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Fabrication of open type carbonizer for the preparation of activated carbon from rice husk

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ABSTRACT

Activated carbon has been prepared from rice husk using laboratory fabricated open type carbonizer. The raw rice husk powder was named as RRH whereas chemically activated rice husk was named as CARH. Both samples were characterized by methylene blue number (MBN), iodine number (IN) and surface area. The MBN and IN of RRH was found to be 83 mg/g and 415 mg/g whereas CARH was 99 mg/g and 716 mg/g respectively which indicate the presence of mesoporosity and microporosity of the samples. The surface area of RRH was found to be 206 m²/g while CARH was found to be 531 m²/g. XRD analysis showed that the prepared materials were amorphous with some crystalline state while FTIR spectra showed the presence of different functional groups such as hydroxyl, carbonyl, Si-O-Si bond and aromatic group on the material. The adsorption properties of prepared samples were studied by using Langmuir and Freundlich isotherm models. Langmuir adsorption isotherm model was found to be best fitted. It showed that prepared materials have homogenous surface with monolayer type of adsorption. The maximum monolayer coverage (Q_m) for RRH was found to be 55 mg/g and for CARH 143 mg/g. Thus, results revealed that laboratory fabricated low cost open type carbonizer is suitable for the preparation of activated carbon.

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1. Introduction

Activated carbon (AC) is an inimitable form of carbon and is generally prepared from carbonaceous materials. Such materials could be obtained from plant resources including agriculture wastes. Some of the agricultural wastes that have been used are saw dust [1-2], rice husk [3], corncob [4], sugarcane [5], waste tea [6] and other by-product such as; almond shell [7], coconut shell [8], hazelnut shell [9], olive

[10], apricot [11] and cherry stones [12]. Among them rice husk is one of the eco-friendly and locally available agricultural waste that has been generated approximately 120 million tons annually from rice milling industries [13] and hence in present work, rice husk has been used as precursor for the preparation of activated carbon.

Rice husk is actually outer most covering of the rice grain. It contains 15-20% hemicellulose, 28-30%

cellulose, 25-30% lignin, 15-20% silica and 10-15% moisture [14]. Hemicellulose, cellulose and lignin are generally considered as a major source of activated carbon. These AC are generally prepared by carbonization technique. For carbonization, instruments like muffle furnace, tube furnace and other furnaces have been used. The temperature ranges from 100 to 1800°C. Such high temperature needs high energy consumption and running cost also get elevated. Hence, we tried to fabricate an efficient, low cost open type carbonizer to prepare AC [15]. Thus prepared activated carbon from open type carbonizer was then activated by phosphoric acid which mainly helps in dehydration of lignocellulosic material and formation of phosphate ester linkage between cellulose rings which inhibits shrinkage of structure during heat treatment.

Actually, activation is the way that is employed to increase surface area and porosity from the carbonized organic precursor [16]. The organic precursor consists of elementary crystallites with a large number of interstices between them. These interstices were filled with disorganized carbon residue that blocks the pore entrances due to which low porosity observed.

The highly porous activated carbon with high surface area has got wider application in various fields like to remove pesticides and organic compounds from aqueous solution, to treat waste water, to purify food, beverage, to remove various dyes, for reducing organic chemicals, chlorine, heavy metals, as catalyst carriers (catalytic support) and as adsorbent for air purification [17]. In present work, activated carbon derived from rice husk was used to study the adsorption of methylene blue dye.

2. Materials and Method

Reagents

The reagents such as orthophosphoric acid (H_3PO_4), methylene blue, iodine used were of analytical grade and procured from Merck Company. All the experiments were carried out in distilled water. Stock solution of methylene blue was prepared by dissolving 1 g of MB in 1000 mL of distilled water in volumetric flask. The 0.1 N of I_2 solutions was prepared by dissolving 1.272 g of I_2 and 5 g of KI in

100 mL of water and left for 24 hrs for complete dissolution.

Instruments

The X-Ray Diffractometer (D2-Phaser, Bruker, Germany) has been used to study the phase state of as prepared activated carbon. It was operated at an accelerating voltage of 40 KV and current 40 mA with Cu-K α radiation ($\lambda=1.5418\text{\AA}$) in the diffraction angle of 10 to 50 degrees. The surface functional group was studied by Fourier Transmission Infrared Spectroscopy (Shimadzu, Model No. IRTracer-100, Japan). The FTIR spectra were recorded at 4000-400 cm^{-1} wave number.

Fabrication of open type carbonizer

Open Type Carbonizer was fabricated by following procedure:

Step 1: Fabrication of chamber

First of all, the chamber was prepared by taking a can having 40 cm height and 20 cm diameter. It has volume of 20 L. Bottom of the can was removed and a hole was made at the top of the can which has diameter of 10 cm. Then, small holes have been made at the surface of the can at every 10 cm distance so that, perforated surface have been obtained. The diameter of hole is 2 cm [15]. The structure of chamber is shown in Fig. 1(a).

Step 2: Fabrication of chimney

Then a chimney was prepared by taking, 30 x 122 cm sized GI sheet. It was folded and clamped together to make a roll having diameter of 10 cm [15]. The figure of chimney is shown in Fig. 1(b).

Step 3: Assemble of chimney and chamber

As prepared chimney was then assembled with prepared chamber by welding on the top of the chamber having hole of 10 cm as shown in Fig. 1(c). In this way, open type carbonizer was fabricated.

Preparation of adsorbent

Preparation of raw rice husk (RRH)

Raw rice husk (RRH) was collected from rice mill. It was washed with water and allowed to dry in sunlight. After complete dryness, it was grinded into fine powder in an electric grinder and sieved through

75µm sized sieve. Thus, obtained powder is named as RRH.

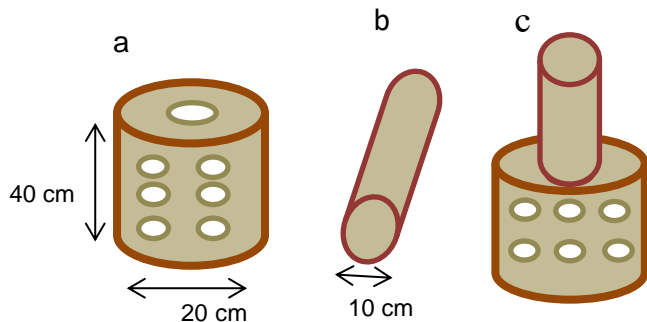


Fig. 1: Fabrication of Open Type Carbonizer.

Preparation of chemically activated rice husk (CARH)

The rice husk was carbonized in open type carbonizer. Then this carbonized carbon was impregnated with phosphoric acid in the ratio of H₃PO₄ 1:1 wt by wt. They were left for 24 hrs for proper soaking. After, that it was cleaned with distilled water till neutral pH. Then the sample was dried at 100°C for 24 hrs. This dried sample was again carbonized at 450°C for 2 hrs in a muffle furnace and then cooled to room temperature. In this way, chemically activated rice husk was prepared and represented as CARH.

Methylene blue number

Methylene blue number is defined as the milligram of methylene blue dye adsorbed by 1g dried activated carbon. It is a measure of the mesopore content in the activated carbon. The amount of methylene blue adsorbed from each was calculated by using equation 1, where, C₀ is the concentration of methylene blue solution (mg/L) at starting time (t=0), C_e is the concentration of methylene blue solution at equilibrium time (mg/L) which can be calculated by equation 2, V is the volume of the solution in liter and M is the mass of the adsorption in g. To determine the methylene blue number, the Langmuir model has been applied. In this model, q_{eq} plot is made as a function of C_e. The Langmuir parameters (q_{max} and K) were obtained by a least square fitting regression method.

$$C_e = \frac{\text{Absorbance}}{\text{Slope}} \dots\dots\dots(1)$$

$$q_{eq} = \frac{C_0 - C_e}{M} \times V \dots\dots\dots (2)$$

Iodine number

Iodine number is the milligram of iodine adsorbed by 1 g of activated carbon from a 0.1N iodine solution when the equilibrium iodine concentration is exactly 0.002N. Iodine number is an indication of micropore content in activated carbon (0-20A⁰ or up to 2 nm) by adsorption of iodine from solution. The concentration of iodine in the solution was then calculated from the total volume of sodium thiosulphate used by using equation 3.

$$X/M = \{ (N_I \times 126.93 \times V_I) - [(V_I + V_{HCl})/V_F] \times (N_{Na_2S_2O_3} \times 126.93) \times V_{Na_2S_2O_3} \} / M_c \dots\dots\dots(3)$$

where,
 N_I = Normality Iodine solution,
 V_I = Added volume of iodine solution,
 V_{HCl} = Added volume of 5% HCl,
 V_F = Filtrate volume used in titration,
 N_{Na₂S₂O₃} = Normality sodium thiosulfate solution,
 V_{Na₂S₂O₃} = Consumed volume of sodium thiosulfate solution,
 M_c = Mass of activated carbon.

Determination of adsorption isotherm

In order to evaluate adsorption capacity of as prepared activated carbon, adsorption isotherms were obtained. Here, Langmuir and Freundlich isotherm model have been applied and the values were then obtained by using the equation 4-8.

Langmuir isotherm

Langmuir isotherm purposes that monolayer adsorption occur on solid surface with identical homogenous sites. Once the active sites are covered with dye molecules, no further adsorption takes place. Langmuir constant can be obtained by using equation 4.

$$Q_e = \frac{Q_m b C_e}{1 + b C_e} \dots\dots\dots(4)$$

The linear form of Langmuir expression is expressed as;

$$\frac{C_e}{q_e} = \frac{1}{Q_m b} + \frac{1}{(Q_m)} C_e \dots\dots\dots (5)$$

where,

C_e = equilibrium concentration of dye solution (mg/L),

Q_e = equilibrium capacity of dye on the adsorbent (mg/g),

Q_{max} = adsorption capacity of the adsorbent (mg/g), and

b = Langmuir adsorption constant.

The essential feature of Langmuir adsorption isotherm can be expressed in terms of dimensionless constant called separation factor or equilibrium parameter (R_L) which is obtained by equation 6.

$$R_L = \frac{1}{1+bC_o} \dots\dots\dots(6)$$

where,

C_o = Initial concentration (mg/L)

b = Langmuir constant

R_L indicates the shape of isotherm and provides the idea of favorability of adsorption. If the R_L value is greater than one, adsorption will be unfavorable. Adsorption is favorable only when R_L less than one and greater than zero.

Freundlich isotherm

It is used for the non-ideal sorption that involves heterogeneous surface energy system and is expressed as equation 7.

$$Q_e = K_F C_e^{\frac{1}{n}} \dots\dots\dots(7)$$

The linear form can be written as;

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \cdot \log C_e \dots\dots\dots(8)$$

where, K_F and n (dimensionless constants) are the Freundlich adsorption isotherm constants, K_F indicates adsorption capacity and n indicates adsorption intensity. As the value of K_F increases the adsorbent capacity of adsorbent also increases. The slope $1/n$ ranging between 0 and 1, is favorable adsorption condition.

Determination of surface area

Surface area of prepared activated carbon was obtained using Langmuir isotherm plot and calculated by using following in equation 9.

$$S_{MB} = \frac{Q_{m \cdot a_{MB}} \cdot N \cdot 10^{-20}}{M} \dots\dots\dots(9)$$

where,

S_{MB} = Surface area

Q_m = Maximum loading

a_{MB} = Cross section area of one molecule of M B = 197.2 \AA^2

N = Avogadro's No = 6.023×10^{23}

M = Molecular weight of MB = $319.84 \text{ g mol}^{-1}$

3. Results and Discussion

Preparation of raw rice husk (RRH) and chemically activated rice husk (CARH)

Powder form of raw rice husk (RRH) and chemically activated rice husk (CARH) was prepared and is shown in Fig. 2.

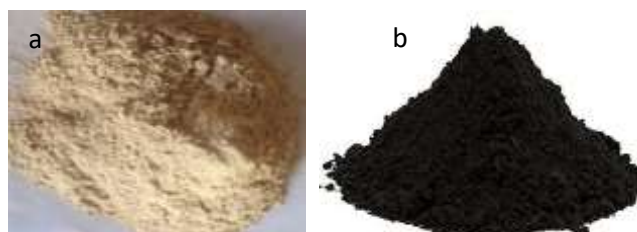


Fig. 2: (a) Raw Rice Husk and (b) Chemically Activated Rice Husk.

Characterization of adsorbents

X-ray diffraction (XRD)

X-ray diffraction analysis of the sample was carried out in order to determine the degree of crystallinity or amorphous nature of the activated carbons. The X-ray diffraction of raw rice husk (RRH) and chemically activated rice husk (CARH) is shown in Fig. 3.

In Fig. 3, pattern **a** is the diffraction pattern of RRH where one can see a distinct peak at $24^\circ 2\theta$ which shows the amorphous nature although, it has some local crystalline structure with high conjugated aromatic compounds. Similarly small peaks could also be observed at 35° and $45^\circ 2\theta$ indicating semi crystalline cellulose structure [18].

The pattern **b** in Fig. 3, is the diffraction pattern of CARH. The peak in between 20° to $30^\circ 2\theta$ indicates the crystalline silicon oxide phase in the tetragonal system (JCPDF file no.01-082-1554) [19]. In comparison to pattern a, pattern b have humplike crystalline peaks or absence of sharp peak. Such a

diminishing of peak may be due to phosphoric acid activation.

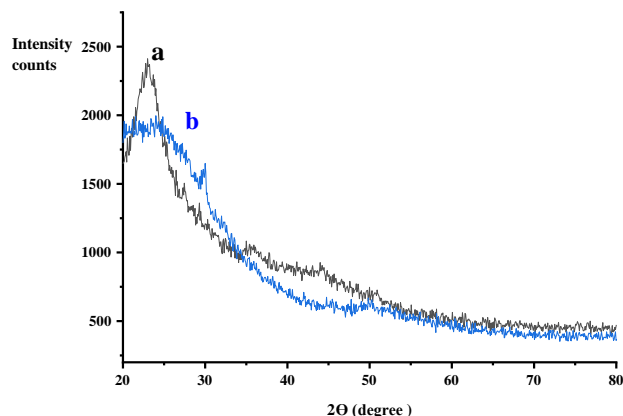


Fig. 3: XRD pattern of (a) RRH and (b) CARH.

Fourier transforms infrared spectroscopy (FTIR)

The FTIR spectra of RRH is shown in **Fig. 4(a)** which indicates the presence of –OH stretching vibration or Si-OH group at around 3724 cm^{-1} . Small band around 2910 cm^{-1} represents C-H stretching of alkanes and stretching aliphatic bond of –CH, –CH₂, –CH₃ was obtained at 2341 cm^{-1} . The band at 1500 cm^{-1} to 1750 cm^{-1} was noted and represents C=C stretching of alkenes and aromatic as well as C=O stretching of aromatic group [20].

At around 1039 cm^{-1} , bending vibration of –CH₃ group or stretching vibration of Si-O-Si bond of siloxane. The band around $(450-800)\text{ cm}^{-1}$ indicate bending vibration of Si-O bond from amorphous silica.

Similarly, Fig. 4(b) shows the FTIR spectra of CARH. The band at 3716 cm^{-1} was found to be weaker in comparison to raw rice husk which was broader which implies dehydration of water. The band at $3000\text{ to }2500\text{ cm}^{-1}$ is due to –C-H stretching vibration, was completely diminished. At around 1576 cm^{-1} a weak band of C=C aromatic groups which may be due to partial modification of husk

texture during impregnation process. Likewise some changes in band could be observed at around 1086 cm^{-1} indicates the bending vibration of –CH₃ group or stretching vibration of Si-O-Si bond of Siloxane. The band observed at the region lower than 1000 cm^{-1} can be attributed to compounds with aromatic ring. The band at $450-800\text{ cm}^{-1}$ is assigned to bending vibration of Si-O bond from amorphous silica and was found to be less intense which may be due to modification of the carbon by phosphoric acid activation [20].

Determination of methylene blue number and iodine number

Porosity was determined by Methylene Blue Number and Iodine Number. The methylene blue number and iodine number of RRH and CARH are presented in Table 1 and Table 2.

Table 1: Methylene Blue Number of RRH and CARH.

S.N	Sample	Methylene Blue Number (mg/g)
1.	RRH	83
2.	CARH	99

Table 2: Iodine Number of RRH and CARH.

S.N	Sample	Iodine Number (mg/g)
1.	RRH	415.1
2.	CARH	716.3

Prepared sample implies that large number of micropores on the surface rather than mesopores i.e. iodine number is found to be greater than methylene blue number. It may be due to easy breakdown of amorphous polymers like lignin and hemicelluloses which produce micropores and crystalline form like cellulose which produce mesoporosity. In case of RRH porosity was low as indicated by low surface area (Table 3) but in

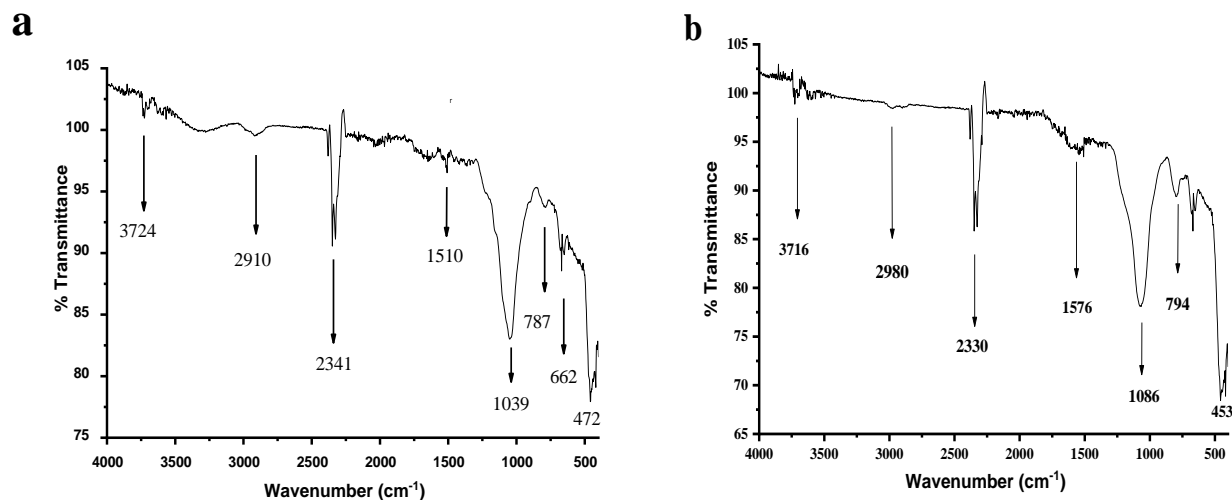


Fig. 4: FTIR spectra of (a) RRH and (b) CARH.

CARH, which was carbonized and activated chemically, there was loss of volatile compounds, dehydration of lignocellulose materials as well as cleavage of the bond takes place. As a consequence, porosity developed.

Determination of surface area

The surface area of RRH and CARH were calculated using equation 9 and are tabulated in Table 3. The surface area of CARH was found to be 531 m²/g which was higher than RRH. It may be due to loss of volatile compounds, dehydration of lignocellulosic materials and cleavage of the bond during chemical activation and carbonization.

Table 3: Surface area of RRH and CARH

S.N	Sample	Surface Area (m ² /g)
1.	RRH	206
2.	CARH	531

Adsorption isotherms

In order to evaluate adsorption behavior of prepared samples, different Isotherm models have been fitted.

Langmuir isotherm of RRH and CARH

Langmuir isotherm of raw rice husk (RRH) and chemically activated rice husk (CARH) was obtained by plotting ce/qe verses ce which is shown in Fig. 5.a and Fig. 5.b respectively. Graph was found to be linear and fitted with Langmuir model. The results or Langmuir parameters which were obtained are presented in Table 4.

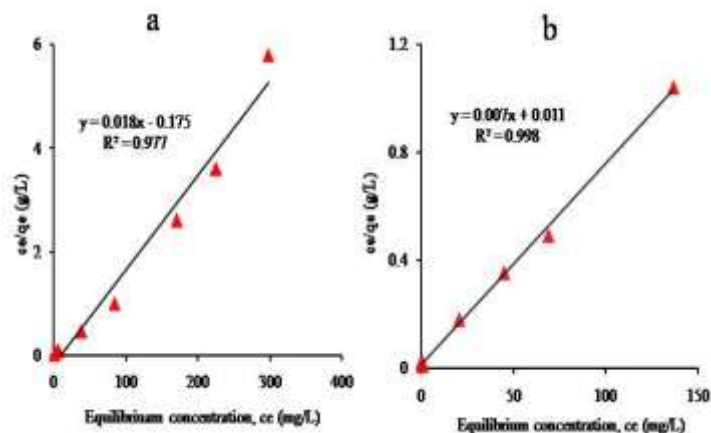


Fig. 5: Langmuir Isotherm of (a) RRH and (b) CARH.

Table 4: Langmuir parameters.

Adsorbents	Langmuir Isotherm			
	B(L/mg)	Qm (mg/g)	R ²	R _L
RRH	-0.3	55.0	0.977	-0.01
CARH	1.82	142.9	0.998	0.3

Table 5: Freundlich parameters.

Adsorbents	Freundlich Isotherm			
	1/n	n	K _F (mg/g)	R ²
RRH	0.126	7.93	1.857	0.959
CARH	0.092	10.87	1.848	0.967

Freundlich isotherm for RRH and CARH

Freundlich isotherm of raw rice husk (RRH) and chemically activated rice husk (CARH) was obtained by plotting log q_e verses log c_e and is shown in Fig. 6 (a) and (b).

From Table 4 and Table 5, the correlation coefficient R² values of Langmuir isotherm and Freundlich isotherm were evaluated. Langmuir isotherm of CARH was found to be 0.998 and of RRH was 0.977 which was higher than the value obtained from Freundlich isotherm i.e. for CARH it was 0.967 and for RRH it was 0.959. It shows that Langmuir adsorption isotherm model was found to be best fitted.

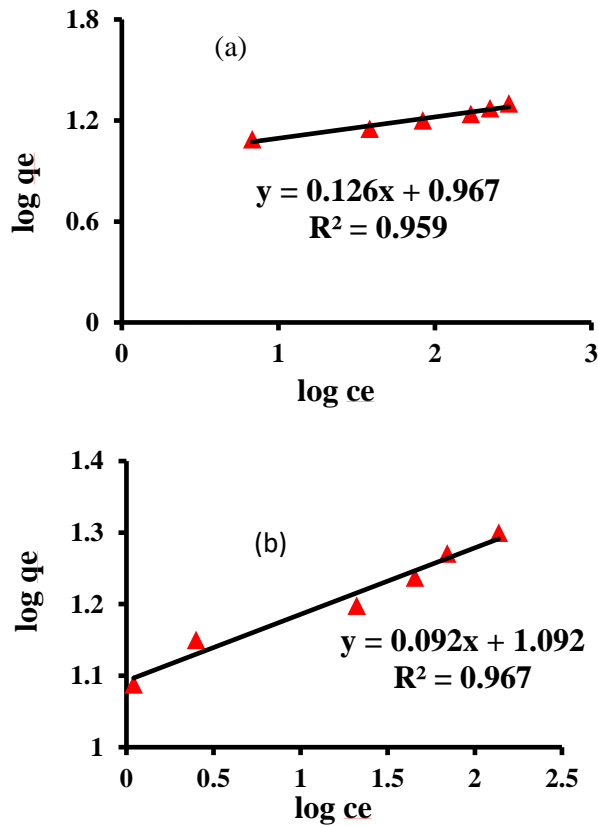


Fig. 6: Freundlich Isotherm of (a) RRH and (b) CARH

The Freundlich parameters obtained are presented in Table 5.

Table 6: Comparison of adsorption capacities of various activated carbons

Precursors	Adsorption capacity Q _m (mg/g)	
Banana stalk waste	243.90	[21]
Modified rice straw	208.33	[22]
Salsola vermiculata plant	130	[23]
Pumpkin seed hull	141.92	[24]
Pineapple stem	119.05	[25]
Coffee husk	90.1	[26]
Tea waste	85.16	[27]
CCRH	143	Present work

The results revealed that CARH has solid surface with identical homogenous sites where monolayer

adsorption took place. The active sites were first covered with dye molecules and there were no further adsorption occurred. The maximum adsorption capacity of CARH was found to be 143 mg/g which was found to be higher than RRH which was also supported by high surface area of CARH (Table 3). Similarly, the equilibrium parameter R_L value was found to be less than one which revealed the favorability of adsorption. The adsorption capacity of CARH was compared with literature values and found to be good (Table 6).

4. Conclusion

It has been concluded that activated carbon can be prepared from low cost laboratory fabricated open type carbonizer. For the preparation of activated carbon, rice husk was used as a precursor. Prepared materials were characterized by MB, IN, surface area, XRD and FTIR spectroscopy. XRD pattern of RRH and CARH showed the amorphous with some crystalline nature of the materials. Similarly, FTIR spectra of RRH and CARH showed the presence of siloxane bond, hydroxyl, carbonyl and Si-O bond from amorphous silica. The adsorption behavior of prepared materials were studied and results revealed that Langmuir model was best fitted in both sample as indicated by the correlation coefficient R^2 value. The dimensionless separation factor $R_L < 1$ indicating a favorable adsorption condition for CARH. Hence, low cost laboratory fabricated open type carbonizer is good for the synthesis of activated carbon from waste product.

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