

Carbon Dioxide Adsorption Studies of Rice Husk Ash Prepared in Different Atmospheres

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ABSTRACT: The existing Carbon dioxide adsorption methods are environmental unfriendly procedures hence forth researchers are in search for new materials and technologies, that are both ecologically safe, inexpensive and able to fulfill its role with little pre-processing is growing. One interesting approach is employing agro bio-waste as adsorbents for CO₂ adsorption which is alarming cause for global warming. Rice husks from local areas are collected and washed with distilled water and subjected to calcination at different temperatures under different atmospheres. Among all the samples Rice husk calcined at 600⁰C in nitrogen and steam is showing promising results interms of texture as well as adsorption of CO₂. All the samples are characterized for measuring surface area, pore diameter, X-Ray diffraction studies, FTIR. The adsorption break through with 10% CO₂ balanced helium at 70⁰C for all the samples are studied. RHNW-6 has shown maximum break through adsorption capacity of 0.86 mmol g⁻¹. Recyclability has been carried out up to 10 cycles.

KEY WORDS: X-Ray Diffraction, Carbon Capture and Sequestration, Calcination, Adsorption

I. INTRODUCTION

Prime energy sources of world are mainly 30% coal, 34% oil and 24% natural gas. When these substances are burnt CO₂ gas is given off in to atmosphere. Due to these human activities, natural climate is being changed. CO₂ is considered as a carbon reservoir that is increasing in size. The main natural sinks are i) Oceans ii) Plants and other organisms that use photosynthesis to remove carbon from the atmosphere by incorporating it in to biomass. The statistics on carbon emission by 2010 shows that China, U.S.A. and Europe are emitting 23.3%, 18.1% and 14.1% carbon dioxide respectively [1]. These three countries are mainly responsible for more than 50% CO₂ emissions worldwide. But U.S.A. is working on CCS-R&D and is successfully capturing 40% CO₂ whereas Europe and China are failing to do so.

Carbon dioxide levels in the atmosphere are rising at a frightening rate with no sign of slowing downbut instead, global temperatures are continuing to rise. The science behind Kyoto was shaky due to the limited availability of crucial data and knowledge at the time, particularly in regard to positive feedback loops in nature being revealed that amplify warming and prevent CO₂ from being absorbed. Scientists studying global warming are finding nature fighting back in ways they never contemplated daily. Some countries want to be able to trade in emission rights in carbon emission markets, to make it possible for one country to buy the benefit of O₂ sinks in another country. If overall limits on greenhouse gas emissions are put in to place, such a “cap-and-trade” market mechanism will tend to find most effective ways to reduce emissions. There is as yet no carbon audit regime for all such markets globally and none is specified in the Kyoto protocol. Sequestration involves trapping CO₂ as it is emitted and storing it in huge reservoirs underground or beneath the sea. It is already being used in some countries like Norway, where the carbon helps to force oil out of partly exploited fields [2]. In its broadest sense, sequestration is any means that prevents carbon dioxide from entering the atmosphere. Realistically, this is equivalent to the permanent storage of carbon dioxide independent of the state of CO₂ or the location of storage. Traditionally, carbon sequestration has referred to the carbon stored in biomass, but the definition has come to include the disposal of CO₂ underground or in the ocean, aswell.

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CO₂ STORAGE MATERIALS

In order to sequester the CO₂ emissions, it is necessary to capture and store it in cylinders and transport them to the site where it is going to be sequestered. To enhance the capability of storage in the cylinders one way is to pack CO₂ adsorbents inside the cylinders. This process enables to store more amount of CO₂ in the cylinders. The storage materials generally work on the principle of adsorption or through a chemical reaction. For example carbon dioxide reacts with quicklime (CaO), to form lime stone (CaCO₃). Separation and capture of CO₂ have been studied in recent times by many researchers and the goal of CO₂ separation and capture is to isolate CO₂ from its many sources in a form suitable for transport and sequestration. There are three pathways for CO₂ separation, they are i) pre-combustion decarbonation, ii) O₂/CO₂ recycle combustion, and iii) post combustion separation [3]. The steam reform of methane is a typical pre-combustion decarbonation process since the fuel is reacted with steam to produce mainly CO and H₂. The CO is processed in a catalytic reactor to give CO₂ and more H₂. The CO₂ is separated and the hydrogen can be used as fuel or in a hydrogen fuel cell [4,5].

Several solid sorbents have been utilized to remove carbon dioxide in post combustion separation processes. Carbon molecular sieve-based material functionalized with amine groups, amine surface-bonded silica gel [6], acrylic ester resin-based solid amine sorbent [7], calcium oxides [8], magnesium silicates, and hydrotalcites [9] are shown to be suitable adsorbents to capture CO₂ in the gas phase. The ability to regenerate an adsorbent and the ease of this regeneration are also important considerations. The need for extreme conditions such as high temperatures or very low vacuum, makes regeneration more complicated and costly.

It has been reported that hydrotalcite is a more suitable adsorbent of CO₂, especially at high temperatures, Hydrotalcites are anionic clays that present layers of positively-charged metallic oxide (or metallic hydroxides) with inter-layer of anions, such as carbonates. These materials have been studied by several authors [4,5,9,10,11,12] for carbon dioxide adsorption, and their applicability in separation-enhanced reaction processes for ethane steam reforming has recently been reported, since these materials adsorb selectively the CO₂ produced by the reactions at high temperature [4,5,12]. The amount of CO₂ removed by hydrotalcite depends on its pretreatment [4] but there is no consensus about the importance of the chemisorptions [13] and the effect of the previous contact with steam or CO₂ [4]. Also the regeneration of these adsorbents is generally difficult since a certain portion of CO₂ could be irreversibly chemisorbed on the material [13]. The increase in atmospheric concentration of carbon dioxide is proving to be detrimental for the environment and will ultimately result in global climate change [14]. It is estimated that since the time of industrial revolution to 2015, atmospheric CO₂ concentration has risen to a value of 401 ppm [15]. This trend will continue to rise if anthropogenic sources of emission are not properly regulated. Different techniques have been proposed in order to capture CO₂ from flue gases on large scale. These techniques include cryogenic distillation, membrane purification, adsorption using liquids and adsorption by employing solid adsorbents [16].

II. RELATED WORK

Rice husk is an important biomass resource in South Asia including India and China. When compared to other agricultural Bio-wastes rice husk is known for low utilization value as husk and highly utilized as ash which is mostly in the form of silica. Organic matter of rice husk can be used as energy source and the inorganic composition has high value added utilization potential. Rice husk ash contains more than 80% of SiO₂(w/w) [17]. Rice husk can also be used as a low-cost CO₂ adsorbent [18].

- i. The major composition of rice husk is silica and several volatile organic compounds (17). By exploring the best surface properties of silica, carbon dioxide adsorption studies are planned to carry out in depth.
- ii. This paper mainly describes the physical characteristics, pyrolysis of rice husk under different atmospheres and their CO₂ adsorption capabilities.
- iii. Surface area and pore volume plays important role in any adsorption studies. Guest molecule CO₂ should fit in to the matrix of the host surface rice husk ash, so CO₂ molecules will hook on to the surface (4).
- iv. Calcination of rice husk at different temperatures in different atmospheres will produce a suitable matrix which removes volatile organic matter. This results in surface exposure due to increase in porosity. Higher the surface area greater will be activity.

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III. MATERIALS AND REAGENTS

The experimental procedure was carried out in three phases: i) Preparation of Rice husk ash samples in different atmospheres at different temperatures ii) Characterization of Rice Husk Ash (RHA) and iii) Carbon dioxide adsorption studies. Rice husk obtained from rice mill near Telaprolu, Vijayawada, India, was washed thoroughly with distilled water to remove adhering soil and dust, and dried at 110°C overnight. Rice husks were calcined at 400°C in pure Nitrogen atmosphere for 4 hours. The temperature was programmed at 10°C per minute and N₂ gas flow maintained at 40 ml per minute. Under same conditions the following samples are prepared.

Table 1: Rice husk samples prepared in different atmospheres and temperatures

S.No.	Sample details	Calcination Temperature	Abbreviation
1	Rice husk+Nitrogen	400 ⁰ C	RHN-4
2	Rice husk+Nitrogen	600 ⁰ C	RHN-6
3	Rice husk+Nitrogen	800 ⁰ C	RHN-8
4	Rice husk+Air	400 ⁰ C	RHA-4
5	Rice husk+Air	600 ⁰ C	RHA-6
6	Rice husk+Air	800 ⁰ C	RHA-8
7	Rice husk+N ₂ +Steam	400 ⁰ C	RHNW-4
8	Rice husk+N ₂ +Steam	600 ⁰ C	RHNW-6
9	Rice husk+N ₂ +Steam	800 ⁰ C	RHNW-8
10	Ricehusk+N ₂ (40ml/min.) + Air(40ml/min.)	400 ⁰ C	RHNA-4
11	Ricehusk+N ₂ (40ml/min.) + Air (40ml/min.)	600 ⁰ C	RHNA-6
12	Ricehusk+N ₂ (40ml/min.) + Air (40ml/min.)	800 ⁰ C	RHNA-8

IV. CHARACTERIZATION

All the Rice Husk Ash samples prepared in different atmospheres at different temperature conditions were characterized for BET Surface area, Pore volume, X-ray diffraction 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 and 70°C temperature. Carbon dioxide adsorption experiment was carried out on a lab made apparatus shown in Fig.1. 1 gram of the sample was loaded in metal reactor between the two quartz plugs and pretreated at 473K for 1 hr in down stream of nitrogen at a flow rate of 40 ml/min. followed by cooling to desired adsorption temperature. Then a mixture of 10% CO₂ 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).

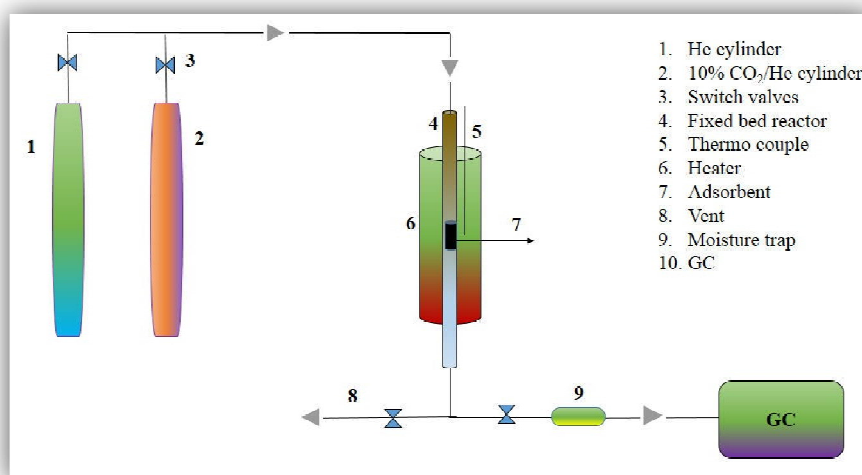


Fig.:1 Schematic diagram of Reactor and GC for CO₂ adsorption studies

4.1 SURFACE AREA AND PORE VOLUME

The surface areas of the samples are shown in Fig.2. It can be noted that the surface areas of all the samples are reasonably high to accommodate required basic groups like OH groups on the matrix of rice husk ash. However, when compared with other series highest surface area was noticed for RHNW series at all temperatures and RHNA series is showing least surface area. It can be seen from Fig.2 that the surface area is gradually increased up to 600^oC and then decreased in all series. The lowering of surface area beyond 600^oC temperature may be due to blockage of small pores by the active components. This can be further clarified by examining the pore volumes. It can be seen from Fig.3 that the pore volume increases with increase in calcination temperature. This may be due to evaporation of volatile matter from the matrix of rice husk. But variation of average pore diameter in all these samples is marginal.

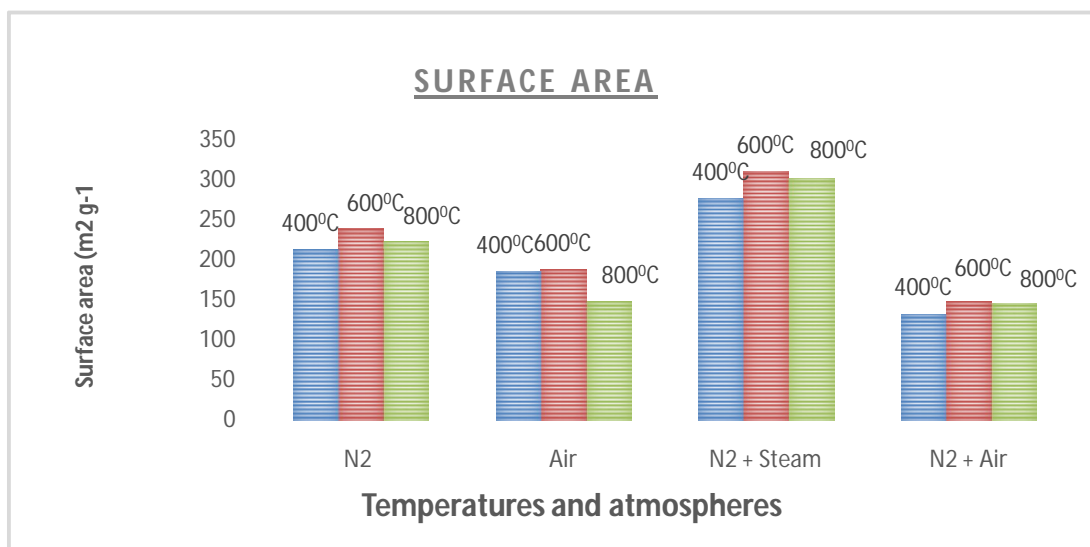


Fig.: 2 Variation of Surface are of Rice Husk ash sampleswith increase in temperature in different atmospheres

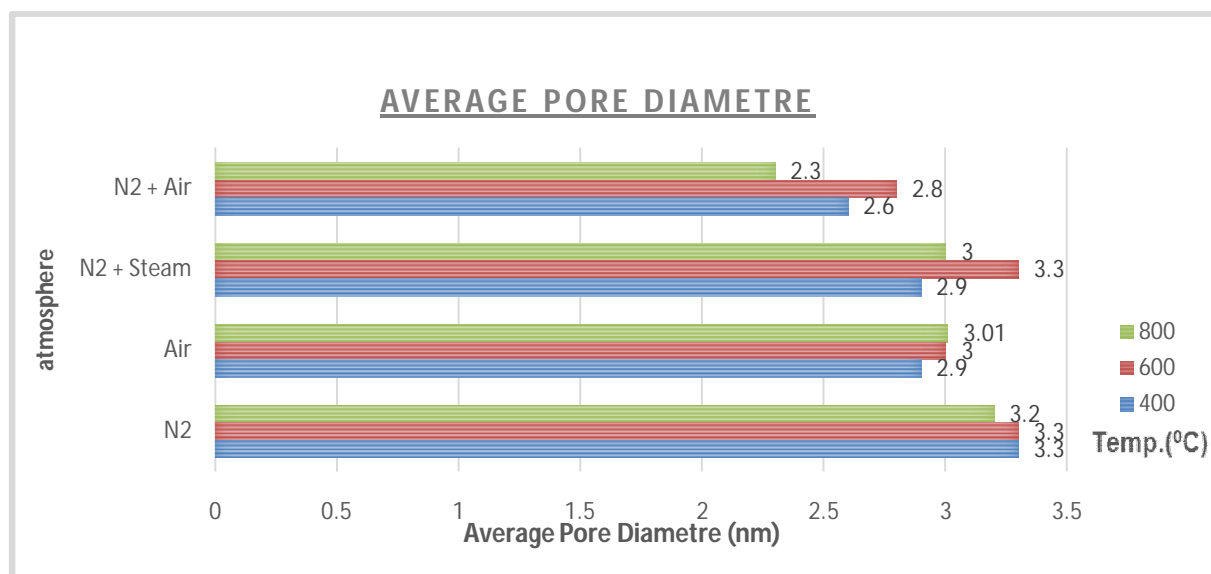


Fig.:3 Variation of average pore diameter of different rice husk ash samples at different temperatures

4.2 X-RAY DIFFRACTION

XRD is a useful technique for identifying various phases of composite materials in rice husk ash especially silica. Diffraction pattern of the treated ash confirmed the presence of silica and observed to be the major phase in the adsorbent. Silica was found to be the only major constituent as shown by the highest peak located and some other elements were also observed but in traces, as shown by small peaks (Fig 4). The sharp peaks observed here and there indicates the traces of cristobalite, a crystalline phase of silica at 30-50 2-theta degree at high temperatures. The X-ray diffractogram of the RHN-4, RHNA-4 and RHNW-8 powders were observed in Fig.4. There is no difference in XRD patterns of the RHNW-4, RHN-6, RHNA-6, RHNW-6, RHN-8 and RHNA-8 and yielded amorphous patterns of silica and no other impurities were detected. These peaks confirmed that silica is mostly amorphous in nature. Earlier studies have proven that RH silica nanoparticles have an amorphous nature [19,20].

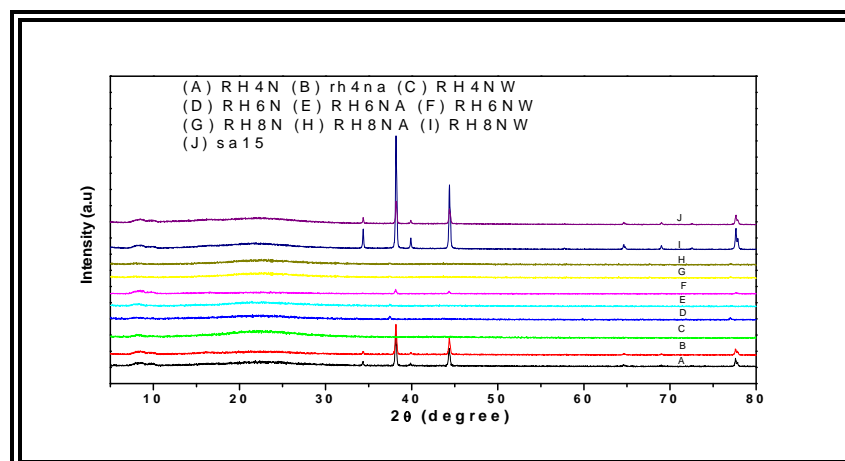


Fig.:4 X-ray diffraction studies

4.3 FT-IR STUDIES

FT-IR patterns of all the rice husk samples calcined at different temperatures and in different atmospheres are shown in Figure-5. The stretching frequencies of (Si-O-Si) near 1205, 1410 cm^{-1} and 1743 cm^{-1} confirm the presence of -OH groups within framework. The stretching and bending vibrational bands in the range of 1800 - 1200 cm^{-1} correspond to carbon-silica composite materials. The small bands around 3000 cm^{-1} confirm the presence of water molecule in the framework [21] and the framework is intact. All these bands indicates the significant effect of thermal treatments on the functionality of the samples. The most obvious change is the sharpness of peaks observed at 600 $^{\circ}$ C temperature. These bands increase with increasing sintering temperatures, confirming the existence of SiO_2 and other impurities like MgO, Al_2O_3 etc. as suggested in previous studies [22,23] even at high temperatures FT-IR spectra showed characteristic bands in the region of 1800-1200 cm^{-1} without any much change in the basic structure of rice husk samples.

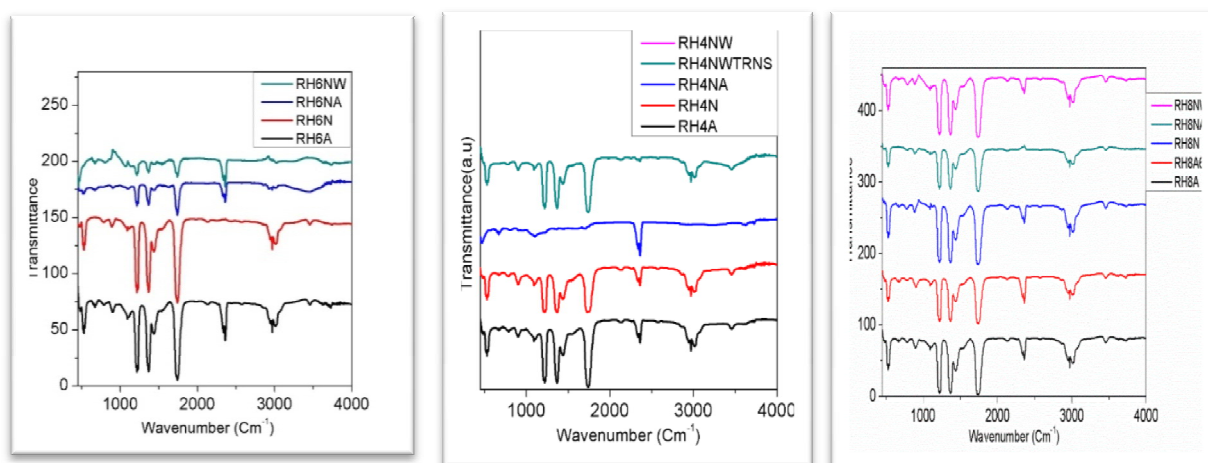


Fig.:5 FT-IR Spectra of Rice husk samples prepared at different temperatures and atmospheres

V.CO₂ ADSORPTION STUDIES

Figure-6 shows CO₂ adsorption capacities of different rice husk samples prepared at different temperatures in different atmospheres. Among all these samples maximum carbon dioxide is absorbed by the sample calcined at 600 $^{\circ}$ C. Increase in trend of CO₂ adsorption is observed from the samples treated at 400 $^{\circ}$ C to 600 $^{\circ}$ C and then decreasing trend is observed for the samples calcined at 800 $^{\circ}$ C. This may be attributed to the maximum surface area associated with the rice husk samples calcined at 600 $^{\circ}$ C. Beyond this temperature the carbon content is exhausted [24] resulting in pore collapse. This lead to decrease in surface area and CO₂ adsorption levels. In a relative comparison though all the samples of rice husk calcined in different atmospheres, maximum CO₂ adsorption is shown by the RHNW-6 sample which shows an adsorption of 0.86 mmol g⁻¹.

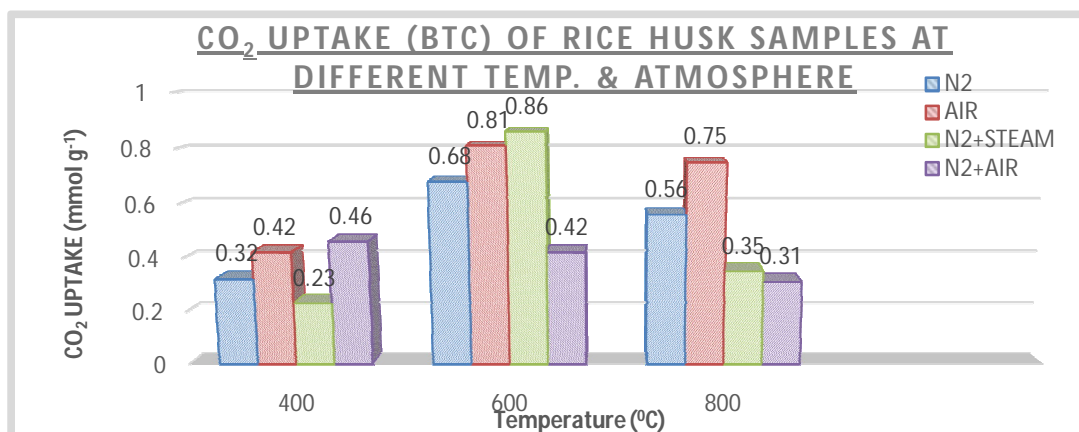


Fig.:6 CO₂ adsorption capacities from BTC of different samples prepared in different atmospheres and temperatures

VI.RECYCLABILITY

Recyclability of adsorbent is an important factor in capture of CO₂. The initial adsorption capacity of RHA-6 sample is 0.86 mmol/gm. Recyclability has been carried out up to 10 cycles, there is marginal variation in activity up to 5 cycles but beyond that gradual decrease in adsorption capacity is depicted and the uptakes in different cycles are shown in Figure-7.

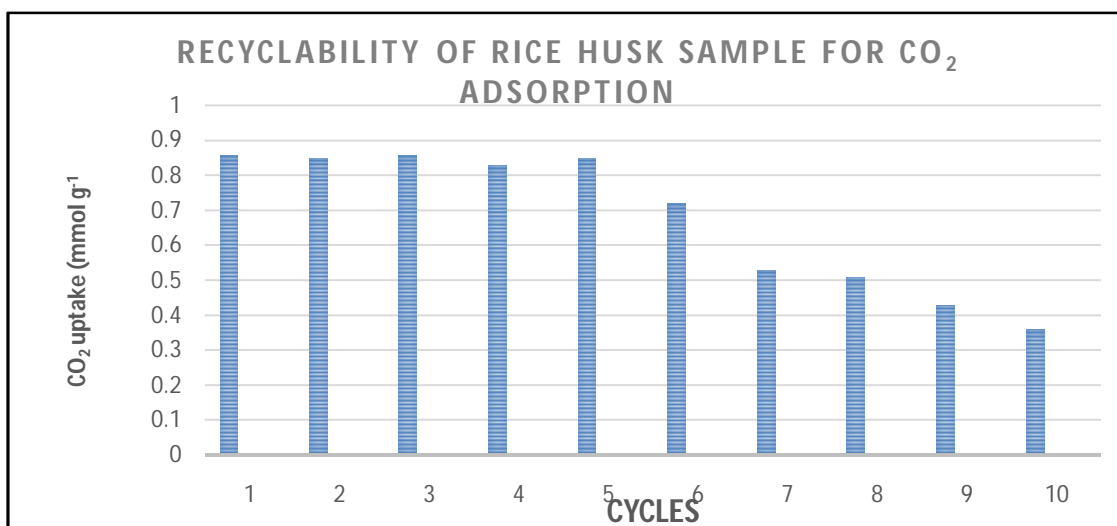


Fig.: 7 Recyclability of RHNW-6 sample for CO₂ uptake

VII.RESULTS AND DISCUSSION

The process of pyrolysis of rice husks is divided into four stages. The first stage is a drying stage that takes place around 100°C where water and small molecules evaporate. Although the rice husks were already dry, there was still a loss of mass, indicating water loss of about 7-10%. The second stage from 100-250°C is when the rice husks began to change their chemical composition. Small amounts of volatile components decompose into low molecular mass compounds. The third stage is the pyrolysis stage that takes place between 250-600°C. The rice husks decompose and generate a lot of heat. Fig.2 and 3 shows that as the calcination temperature increases the surface area and porevolume

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increases up to 600⁰C temperature, beyond this temperature both the properties are decreased which is in agreement with several earlier studies [25-27]. This is attributed due to the evaporation of organic matter and carbon content from the matrix of rice husk ash which leads to collapsing of pores. X-ray diffraction patterns occur at same angle for almost all samples, with low intensity peaks. This typical observation indicates that there is no substantive change in pore separation though the calcination temperature is increased up to 800⁰C. The reduction in diffraction intensity is probably due to partial filling of pores with carbonaceous matter or impurities during evaporation of organic matter. Fig.6 illustrates CO₂ adsorption capacity on rice husk ash samples in anhydrous condition. Each material was found to absorb reasonable amount of carbon dioxide. However the amount of CO₂ adsorption is maximum for RHNW-6 sample which is 0.86 mmol g⁻¹. These results show that RHNW-6 surface is providing maximum number of active sites which binds carbon dioxide molecules more strongly than other samples. However it is noted that the adsorption capacity is remaining almost constant up to 5 cycles, but after that drastic decrease is observed in CO₂ adsorption capacities.

VIII.CONCLUSIONS

The Rice husk ash is a agricultural waste which is locally available in large quantity. The result indicates that rice husk calcined in different atmospheres and at different temperatures is producing good surface materials for adsorption of carbon dioxide. Among all the samples rice husk ash produced at 600⁰C in nitrogen and steam atmosphere is showing promising results for adsorption. The XRD and FTIR study indicates the presence of silica and Si-O-Si group. Thus, the result of the study suggests that the RHNW-6 has the potential to be used as a low-cost adsorbent for the CO₂ adsorption. As a part of future plan of action, these samples of rice husk ash can be impregnated with amine functional groups to extend the study of CO₂ adsorption. Further, the utilization of agro-waste rice husk based adsorbent will also solve its disposal problem.

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