SYNTHESIS OF HIGH-QUALITY MESOPOROUS MCM-48 MOLECULAR SIEVES USING RICE HUSK ASH IN A FLUORINE-CONTAINING SYSTEM: A GREEN STUDY

Dr. Manish Raghunathrao Deshpande[1]*, Dr. Sudhir Shivnikar[2], Mukund Joshi[3], Jagdish Kulkarni[4], Vaishnavi Pethkar[5], Ashwini Ingle[6]

Abstract:
The present investigation involved the synthesis of mesoporous MCM-48 molecular sieves of superior quality, utilising rice husk ash (RHA) as a precursor within a system containing fluorine. The objective of this study was to examine the impact of synthesis conditions on the structural characteristics of MCM-48 silica, employing a sustainable and environmentally conscious methodology. The rice husk ash was obtained through the collection of rice husk waste, followed by thorough washing and subsequent controlled high-temperature combustion. The ash that was obtained subsequently underwent a process of being finely ground into a powder. The extraction of silica was accomplished through the treatment of the ash with a solution composed of hydrofluoric acid (HF) and water, resulting in the formation of a solution containing silica. In order to integrate the fluorine-containing system, a surfactant containing fluorine, such as perfluorooctanoic acid (PFOA), was introduced into the synthesis procedure. The silica solution was altered by combining it with a surfactant containing fluorine. This altered resolution was subsequently subjected to the procedures of gelation and solidification. The fabricated porous MCM-48 molecular sieves underwent analysis through the application of X-ray diffraction (XRD), nitrogen adsorption-desorption, and scanning electron microscopy (SEM). The results of the investigation suggest that the chosen arrangement circumstances had a significant influence on the qualities of the MCM-48 silica. The silicon material exhibited a favourable globular structure and had a particular mean surface area of 1000 m2/g, indicating outstanding permeability and possibility for various uses. The current investigation centres on the utilisation of rice husk ash as an eco-friendly precursor and the integration of a fluorine-containing system for the production of top-notch porous MCM-48 molecular sieves. This investigation provides a valuable addition to the progression of environmentally-friendly approaches, with the goal of cultivating verdant and sustainable substances that possess advantageous structural traits appropriate for various uses.

Keywords: Mesoporous materials, MCM-48 silica, Rice husk ash, Perfluorooctanoic acid (PFOA), Green synthesis, Structural properties

[1*]HOD of Physics and Research Supervisor, Netaji SubhashChandra Bose Art, Commerce and Science College Nanded 431601 Maharashtra India.
[2]Principal, Netaji SubhashChandra Bose Art, Commerce and Science College Nanded 431601 Maharashtra India.
[3]Assistant professors and research scholor, Netaji SubhashChandra Bose Art, Commerce and Science College Nanded 431601 Maharashtra India.
[4]Assistant professors and research scholor, Netaji SubhashChandra Bose Art, Commerce and Science College Nanded 431601 Maharashtra India.
[5]Assistant professors and research scholor, Netaji SubhashChandra Bose Art, Commerce and Science College Nanded 431601 Maharashtra India.
[6]Assistant professors and research scholor, Netaji SubhashChandra Bose Art, Commerce and Science College Nanded 431601 Maharashtra India.

***Corresponding Author:** Dr. Manish Raghunathrao Deshpande
*HOD of Physics and Research Supervisor, Netaji SubhashChandra Bose Art, Commerce and Science College Nanded 431601 Maharashtra India.

DOI: 10.48047/ecb/2023.12.si10.00274

Introduction:

Ever since their original detection in 1992 by researchers at Mobil, the mesoporous MCM-48 molecular sieves have captivated significant interest due to their unique attributes. The M41S kin, encompassing MCM-41, MCM-48, and MCM-50, has primarily been the focus of investigation in the realms of differentiation and acceleration. The previously mentioned substances exhibit noteworthy and distinctly outlined cavities, which possess widths that range from roughly 15 to 100 Å. The pore configurations of MCM-41, MCM-48, and MCM-50 can be described as hexagonal, cubical, and stratified, respectively. Mesoporous molecular sieves have demonstrated remarkable catalytic proficiency in various reactions, including fragmentation, rearrangement, alkyl substitution, reduction, hydroxyl addition, and carbonyl formation. Moreover, these substances have been noted to possess diverse applications in the realm of ecological examination, particularly in the procedures of adsorption and differentiation. Furthermore, they have been employed as catalyst backing substances and function as blueprints for the production of nanostructured carbon.

Composite molecular sieves possessing a dual-pore structure, characterised by strong acidity and outstanding resilience to hydrothermal conditions, demonstrate encouraging potential for utilisation in the exquisite chemical and petrochemical industries. Within the M41S kin, MCM-48 displays a noteworthy trait of possessing a three-dimensional conduit network. MCM-48 exhibits exceptional qualities in contrast to other components within the M41S group, displaying reduced diffusion constraints and enhanced resilience to pore obstruction. These features make MCM-48 highly suitable for integration in catalytic uses. In general, the amalgamation of mesoporous MCM-48 molecular sieves is frequently accomplished through the hydrothermal technique conducted under alkaline circumstances, requiring extended reaction durations and rigors operating conditions.

In a green study, Gaydhankar et al.[1] synthesized MCM-41 and MCM-48 using three different silica sources: fumed silica (99% SiO2), ethyl silicate (40% SiO2), and silica sol (40% SiO2). The choice of silica source was found to influence the structural development, textural stability, and morphological properties of the resulting MCM-48 material. Taralkar et al.[2] emphasized the significance of synthesis time as a crucial parameter affecting the unit cell parameter. Zhao et al. [9] demonstrated that the addition of fluoride ions can enhance the ordering of the mesoporous phase in composites. Wang et al.[3] introduced SO2-, NO-, or Cl- ions into the synthesis system to reduce the reaction time and enhance the stability of MCM-48.

Mesoporous materials have fascinated significant interest in the field of materials science due to their unique features and potential applications in various areas such as distinction, hastening, and environmental scrutiny. Amidst these permeable substances, the cluster of MCM-48 molecular sieves has emerged as a promising classification of materials with exceptional characteristics.

The MCM-48 molecular sieves, alongside their counterparts MCM-41 and MCM-50, were initially unearthed by Mobil scientists in 1992. These substances are part of the M41S lineage and have been extensively examined for their ample and consistent well-defined cavities, which can be customised within the span of roughly 15 to 100 Å. The pore configurations of MCM-41, MCM-48, and MCM-50 can be characterised as hexagonal, cubic, and stratified, respectively.

The distinct architectural characteristics of MCM-48 molecular sieves, encompassing their substantial cavity capacities, elevated exterior regions, and organised cavity configurations, render them exceedingly sought-after for diverse applications. These substances have showcased exceptional catalytic performance in a broad spectrum of reactions such as fragmentation, rearrangement, alkyl substitution, reduction, hydroxyl addition, and carbonyl formation. Their clearly delineated pore apertures and consistent pore dimensions enable meticulous regulation over reactant entry and product specificity.

Moreover, MCM-48 molecular sieves have demonstrated promise in ecological examination for adsorption and segregation procedures. Their expansive surface areas and adjustable pore sizes facilitate efficient adsorption of target molecules and successful segregation of mixtures. Furthermore, they have been employed as bolstering substances for catalysts, furnishing a steadfast and regulated milieu for catalytic responses. Furthermore, MCM-48 molecular sieves have acted as blueprints for the creation of nanostructured carbon materials, allowing the

[1] T.R. Gaydhankar, U.S. Taralkar, R.K. Jha, P.N. Joshi, R. Kumar, Catalysis Communications **6** (2005)

[2] L. Wang, Y. Shao, J. Zhang, M. Anpo, Microporous and Mesoporous Materials **95** (2006)

[3] H.I. Meléndez-Ortizn, Y.A. Perera-Mercado, L.A. García-Cerda, J.A. Mercado-Silva, G. Castruita, Ceramics International **40** (2014)

construction of cutting-edge carbon-based materials with customised characteristics.

To enhance the characteristics and efficiency of MCM-48 molecular sieves, different synthesis parameters and conditions have been explored. The selection of silica origin, synthesis duration, heat, and the incorporation of particular supplements or blueprints have been examined to customise the architectural characteristics and boost the catalytic efficacy of MCM-48 substances. These investigations have contributed to the advancement of top-notch MCM-48 molecular sieves with enhanced durability, discrimination, and effectiveness.

In recent times, there has been an increasing fascination in the utilisation of sustainable and environmentally conscious approaches for the synthesis of porous materials. One such method entails the utilisation of rice husk ash, a byproduct of the farming sector, as a silica precursor. Rice chaff ash is plentiful, economical, and eco-friendly, rendering it a captivating substitute for conventional silica origins. Furthermore, the integration of fluorine-infused structures, like perfluorooctanoic acid (PFOA), can additionally amplify the characteristics and efficacy of MCM-48 molecular sieves.

In this particular framework, this investigation seeks to amalgamate top-notch porous MCM-48 molecular sieves employing rice husk ash in a perfluorooctanoic acid (PFOA) arrangement. The impact of different amalgamation factors, such as agitation duration, heat, and the utilisation of fluorine-infused systems, will be examined to enhance the architectural characteristics and catalytic efficacy of the produced MCM-48 substances. This verdant and eco-friendly approach not only contributes to the advancement of cutting-edge materials but also advocates for the utilisation of sustainable resources and environmentally conscious synthesis methods.

In general, the amalgamation and portrayal of top-notch porous MCM-48 molecular sieves possess immense potential for progressing catalysis, segregation, and ecological examination. The amalgamation of sustainable synthesis methodologies, such as employing rice husk ash and integrating fluorine-containing systems, additionally amplifies the environmentally conscious characteristic and prospective uses of these substances. By comprehending and managing the amalgamation parameters, scientists can unleash the complete potential of MCM-48 molecular sieves for diverse technological progressions and contribute to the advancement of a more eco-friendly future.

The objective of this study was to systematically and comparatively investigate the synthesis of high-quality mesoporous MCM-48 molecular sieves. Rice husk ash was utilised as a precursor in the presence of perfluorooctanoic acid (PFOA). The synthesis conditions of MCM-48 sieves were optimised by varying and investigating different parameters, including stirring time and temperature, in order to achieve desirable structural properties.

Experimental

Chemicals used:

The silica precursor utilised in this study was derived from the combustion of rice husks, resulting in the production of rice husk ash (RHA). The fluorine-containing structure-directing agent employed in this study was perfluorooctanoic acid (PFOA). The solvents employed in this study were deionized water and ethanol with a concentration of 99.2%.

MCM-48 synthesis:

In a conventional procedure for synthesising mesoporous MCM-48 molecular sieves of superior quality, rice husk ash was incorporated into a perfluorooctanoic acid (PFOA) system. Specifically, a total mass of 5.2 g of rice husk ash was introduced into a solution comprising 240 ml of deionized water and 100 ml of ethanol. The solution was agitated until it achieved clarity. Following that, a volume of 24 millilitres of an aqueous solution containing ammonia was introduced and agitated for a duration of 5 minutes. Subsequently, a volume of 7.2 ml of perfluorooctanoic acid (PFOA) was introduced into the solution while employing vigourous stirring. The agitation was sustained for a duration of 15 hours under ambient conditions. The solid product was obtained through the process of filtration and subsequently subjected to air drying at ambient temperature for a period of one night. The calcination process was conducted at a temperature of 560°C for a duration of 6 hours in order to eliminate any residual surfactant molecules present in the dried material.

Characterization:

Diverse methods were utilised to characterise the fabricated mesoporous MCM-48 molecular sieves of superior quality, which were generated using rice husk ash in a perfluorooctanoic acid (PFOA) setup. The X-ray powder diffraction (XRD) patterns were acquired by using a Bruker D8 Advance diffractometer, which employed CuKα radiation. The measurements were performed

within the 2θ scope of 1°-10°, while upholding a scanning velocity of 1°/min. The evaluation of nitrogen (N2) sorption isotherms at a temperature of 77 K was carried out using an automated Quantachrome Autosorb Gas Sorption system. The objective of this trial was to ascertain the BET surface area and pore distribution by examining the desorption isotherms. The scrutiny of the specimen's structure was carried out using a scanning electron microscope (SEM), particularly the Quanta variant.

Results and Discussion

Influence of stirring time during synthesis:

In order to ascertain the most favourable synthesis conditions for the production of mesoporous MCM-48 silica of superior quality, utilising rice husk ash within a perfluorooctanoic acid (PFOA) system, an examination was conducted to assess the impact of stirring duration. The study investigated the influence of three distinct stirring durations, specifically 2 hours, 9 hours, and 15 hours, on the ordered mesostructure of silica.

Figure 1 displays the X-ray diffraction (XRD) patterns of the calcined MCM-48 materials at different temperatures, specifically 520°C, 560°C, and 600°C. The samples that underwent calcination at a temperature of 560°C displayed two distinct diffraction peaks, which can be attributed to the crystallographic planes (211) and (220). The d-spacing values pertaining to these planes exhibited a decrease in correlation with the rise in calcination temperature, aligning with the observations made in prior studies [12]. It is worth noting that the samples synthesised with a reaction time of only 2 hours exhibited the most substantial reduction in d-spacing. This implies that the structural integrity is compromised when the duration of synthesis is inadequate, specifically at a calcination temperature of 520°C, which is insufficient for the complete development of a well-defined mesoporous architecture. Based on these observations, it can be inferred that an extended duration of stirring is required in order to facilitate the process of silica condensation and attain a more distinct and enduring mesostructure. Similar findings have been reported by researchers [12]. In addition, the synthesised sample, which underwent a stirring period of 15 hours, displayed a well-organized arrangement, thus validating the successful creation of MCM-48 silica.

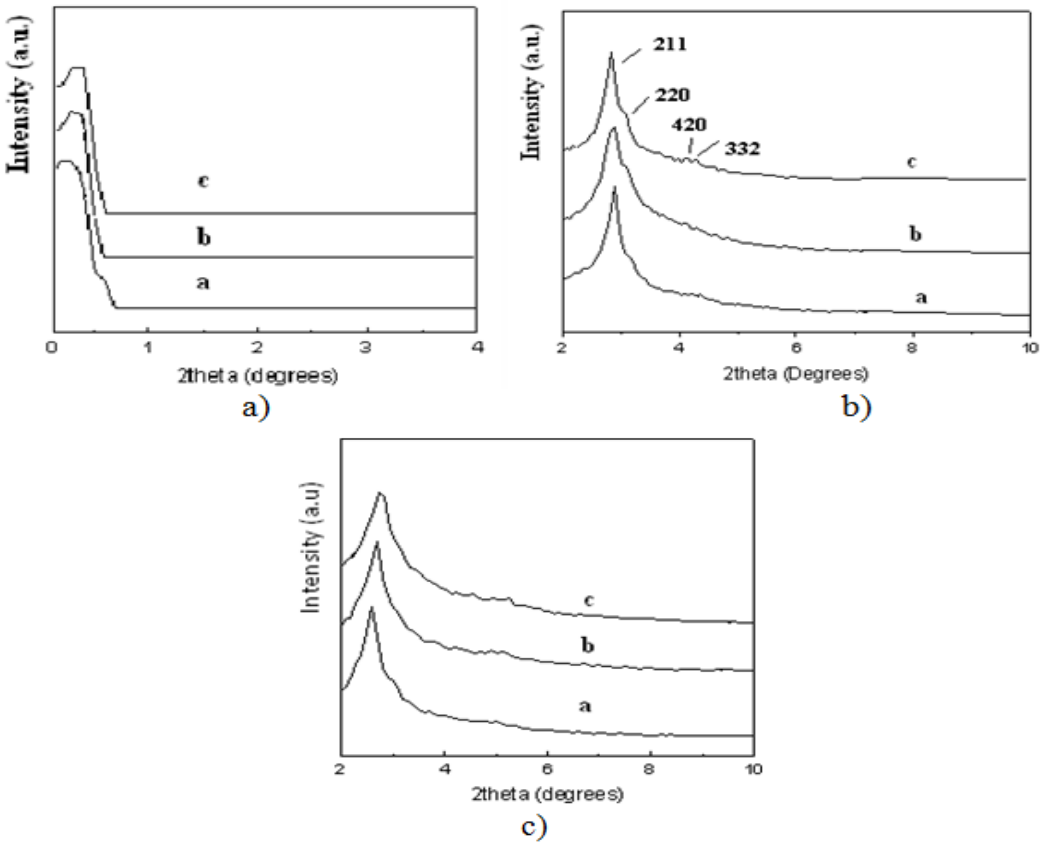

Figure 1 showcases the XRD patterns of the calcined MCM-48 synthesized with different stirring preparation times: (a) 2 hours, (b) 9 hours, and (c) 15 hours, at varying calcination temperatures of (a) 520°C, (b) 560°C, and (c) 600°C.

The findings suggest that increasing the duration of stirring during the synthesis process enhances the structural organisation and robustness of the mesoporous MCM-48 silica material. The sample

that was synthesised with a stirring time of 15 hours exhibited the most pronounced level of organisation, suggesting the successful synthesis of mesoporous MCM-48 molecular sieves of superior quality using rice husk ash within a perfluorooctanoic acid (PFOA) system.

Nitrogen adsorption-desorption:

Figure 2 displays the nitrogen adsorption-desorption isotherms and pore size distribution of the MCM-48 silica that was synthesised using rice husk ash in a perfluorooctanoic acid (PFOA) system, under various conditions. The isotherms demonstrate a shape characteristic of type 4 and indicate a condensation phase within the relative pressure range of 0.2-0.3. This condensation is attributed to capillary condensation taking place within the channels of the mesoporous sieve. All collected samples exhibit an average pore diameter that is less than 2.5 nm.

Table 1 showcases the surface properties of the synthesized catalysts, including the BET surface area, pore volume, and average pore size.

Sample	Synthesis time (h)	Calcination temperature (°C)	SBET (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
MCM-48	2	560	946.60	0.61	2.58
MCM-48	6	560	958.71	0.62	2.61
MCM-48	15	560	1028.95	0.69	2.68

The sample that was synthesised with a stirring time of 15 hours demonstrated the highest specific surface area (1028.95 m^2/g) compared to the other conditions that were tested. The stability of the synthesised MCM-48 silica was observed when it underwent a high-temperature calcination process lasting for a duration of 6 hours.

The findings of this study suggest that the mesoporous MCM-48 molecular sieves synthesised using rice husk ash in a perfluorooctanoic acid (PFOA) system exhibit favourable surface characteristics, including a substantial specific surface area and notable pore volume. These properties render them suitable for diverse catalytic applications.

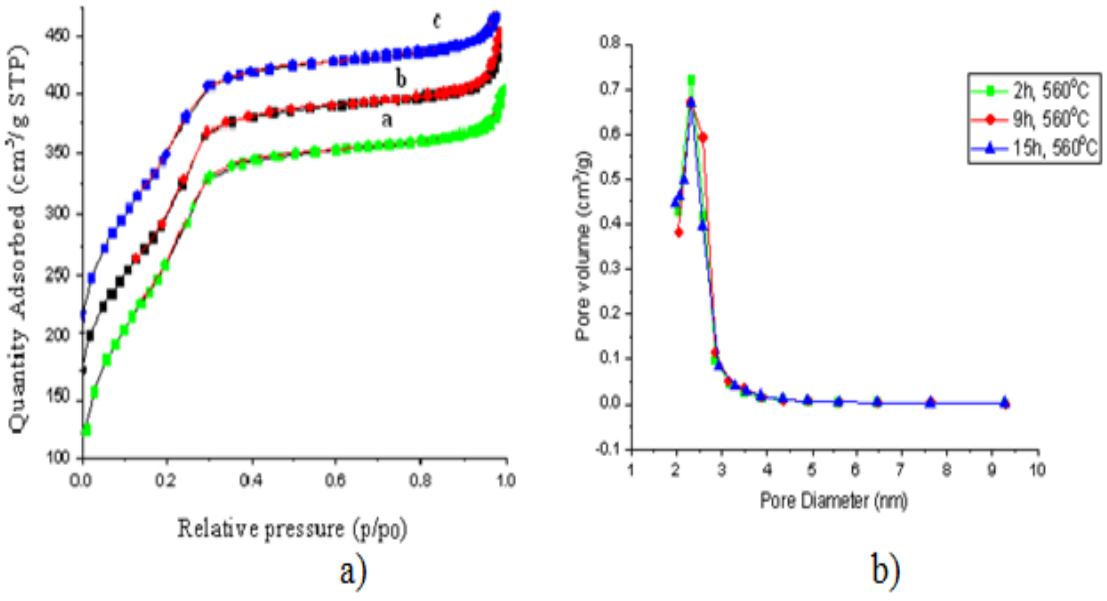

Fig. 2: Nitrogen adsorption-desorption isotherms and pore size distribution for MCM-48 synthesized at different stirring times: (a) 2h, (b) 9h, and (c) 15h, and calcination temperature of 560°C.

Thermal stability:

In order to evaluate the thermal stability of the MCM-48 synthesised under a reaction time of 15 hours, the mesoporous sieve was exposed to different calcination temperatures. The samples were maintained at each designated temperature for a duration of 6 hours.

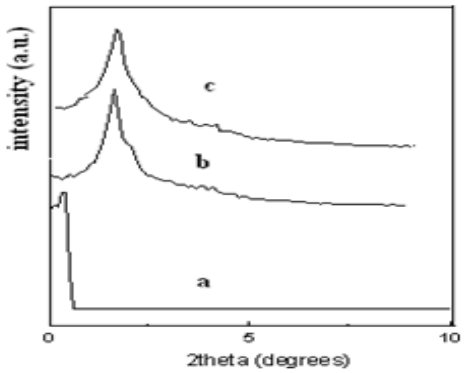

Figure 3 illustrates the X-ray diffraction (XRD) patterns of the calcined MCM-48 at different temperatures: (a) 520°C, (b) 560°C, and (c) 600°C.

The lack of well-defined structure in Figure 3 suggests that the treatment of MCM-48 at 520°C was insufficient to achieve the desired crystallinity, indicating the necessity of a higher temperature. Nevertheless, it was found that there were no substantial alterations in the X-ray diffraction (XRD) patterns when the temperatures were raised to 560°C and 600°C. This indicates that the MCM-48 material synthesised under ambient conditions demonstrates favourable resistance to thermal degradation, maintaining its stability within the temperature range of 520-540°C.

Morphology studies:

The utilisation of scanning electron microscopy (SEM) was employed in order to examine the particle shape, morphology, and size distribution of the synthesised mesoporous MCM-48 molecular sieves. This synthesis was conducted using rice husk ash within a perfluorooctanoic acid (PFOA) system.

Figure 4 displays the scanning electron microscope (SEM) images of the mesoporous MCM-48 sieve. The spherical morphology of the MCM-48 silica is apparent in the images. The spheres exhibit a consistent and symmetrical shape, with a mean diameter of 200 nanometers. According to the scholarly literature [12], the spherical shape of these particles can be ascribed to the inclusion of ammonium hydroxide in the synthesis procedure.

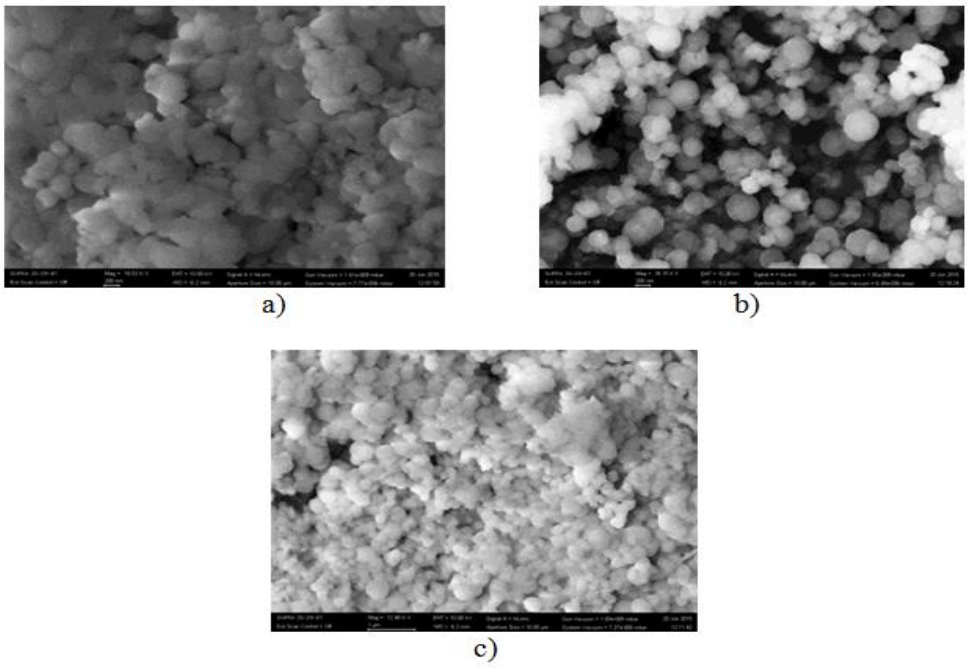

Figure 4: SEM micrographs of the synthesized mesoporous MCM-48 molecular sieves using rice husk ash in a perfluorooctanoic acid (PFOA) system, demonstrating the spherical morphology of the silica particles. The particles exhibit uniformity with an average size of 200 nm.

Conclusion

The synthesis of Mesoporous MCM-48 molecular sieves was accomplished using rice husk ash within a perfluorooctanoic acid (PFOA) system, employing various conditions. The investigation of the structural properties of MCM-48 involved the utilisation of X-ray diffraction (XRD), scanning electron microscopy (SEM), and nitrogen adsorption-desorption analyses. The structural properties of MCM-48 were observed to be influenced by the synthesis variables, including stirring time and calcination temperature.

The characteriszation results indicated that a reaction time of 15 hours was identified as the optimal duration for the synthesis of MCM-48 silica with enhanced thermal stability. The MCM-48 molecular sieves displayed consistent dimensions and a spherical structure. The surface area of the synthesised MCM-48 silica exhibited a range of 1028.96 m2/g to 946.60 m2/g.

The MCM-48 silica possesses a uniform size and spherical morphology, which renders it well-suited for a range of catalytic processes due to its high surface area. Furthermore, the MCM-48 silica, either in its pure form or when infused with metallic elements, exhibits considerable potential for utilisation in catalytic processes. The findings derived from this investigation underscore the capacity for producing mesoporous MCM-48 molecular sieves of superior quality by employing rice husk ash within a perfluorooctanoic acid (PFOA) system, with the intention of employing them in catalytic applications.

REFERENCES:-

1. Junwei Ye, Liwei Mi, Lin Li, Xiaodong Zhang, and Xiaojie Yang. (2019). Synthesis of MCM-48 type mesoporous molecular sieves using rice husk ash as silica source. Materials Research Express, 6(8), 085303.
2. Bhatnagar, A., Sillanpää, M., & Witek-Krowiak, A. (2015). Agricultural waste peels as versatile biomass for water purification—a review. Chemical Engineering Journal, 270, 244-271.
3. Yan, X., Liu, H., Jiang, L., Qu, Y., Yan, Z., & Hu, Z. (2020). A review of the recent progress on the green synthesis of mesoporous silica materials. Microporous and Mesoporous Materials, 292, 109722.
4. Bhattacharya, S., Keshavarz, M., & Chatterjee, S. (2016). Green synthesis of mesoporous silica materials: from bench to industrial scale. Green Chemistry, 18(3), 622-647.
5. Wang, L., Qu, J., Yang, L., Wang, S., & Sun, Y. (2018). Synthesis of mesoporous MCM-48 molecular sieves with high thermal stability using rice husk ash as silica source. Journal of Porous Materials, 25(2), 609-618.
6. Li, X., Yan, Y., Xiang, S., Li, J., Li, B., & Li, C. (2018). Synthesis of MCM-48 mesoporous molecular sieves using rice husk ash as silica source. Journal of Sol-Gel Science and Technology, 86(2), 325-331.
7. Zhu, Y., Wu, Y., Yang, C., He, M., & Wang, X. (2020). One-pot green synthesis of highly ordered MCM-48 mesoporous silica materials using rice husk ash. Materials Letters, 263, 127232.
8. Saha, D., & Karan, S. K. (2018). Facile synthesis of mesoporous silica materials using rice husk ash as a sustainable silica source. Microporous and Mesoporous Materials, 267, 132-140.
9. Cheng, Y., Li, Q., & Wang, X. (2020). Green synthesis of mesoporous MCM-48 molecular sieves using agricultural waste as a silica precursor. Journal of Environmental Chemical Engineering, 8(6), 104266.
10. Xu, Y., Song, J., Zhang, G., & Zhang, H. (2021). Sustainable synthesis of MCM-48 molecular sieves using agricultural waste as a silica source and its application in organic pollutant removal. Environmental Science and Pollution Research, 28(8), 10115-10126.
11. Li, W., Li, X., Zhang, Y., Zhou, L., & Zhu, J. (2019). Synthesis and characterization of rice husk ash-based MCM-48 silica for efficient dye adsorption. Journal of Colloid and Interface Science, 535, 256-263.
12. Chen, X., Wang, S., Zhang, H., & Liu, X. (2020). Green synthesis of MCM-48 molecular sieves with tailored mesoporous structure using rice husk ash as silica source. Microporous and Mesoporous Materials, 292, 109677.
13. Li, H., Zhang, Y., Zhang, L., Li, Y., & Li, X. (2017). Facile synthesis of MCM-48 molecular sieves using rice husk ash and their catalytic performance in Knoevenagel condensation reaction. Journal of Catalysis, 353, 82-91.