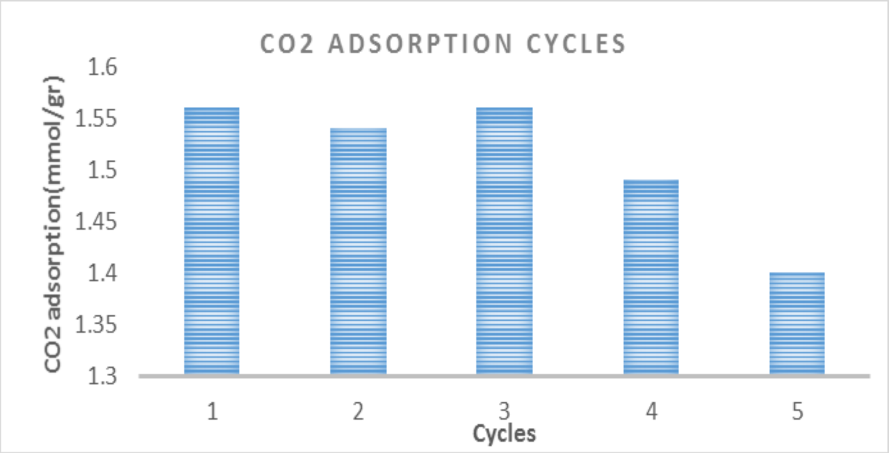

Fig.6 Recyclability of TEPA-RHAAC catalyst

Table:1 Surface area and average pore size distribution of activated carbons

S.No.	**Activated Carbon**	**Surface Area (m^2g^{-1})**	**Average pore size (nm)**
1	RHAC	863.0	2.9
2	RHPAC	1408	3.2
3	RHAAC	1379	3.01
4	TEPA-RHPAC	1264	2.76
5	TEPA-RHAAC	1243	2.69

V. Conclusions

Activated carbons are prepared from rice husk by treating with phosphoric acid and ammonium hydrogen phosphate. Both the samples have shown good improvement in surface properties. The surface area is almost enhanced by 62% but there is no much change in average pore size distribution. CO_2 adsorption studies on Rice husk activated carbons have been carried out and the adsorbents are characterized by BET, XRD, FT-IR and TGA. Non impregnated activated carbons shows low CO_2 adsorption. Modification of RHAC with tetraethylenepenta amine, decreases the BET surface area and pore volume due to attachment of amine group to the active site of RHAC is observed. CO_2 adsorption have been done on all adsorbents under volumetric conditions. TEPA-RHACC has shown an adsorption capacity of 1.56mmol/gm at 70^0C. Presence of moisture increases the adsorption capacity of TEPA-RHAAC to 1.89mmol/g. The adsorbent shows the recyclability with a marginal 10% loss of adsorption capacity up to 5 cycles. The loss in adsorption capacity due to cyclic adsorption desorption procedures can be overcome with further stabilization of the surface of activated carbons with Helium treatments. The rate of adsorption increases with increase in temperature up to 70^0C and beyond that there is decrease in adsorption is noted. From this in can be concluded that 70^0C temperature is an optimum temperature for adsorption of CO_2 on activated carbons.

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