



## SUSTAINABLE APPROACH TOWARDS THE SYNTHESIS OF MESOSTRUCTURED MOLECULAR SIEVES MCM-48 FROM RICE HUSK ASH.: A GREEN PATHWAY

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### ABSTRACT

Rice Husk is the by-product produced during rice milling. Sustainable use of Rice Husk Ash (RHA) and Rice Husk (RH) in Industrial Sector and other fields depends upon its physical and chemical properties. This research contributes holistic approach to the potential use of rice husk towards synthesis of meso-porous material than the traditional uses of husks. It not only reduces the cost of material but also results in the reduction of the environmental greenhouse effects. Attempts have been made to investigate crystallization kinetics of MCM-48. The various synthesis parameters were investigated during crystallization of MCM-48. The activation energy of crystallization kinetics of MCM-48 was calculated using Arrhenius equation and found to be 179.07 kJ / mole in the present system of synthesis.

**KEYWORDS:** Rice Husk Ash, MCM-48, Crystallization Kinetics, Activation Energy.

### 1. INTRODUCTION:

Hazardous wastes are generated annually throughout the world by all industries and their disposal poses major challenges and serious environmental problems. In the recent years, there has been a growing interest to find creative ways not only to reduce natural waste and industrial hazard to overcome environmental pollution but also its effective utilization<sup>1</sup>.

As we know that, Rice is a primary source of food. Its production covers almost 1% of the Earth's surface. Globally, approximately 800 million tons of rice<sup>2</sup> is produced every year. India is a major rice producing country and annual production of rice husk is approximately 20 million tons<sup>3</sup>.

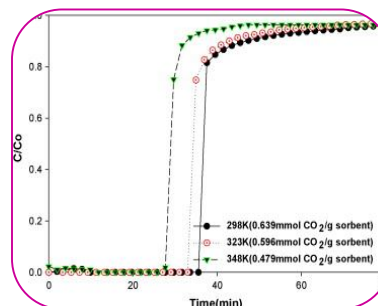
For every 100 kg of paddy milled, about 22.8% of husk is produced<sup>2</sup>. Even though some of this husk is converted into end product such as feedstock and adsorbent but most is either dumped as a waste or burnt openly, causing environmental and health problems.

Therefore, one of the chief principles of green technology is to utilize the RHA as a raw material or renewable resource for making high value added, versatile materials rather than depleting, as it has high silica content (>90%).

Quite a lot of research groups have taken the advantage of this silica composition and made endeavors in making micro<sup>4</sup> and mesoporous<sup>5</sup> zeolitic materials synthesized from extracted silica through them.

These materials have wide applications as adsorbents, in ion exchange, as molecular sieves, catalysts etc. Compared to conventional microporous zeolites, mesoporous materials possess many advantages such as high surface area (more than 980m<sup>2</sup>/g), large pore size and an ordered structure<sup>6,7</sup> which is attractive for designing new selective heterogeneous catalyst in production of fine chemicals on large scale.

In 1992, scientist at Mobil Oil Corporation discovered new family (M41S) of mesoporous materials, among them MCM-48



possesses hexagonal molecular sieves having fairly uniform pores with pore diameter of 20-100Å. Our research endeavors the use of no-cost raw materials such as agro waste rice husk for our further investigations because it add value; reduce the cost and create effective utilization to protect the environment.

## 2. Experimental: Materials and Methods for Synthesis of mesoporous MCM-48 from RHA in alkaline medium:

Hydrothermal synthesis of RHA-MCM-48 was carried out in hydrothermal reactor at autogenous pressure under stirring conditions. The chemicals used during synthesis were TritonX, Sodium hydroxide, Hydrochloric acid, Deionized water etc. The rice husk silica extraction was carried out using acid hydrolysis method. Protocol is as follows.

|   |
|---|
| Rice husk→ washed with deionized water and dried at 80 <sup>0</sup> C for 24h   |
| → Treated with 3.0 M HCl with heating at 100 <sup>0</sup> C   |
| →Rinsed with distilled water until pH reaches to 7  |
| → Dried at 100 <sup>0</sup> C for 24 h  |
| → Finally, calcined at 800 <sup>0</sup> C for 4h.   |
| → Mixed with 3.75 M NaOH solution and stirred overnight to extract the silicate from the ash  |
| →Triton-X was dissolved and stirred for 1hr at different synthesis temperatures (80 <sup>0</sup> C, 100 <sup>0</sup> C and 120 <sup>0</sup> C). |
| →pH of the mixture was adjusted to 10.2 to obtain a white precipitate by adding 3.0 M HCl solution  |
| → Heated in microwave oven at 100 <sup>0</sup> C for 30min for crystallization.   |
| →The solid was recovered and was dried in oven overnight at 100 <sup>0</sup> C and then it was calcined at 550 <sup>0</sup> C for 6h.           |
| →These synthesized samples were designated as RHA-MCM-48 (a, b, c) respectively.  |
| → The molar composition of the synthesis gel was as follows:<br><b>1.0SiO<sub>2</sub>: 1.09 NaOH: 0.13 CTAB: 50.12H<sub>2</sub>O.</b>           |
| → Formation of the materials has been evaluated by X-ray diffraction and N <sub>2</sub> .sorption studies.                                      |

## 3. CHARACTERIZATION:

To elucidate the structural features<sup>8</sup>, morphology<sup>9</sup>, pore architecture<sup>10</sup>, thermal stability<sup>11</sup>, adsorptive<sup>12</sup> and catalytic behavior<sup>13</sup>, surface area<sup>14</sup> etc: the synthesized samples are characterized by techniques such as XRD, N<sub>2</sub>-sorption, FTIR, etc.

## 4. RESULTS AND DISCUSSION:

### I) XRD-studies:

The XRD scans were recorded from 10<sup>0</sup>-70<sup>0</sup> with 0.2<sup>0</sup> step-width and 5.1s counting time for every step. The X-ray diffraction patterns of treated RHA are shown in Fig.1 indicates the presence of quartz (21.31<sup>0</sup>, 25.45<sup>0</sup> and 41.31<sup>0</sup> 2θ peaks). From these XRD patterns it can be seen that a broad peak at 2θ = 20<sup>0</sup> clearly indicates that silica obtained after fusion and burning of rice husk ash was in the amorphous nature.

In the XRD pattern of the calcined RHA-MCM-48 (a), the prominent presence of (100) reflection suggests that this material is likely to possess but not well defined hexagonal arrays after calcination. The maximum contraction is observed in the case of RHA-MCM-48 (a), which may be due to the poorly ordered

arrangement of the mesopores. However, the long range order in hexagonal symmetry is maintained in the calcined forms of RHA-MCM-48 (b, c) which is indicated by the presence of the four or three peaks respectively in their XRD patterns.

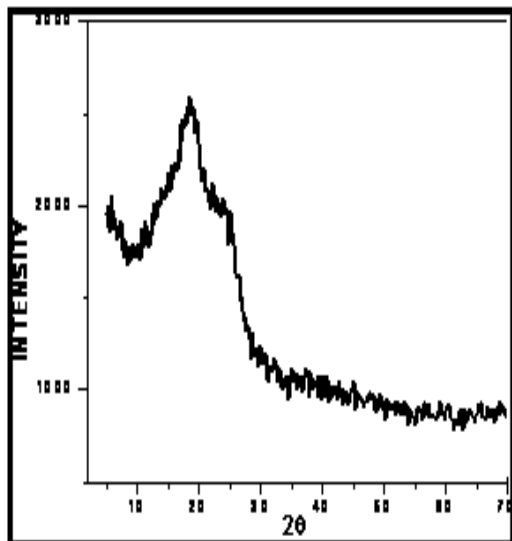


Fig. 1: XRD Pattern of treated RHA

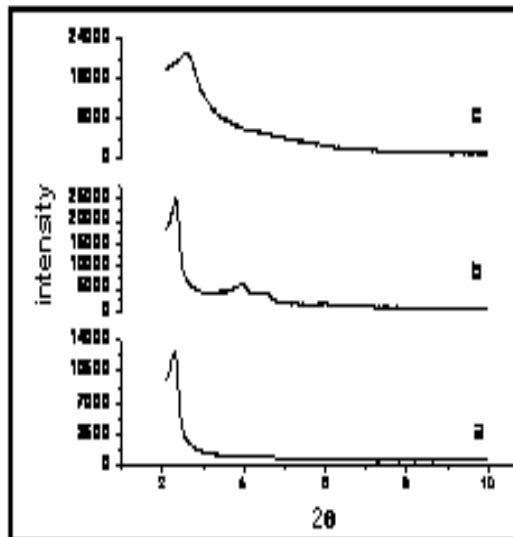


Fig. 2: XRD patterns of calcined samples of RHA-MCM-48 (a, b, c) synthesized at 80, 100 and 120°C

In calcined sample (b) at 100°C, the most intense peak with (100) reflection is shifted to higher  $d_{100}$  spacing values and afterwards it lowers as in Fig.2-c this is because the calcination causes condensation of internal Si-OH groups giving rise to a contraction of the unit cell.

A significant increase in the intensity of this peak in calcined samples b and c indicates that an atomic reorganization occurs during the removal of the surfactant molecules in the calcinations process.

## II) FTIR-studies :

Fig.3 and Fig.4 shows the IR spectra of rice husk ash and RHA-MCM-48(b) after calcination. A broad band between 3300  $\text{cm}^{-1}$  - 3400  $\text{cm}^{-1}$  is attributed to surface -OH groups of silanol groups (-Si-OH) and adsorbed water molecules on the surface. The broadness of band indicates the presence of strong hydrogen bonding.

In the calcined sample a very small peak in the same range confirms the retention of the silanols group resembling the hydrophilicity of the material. Peak at 2854  $\text{cm}^{-1}$  could be assigned to C-H stretching vibration of organic contaminants which may be introduced during sample handling or some hydrocarbon present in rice husk.

A broad band ranging from 1070  $\text{cm}^{-1}$  to 1170  $\text{cm}^{-1}$  due to Si-O-Si asymmetric stretching vibrations of silica is present in uncalcined and calcined rice husk samples. The effect of the higher reaction temperature was a large amount of silanol group. The effect observed for RHA-MCM-48 (b) is noticeable, which is also supported by the XRD analysis and sorption studies of the samples.

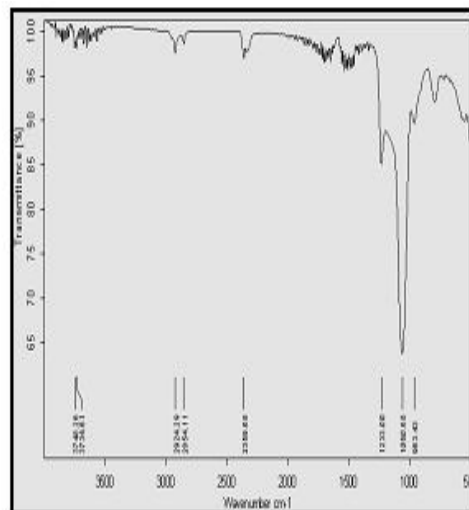
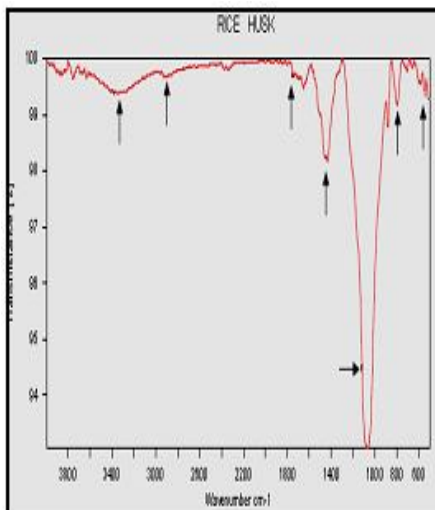


Fig. 3: FTIR spectrum of treated RHA Fig. 4: FTIR spectrum of RHA-MCM-48 (b)

### III) N<sub>2</sub>-Sorption studies

The sample (b) synthesized at temperature 100°C have been characterized by N<sub>2</sub>-adsorption-desorption isotherms and the corresponding BJH pore size distribution was shown (Fig.5 A, B). According to IUPAC classification, all the isotherms of RHA-MCM-48 are of type IV, which is the characteristic of mesoporous material.

The isotherms exhibit three stages. The first stage is a linear part almost going through the origin, which is due to monolayer adsorption of nitrogen on the walls of the mesopores ( $p/p_0 < 0.2$ ). The second stage is characterized by a steep increase in adsorption (within the relative pressure  $p/p_0$  range of 0.2-0.4) due to capillary condensation of N<sub>2</sub> in the pore channels.

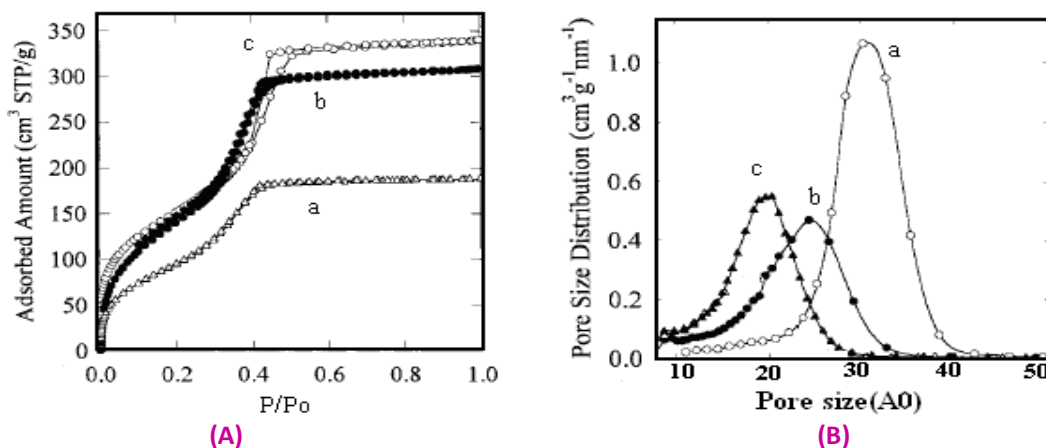


Fig. 5: (A) N<sub>2</sub> adsorption-desorption isotherms and (B) pore size distribution of RHA-MCM-48(a, b, c) synthesized at 80, 100 and 120°C

The  $p/p_0$  value at which the inflection starts is related to the diameter of the mesopores. The sharpness in this step indicates the uniformity of the pore size distribution. The third stage in the adsorption isotherm is an almost horizontal part after the relative pressure  $p/p_0$  of  $\sim 0.38$  and is due to multilayer adsorption on the outer surface of the particles.

In addition, a hysteresis loop at relative pressure  $p/p_0 > 0.8$  corresponds to capillary condensation in

the inter particle pores. The hysteresis loop is found over a wide range of relative pressures,  $p/p_0$  (0.35-1.00). The shape of the hysteresis loop confirms the formation of a lamellar phase.

The pore size distribution becomes broader. Thus, the XRD results are confirmed by N<sub>2</sub>-adsorption-desorption data. We noted that the surface areas of calcined RHA-MCM-48 samples are increasing with the increase in crystallization temperature up to 100°C. The more surface area (933.27m<sup>2</sup>/g) is an indication of narrow pore size distribution.

**Table.1: Data obtained from XRD and N<sub>2</sub>-sorption studies**

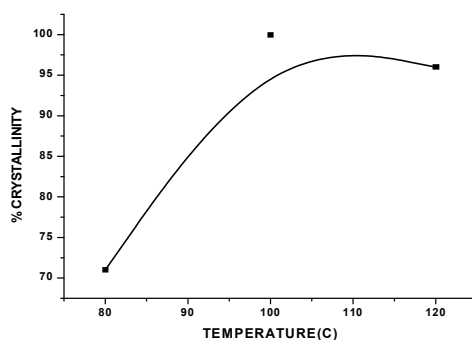
| Sample name    | d <sub>100</sub> | Unit cell parameter | S.A. (m <sup>2</sup> /g) | Average pore diameter (Å) | Pore volume (ml/g) | Average wall thickness (Å) | % Crystallinity |
|----------------|------------------|---------------------|--------------------------|---------------------------|--------------------|----------------------------|-----------------|
| RHA-MCM-48 (a) | 33.6             | 39.2                | 571.4                    | 31.3                      | 0.38               | 8.0                        | 74              |
| RHA-MCM-48 (b) | 36.3             | 42.1                | 933.3                    | 28.6                      | 0.49               | 14.4                       | 100             |
| RHA-MCM-48 (c) | 34.8             | 41.6                | 761.4                    | 30.0                      | 0.45               | 11.5                       | 92              |

### 5. STUDY OF KINETICS OF CRYSTALLIZATION OF RHA-MCM-48:

The percent crystallinity of the samples drawn at different synthesis temperatures in the crystallization kinetics was obtained by the following relation.

$$\% \text{ Crystallinity} = \frac{\text{Sum of the peak heights of unknown material} \times 100}{\text{Sum of peak heights of standard material}}$$

The obtained values of % crystallinity were further plotted as a function of temperature from which the gradient of crystallization has been evaluated. The percent conversion from amorphous to 100 % crystalline product of RHA-MCM-48 phase is shown in the Fig.6 indicates that the rate of conversion of amorphous to crystallization of RHA-MCM-48 phase was initially slow and then it is increased sharply followed by subsequent slow down. Therefore, the rate of crystallization decreases as the process approaches to the completion indicated by constancy (100 %) in percent crystallization. The apparent activation energy for conversion was estimated from the slope of linear plot of  $\ln K$  vs.  $(1/T)$  by applying the Arrhenius equation  $d \ln K/d (1/T) = E_{ac}/RT$ , Where,  $K$  is the rate of conversion,  $E_{ac}$  is the energy of crystallization/ conversion,  $R$  is the gas constant. The apparent activation energy of conversion of silicate gel to 100 % crystalline RHA-MCM-48 phase was calculated and found to be 179.07 kJ/mole in the present crystallization system.



**Fig.6 Kinetics of crystallization of RHA-MCM-48**

## 6. CONCLUSION:

All the characterization techniques performed in this study reveals that well ordered mesoporous material of uniform hexagonal array can be synthesized very conveniently and in a very short span of time from an agro waste rice husk ash instead of commercial expensive silica sources.

The parametric variation such as change of synthesis temperature helps to optimize the synthesis conditions. The well ordered mesoporous material CFA-MCM-48 can be synthesized at 100°C for 6h keeping pH of gel 10.2 and calcined at 550°C. The apparent activation energy of conversion of synthesis gel to 100 % crystalline CFA-MCM-48 phase was 184.62kJ/mole calculated by Arrhenius equation.

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