Research Article

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# Mesoporous 3D Carbon Foam, Pellets and Composite Monolith using Multi-Walled Carbon Nanotube Derived from Methyl Ester of *Jatropha curcas* Oil

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## ABSTRACT

In this research work, Multi-walled Carbon Nanotubes (MWNTs) were synthesized from the methyl ester of *Jatropha curcas* oil on Fe, Co and Mo catalyst-supported Alumina using Spray Pyrolysis process at temperatures of 650 °C under $N_2$ atmosphere. MWNTs/C composite foam was prepared using resorcinol and formaldehyde as a binder with polyurethane as a sacrificial scaffold by Evaporation Induced Self-assembly (EISA) method, MWNTs/C composite pellets were prepared using coal tar pitch-based Meso Carbon Micro Beads (MCMB) as a binder by Extrusion-Spheronization process followed by Carbonization and MWNTs/C composite monolith was prepared using Microcrystalline Cellulose (MCC) as a binder by Extrusion-Spheronization process followed by Carbonization were successfully reported. The micro and mesoporous composition of the MWNTs/Carbon composite foam had a high surface area of 551.21 $m^2/g$, which was verified by $N_2$ adsorption-desorption measurements. Micro and mesoporous structures with a high surface area and low density were achieved in MWNTs/Carbon Composite pellets. Pore structure was evident in the MWNTs/Carbon Composite monolith.

**Keywords:** Composite monolith; *Jatropha curcas* oil; Multi-walled Carbon Nanotube; MWNTs/Carbon composite foam; Pellet.

## 1. INTRODUCTION

Carbon materials have received enormous attention because of their adjustable thermal and electrical conductivity, low thermal expansion coefficient and large surface area. Carbon materials are discovered in various forms like diamond, carbon fibers, graphite and carbon nanotube, graphene and so on (Lee *et al.* 2006; Zhu *et al.* 2011). Three-dimensional (3D) mesoporous carbon foams with an integrated nanoporous network have excellent properties such as high porosity, low density, low-pressure drop, strong thermal/electrical transport properties and high thermal stability (Chen *et al.* 2013). The above-mentioned peculiar and extraordinary physical properties make them useful as adsorbents for separation processes and gas storage, electrode materials for batteries and supercapacitors, insulators, inclusion material for thermal managements and supports for a variety of critical catalytic processes (Straatman *et al.* 2007; Zhai *et al.* 2011; Song *et al.* 2012).

Graphitic carbon foams are usually made by foaming coal, coal tar pitch and petroleum pitch, then calcining and graphitizing were carried out at high temperatures. Compared to non-graphitic carbon foams, these materials have high electrical and thermal conductivity, a well-aligned crystalline structure and excellent thermal stability (Wang *et al.* 2008; Wang *et al.* 2009).

In this present study, MWNTs were synthesized from methyl ester of *Jatropha curcas* oil. MWNTs/Carbon Composite foam was prepared using resorcinol and formaldehyde as a binder with polyurethane as a sacrificial scaffold by Evaporation Induced Self-assembly (EISA) method, MWNTs/Carbon Composite pellets were prepared by coal tar pitch-based Meso Carbon Micro Beads (MCMB) as a binder by Extrusion-Spheronization process followed by Carbonization and MWNTs/Carbon Composite monolith was prepared with microcrystalline cellulose (MCC) as a binder by Extrusion- Spheronization process followed by Carbonization . SEM and HR-TEM were used to describe the morphological composition of as-grown Multi-walled carbon nanotube-based carbon foam/pellet/composite monolith. Raman spectral experiments and the Brunaur-Emmett-Teller approach were used to investigate the graphitization and pore size distributions of carbon composites in the forms of foam, pellets and monolith.

## 2. MATERIALS AND METHODS

### 2.1 Preparation of MWNTs

In the quartz boat, the Fe-Co-Mo catalyst-assisted Alumina (0.5 g) were incorporated into the middle of a quartz tube mounted in the electrical heating furnace. To expel air and create a nitrogen atmosphere, the reaction furnace was passed through with the carrier gas nitrogen (100 mL $min^{-1}$). The temperature was raised from room temperature to 650 °C, which is the ideal temperature for MWNTs development. The carbon precursor (methyl ester of *Jatropha curcas* oil) was then sprayed into the quartz tube at a rate of 20 mL per hour using a spray nozzle. At the chosen temperature, the deposition time was 60 minutes. The supply of nitrogen was sustained until the furnace reached room temperature. After that, the sample was weighed and placed in an airtight container for further analysis.

### 2.2 Preparation of MWNTs/Carbon Composite Foam

The following procedure was used to make MWNTs/Carbon Composite foam with uniform mesopore walls using Evaporation Induced Self-assembly (EISA) system and polyurethane foam (PU) as the sacrificial scaffold. The mixture was mixed for 15 minutes after resorcinol (1.65 g) and pluronic F127 (2.5 g) were dissolved in a 20 ml/20 ml water/ethanol solution. The above mixture was then stirred for 1 hour with 0.2 g of 37 wt. percent hydrochloric acid. Under stirring, 2.5 g of 37 wt. percent formaldehyde solution was applied drop by drop. A homogeneous solution was obtained after actively stirring the reaction mixture for another 1 hour. After that, the solution was put in a Teflon-lined autoclave bottle. In order to impregnate polyurethane foam (1.5 g) with the polymeric solution inside the enclosed autoclave, the foam was treated with ethanol and added to the polymeric solution. After that, hydrothermal therapy was performed in an autoclave inside a hot air oven for two days at 50 °C. Filtration was done at ease to extract the resin-coated polymeric foam, which was then dried in an oven at 50 °C for 12 hours and then 80 °C for 12 hours. The polymeric foam's color changed to dark reddish-brown. Finally, the impregnated polymeric foam was carbonized in a tubular furnace at 800 °C for 1 hour at a heating rate of 1 °C/min under $N_2$ flow. The above-mentioned carbonized mesoporous carbon foam was impregnated with a solution of iron nitrate in ethanol (3 mmol metal/g) and the impregnated carbon foam was graphitized in a tubular furnace at 1000 °C for 1 h at a heating rate of 1 °C /min under $N_2$ flow. Finally, MWNTs based graphitized mesoporous carbon foam was washed with HCl (5–10%) solution in order to remove the metal particles (Karthik *et al.* 2015).

### 2.3 Preparation of MWNTs/C Composite Pellets

To achieve a fine powder, the carbonized MCMB was ball milled for 3 hours with as-grown MWNTs using methyl ester of *Jatropha curcas* oil. This material was mixed in acetone for 2 hours with an ultrasonicator, then homogenized for 10 minutes to achieve uniform dispersion. A solid sample of MCMB-MWNTs composite is placed in a mortar and ground thoroughly with a pestle. Then the sample was placed underneath a piston and pressures ranging from 5000 to 10000 psi were applied. Finally, the MWNTs/C composite pellets were dried at room temperature overnight.

### 2.4 Preparation of MWNTs/Carbon Composite Monolith

The extrusion-Spheronization process was used to make the MWNTs/Carbon Composite monolith. As-grown MWNTs derived from methyl ester of *Jatropha curcas* oil were mixed with MCC in a high-speed grinder and the solid mixture was moistened with deionized water. At a rotating speed of 50 rpm, the wet mixture was inserted into the extruder to provide noodle-like extrudates. The extrudates were fed into a spheronizer, where they were sliced into small columnar fragments at a faster rotational speed. Subsequently, the rotation speed was held at a medium setting until spherical pellets with smooth surfaces in the diameter range of 0.8–1.2 mm were obtained. By adjusting the screen of the Extrusion-Spheronization system, the particle sizes of the composite monolith spheres could be conveniently adjusted; particles with diameters ranging from 0.5 mm to 2 mm could be collected. Until lyophilization, a freeze-casting post-treatment was conducted on the as-prepared water-containing MWNTs/Carbon Composite monolith to further change the pore structures of the final composite spheres. Then, the freeze-dried MWNTs/Carbon Composite monolith was carbonized for 1 hour in a tube furnace with $N_2$ flow at 800 °C. Bai *et al.* (2018) obtained the MWNTs/Carbon Composite monolith after carbonization (Fig. 1).

### 2.5 Characterization

Surface morphological structure of as-grown multi-walled carbon nanotube-based carbon foam/pellets/composite monolith characterized by SEM and HR-TEM. Graphitization of carbon foam, pellets and composite monolith were analyzed by Raman spectral studies. Pore size distributions of carbon foam/pellets/composite monolith were studied by the Brunaur-Emmett-Teller method (BET).

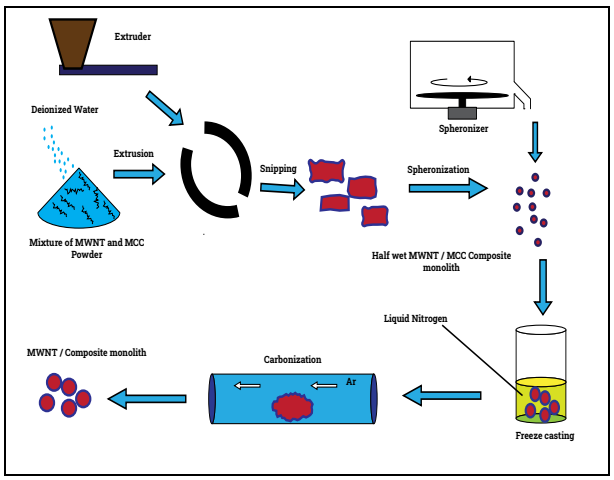



**Fig. 1: Schematic diagram of MWNTs/Carbon composite monolith**

## 3. RESULTS AND DISCUSSION

### 3.1 Optimization of Temperature for Maximum Yield of MWNTs and its Characterisation

The effect of temperature on the yield of MWNTs from vapor phase decomposition of methyl ester of *Jatropha curcas* oil over Fe-Co-Mo catalyst-assisted Alumina at a feed rate of 20 mL per hour is investigated. At 550 °C, a low yield of carbon deposit was provided in this analysis. The yield of carbon deposits was noticeably high at 650 °C, but when the temperature was increased to 750 °C, the yield decreased. Zhn et al. (2007) found a related pattern in their analysis of CNT synthesis by catalytic decomposition of methane with a high yield of MWNTs at 900 °C.

The SEM picture in Fig. 2 shows the development of untangled MWNTs with a diameter in the region of 20-40 nm. The HR-TEM picture in Fig. 2 clearly shows the well-crystalline graphitic layers of MWNTs grown at 650 °C. The inner and outer diameters of the MWNTs produced are 4 and 14-25 nm, respectively. The number of graphitic layers contained in MWNTs is approximately eighteen. The interlayer space of the synthesized MWNTs is 0.34 nm, which compares to the interlayer space of graphene sheets in a graphite structure. Hsieh *et al.* (2009) obtained similar results in their study of the development of CNTs from acetylene over Ni/alumina catalyst in a fluidized bed reactor.

For the MWNTs grown at 650 °C shown in Fig. 3, D and G peaks were observed at about 1343 $cm^{-1}$ and 1582 $cm^{-1}$ in Raman spectral studies. The estimated IG/ID value for the peaks is 1.2. This suggests that the MWNTs were grown at 650 °C and were well graphitized.

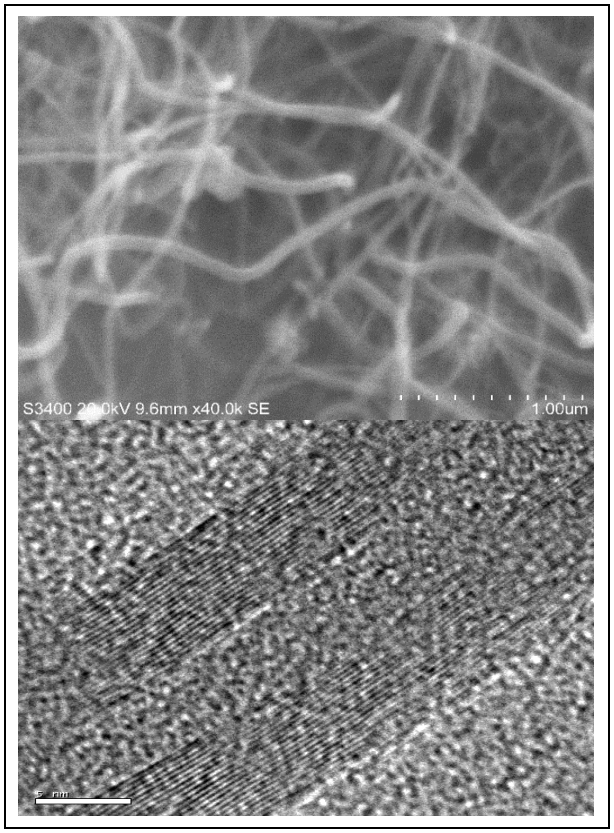



**Fig. 2: SEM and HR-TEM image of MWNTs grown at 650 °C**

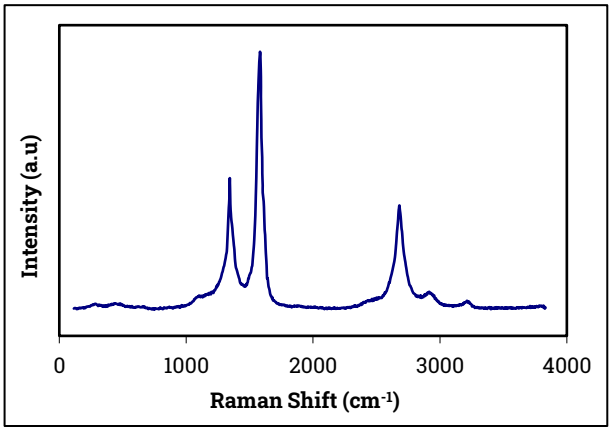



**Fig. 3: Raman Spectra of MWNTs grown at 650 °C**

### 3.2 Morphology Composite Foam of MWNTs/Carbon

In the SEM and HR-TEM photos seen in Fig. 5, the macroporous interconnected 3D network architecture and mesoporous walls of the MWNTs/C composite foam are visible. It's worth noting that the volume of binder and graphitization temperature plays a big role in creating graphitic layers on the pore walls of carbon foam. In the literature, similar findings on the catalytic graphitization of porous carbons have been published.

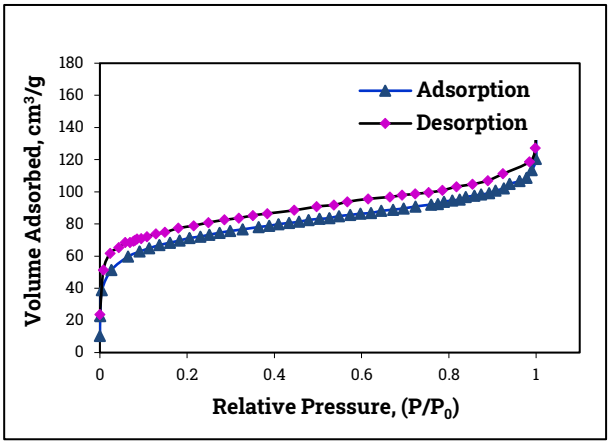



**Fig. 4: $N_2$ adsorption-desorption isotherm of MWNTs/Carbon composite foam**

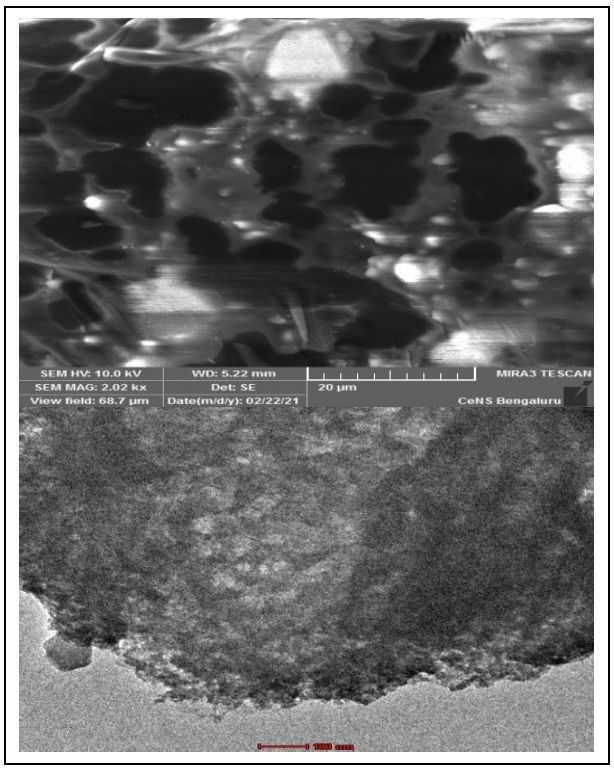



**Fig. 5: SEM and HR-TEM image of MWNTs/Carbon composite foam**

The nitrogen adsorption isotherm data of MWNTs/C Composite foam prepared by EISA method and its corresponding isotherms at liquid nitrogen temperature (77 K) revealed that the majority of the adsorption isotherms of carbon foam samples prepared by various processes are Type 1 according to IUPAC classification. The plateaus of the isotherms are not high, which reflects a small volume of micropores. Pore filling by condensation is responsible for the portion of the isotherm that runs parallel to the pressure axis. Furthermore, visible hysteresis loops for the MWNTs/C Composite foam confirm the presence of mesopores with pore widths ranging from 2 to 50 nanometers.

Fig 4. represents the BET surface area plots for MWNTs/C Composite foam, which revealed a greater BET surface area, micropore volume, and mesopore volume. Because there are more contact points between the adsorbent and the adsorbate, compounds are preferentially adsorbed into pores that are similar in size to the adsorbate, according to (Pelekani *et al.* 1999). Under nitrogen atmosphere, the MWNTs/C Composite foam had the highest surface area of 551.21 $m^2/g$.

## 3.3 Morphology of MWNTs/Carbon Composite Pellets

Fig. 6 shows SEM and HR-TEM images of MWNTs/Carbon composite pellets. SEM revealed the mesoporous carbon architecture of the MWNTs/C Composite pellets. HR-TEM and $N_2$ adsorption-desorption measurements both confirm that the pellets have a uniform mesoporous structure.

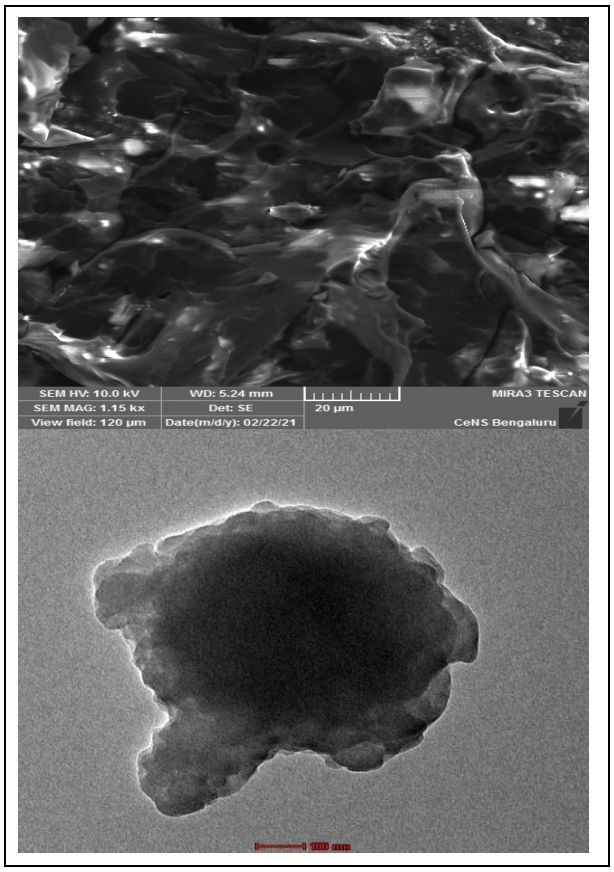



**Fig. 6: SEM and HR-TEM image MWNTs/Carbon composite pellets**

The Raman spectra clearly show three bands at 1351, 1597, and 2660 $cm^{-1}$ for D, G, and G' peaks,

respectively, as shown in Fig 7. The formation of graphite structure can be seen in the G band. The calculated IG/ID value for the peaks is 0.9. When compared to MWNTs/C composite foam prepared using the EISA method, this indicates that it does not contain well graphitization of MWNTs/C composite pellets.

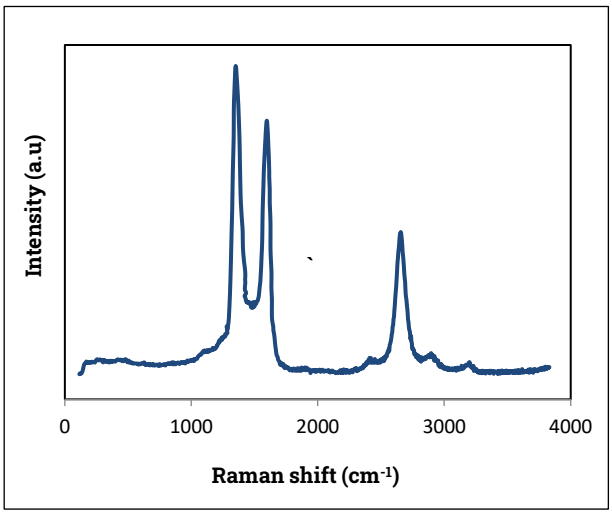



**Fig. 7: Raman spectra of MWNTs/Carbon composite pellets**

The hysteresis of the isotherm of MWNTs/C composite pellets by coal tar pitch with meso carbon microbeads (MCMB) as a binder is very low relative pressure. Such hysteresis, according to Gregg *et al.* 1982), is associated with very narrow micropores. The BET surface area plots for MWNTs/C composite pellets revealed that the BET surface area and micropore volume of MWNTs/C composite pellets were higher than MWNTs/C composite foam by EISA but lower than MWNTs/C composite using MCC.

## 3.4 Morphology of MWNTs/Carbon Composite monolith

In the SEM and HR-TEM images shown in Fig.8, the macroporous carbon architecture of MWNTs/C Composite monolith was clearly visible.

Fig. 9 shows the Raman spectrum obtained for the MWNTs/C composite. Three bands appeared at 1361, 1600, and 2660 $cm^{-1}$ of D, G and G' peaks, respectively, as seen in the Raman spectra. The formation of graphite structure is indicated by the G band. The calculated $I_G/I_D$ value for the peaks is 0.9.

The nitrogen adsorption-desorption isotherm of MWNTs/Carbon Composite monolith made with microcrystalline cellulose (MCC) as a binder and carbonized using an Extrusion-Spheronization process reveals significant nitrogen uptake at a low relative pressure (Fig. 10). The strong interaction between nitrogen molecules and the walls of the mesopores is responsible for this. As a result, the pore volume of the MWNTs/C Composite is negligible. The BET surface area plots for MWNTs/Carbon Composite revealed that MWNTs/C composite might have a higher BET surface area, as well as a higher micropore volume than MWNTs/C composite foam and MWNTs/C Composite pellets.

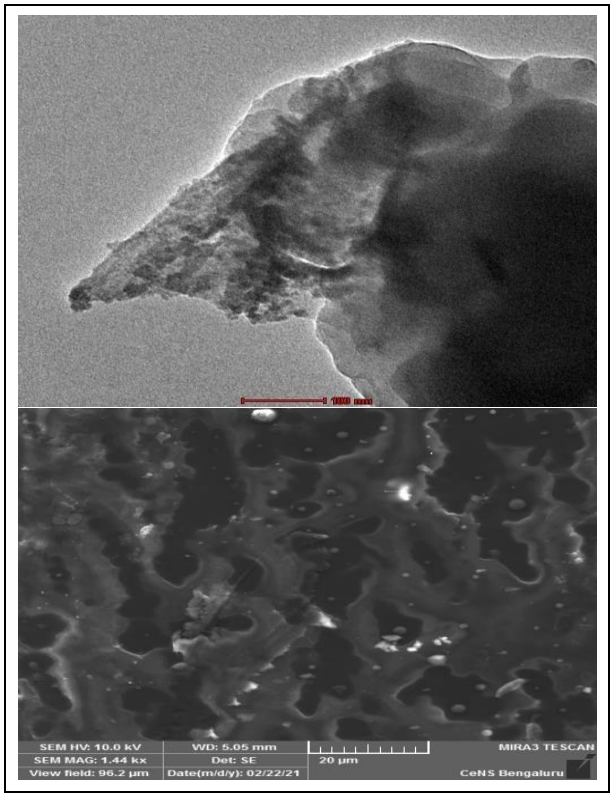



**Fig. 8: SEM and HR-TEM image MWNTs/Carbon composite monolith using nicrocrystalline cellulose**

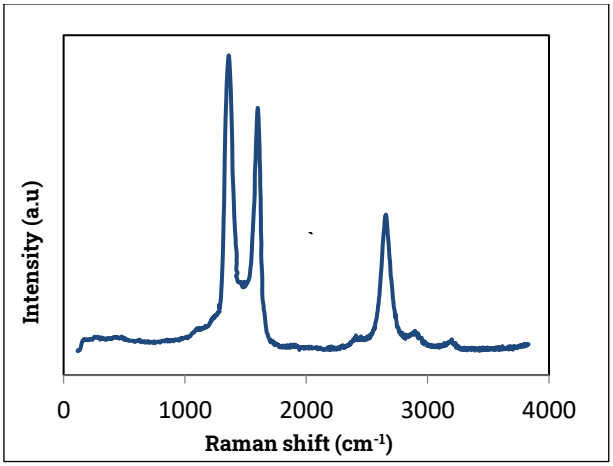



**Fig. 9: Raman spectrum of MWNTs/Carbon composite using microcrystalline cellulose**

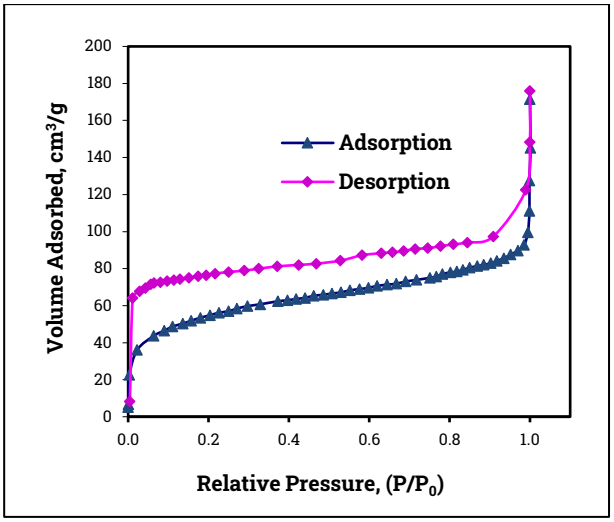



**Fig. 10: Nitrogen adsorption-Desorption isotherm for MWNTs/Carbon composite**

## 4. CONCLUSION

The effect of temperature on the yield and morphology of MWNTs synthesized from natural oil has revealed that 650 °C appears to be the most favorable temperature for producing high yields of well-graphitized MWNTs. Under the experimental conditions for the precursors, Fe-Co-Mo catalyst-supported Alumina is found to be a more active catalyst for producing well-graphitized MWNTs with high yield. The current study discovered that botanical-plant-based oil could be an effective carbon precursor for the spray pyrolysis method of MWNT synthesis.

The prepared as-grown MWNTs/Carbon Composite foam (MWNTs/C composite foam) with uniform mesopore walls have been fabricated using resorcinol and formaldehyde as a carbon binder by EISA method. The well-defined graphitic framework was confirmed by SEM, HR-TEM and Raman studies. The prepared as-grown MWNTs/C composite foam shows both micro and mesoporous structure providing a high surface area 551.21 $m^2/g$, which is confirmed by $N_2$ adsorption-desorption measurement and mesopore width range from 2-50 nm.

MWNTs/Carbon Composite pellets prepared using coal tar pitch-based Meso Carbon Micro Beads (MCMB) as a binder by Extrusion-Spheronization process followed by Carbonization shows both micro and mesoporous structure providing a high surface area with low density has been achieved. A novel approach is used to prepare free-standing, lightweight MCMB-MWNTs Composite pellets, which show promising structured properties with a high surface area of 391.26 $m^2/g$, which is confirmed by $N_2$ adsorption-desorption measurement.

Extrusion-Spheronization followed by Carbonization produced MWNTs/Carbon Composite monolith with a significant pore structure using microcrystalline cellulose (MCC) as a binder. The MWNTs/Carbon Composite monolith have significant adsorption capacities, according to the pore size distribution analysis.

The above results indicate that a simple strategy based on freestanding, lightweight, thin multi-walled carbon nanotubes-based carbon foam/pellets/composite monolith with a high surface area can be used for stealth technology, civil, military, and next-generation flexible electronic devices.

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## CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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## REFERENCES

Bai, J., Huang, Y., Gong, Q., Liu, X., Li, Y., Gan, J., Zhao, M., Shao, Y., Zhuang, D. and Liang, J., Preparation of porous carbon nanotube/carbon composite spheres and their adsorption properties, *Carbon*, 137, 493–501 (2018). https://dx.doi.org/10.1016/j.carbon.2018.05.058

Chen, S., He, G., Hu, H., Jin, S., Zhou, Y., He, Y., He, S., Zhao, F. and Hou, H., Elastic carbon foam via direct carbonization of polymer foam for flexible electrodes and organic chemical absorption, *Energy Environ. Sci.*, 6(8), 2435 (2013). https://dx.doi.org/10.1039/c3ee41436a

Gregg, S. J. and Sing, K. S. W., Adsorption, surface area and porosity. 2. Auflage, Academic Press, London 1982. 303 Seiten, Preis: $ 49.50, *Berichte der Bunsengesellschaft für Phys. Chemie*., 86(10), 957–957 (1982). https://dx.doi.org/10.1002/bbpc.19820861019

Hsieh, C.-T., Lin, Y.-T., Chen, W.-Y. and Wei, J.-L., Parameter setting on growth of carbon nanotubes over transition metal/alumina catalysts in a fluidized bed reactor, *Powder Technol.*, 192(1), 16–22 (2009). https://dx.doi.org/10.1016/j.powtec.2008.11.004

Karthik, M., Redondo, E., Goikolea, E., Roddatis, V. and Mysyk, R., Large-scale hydrothermal synthesis of hierarchical mesoporous carbon for high-performance supercapacitors, *Energy Environ. Focus.*, 4(3), 201–208 (2015). https://dx.doi.org/10.1166/eef.2015.1160

Lee, J., Kim, J. and Hyeon, T., Recent progress in the synthesis of porous carbon materials, *Adv. Mater.*, 18(16), 2073–2094 (2006). https://dx.doi.org/10.1002/adma.200501576

Pelekani, C. and Snoeyink, V. L., Competitive adsorption in natural water: Role of activated carbon pore size, *Water Res.*, 33(5), 1209-1219(1999). https://dx.doi.org/10.1016/S0043-1354(98)00329-7

Song, J., Guo, Q., Zhong, Y., Gao, X., Feng, Z., Fan, Z., Shi, J. and Liu, L., Thermophysical properties of high-density graphite foams and their paraffin composites, *New Carbon Mater.*, 27(1), 27–34 (2012). https://dx.doi.org/10.1016/S1872-5805(12)60002-X

Straatman, A. G., Gallego, N. C., Yu, Q. and Thompson, B. E., Characterization of porous carbon foam as a material for compact recuperators, *J. Eng. Gas Turbines Power.*, 129(2), 326–330 (2007). https://dx.doi.org/10.1115/1.2436562

Wang, M., Wang, C.-Y., Li, T.-Q. and Hu, Z.-J., Preparation of mesophase-pitch-based carbon foams at low pressures, *Carbon.*, 46(1), 84–91 (2008). https://dx.doi.org/10.1016/j.carbon.2007.10.038

Wang, S. and Zhao, X., On the potential of biological treatment for arsenic contaminated soils and groundwater, *J. Environ. Manage.*, 90(8), 2367–2376 (2009). https://dx.doi.org/10.1016/j.jenvman.2009.02.001

Zhai, Y., Dou, Y., Zhao, D., Fulvio, P. F., Mayes, R. T. and Dai, S., Carbon materials for chemical capacitive energy storage, *Adv. Mater.*, 23(42), 4828–4850 (2011). https://dx.doi.org/10.1002/adma.201100984

Zhu, M. and Diao, G., Review on the progress in synthesis and application of magnetic carbon nanocomposites, *Nanoscale.*, 3(7), 2748 (2011). https://dx.doi.org/10.1039/c1nr10165j