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Carbon Ratio Controlled *in-situ* Synthesis of Ordered Mesoporous Hybrid Silica/Carbon Materials *via* Soft Template Method

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Abstract: A strategy for synthesizing the ordered mesoporous hybrid silica-carbon materials with moderate pore volume and surface area are developed from the dry leaves powder of *Tectonagrandis* (TG) as carbon precursor by direct carbon loading method. Pre-activated carbon (PAC) has been generated from the dry leaves powder of TG by sulphuric acid assisted partial chemical activation method. The carbon content in silica matrix of the material is fixed up to 50 weight percentages with respect to silica which renders a novel and highly ordered hybrid Si/C mesoporous material by this direct carbon loading strategy. The physical-chemical analyses are supported that the synthesized hybrid Si/C materials are completely different from carbon coated hybrid Si/C materials. Among the synthesized materials, high surface area containing Si/C material has been chosen for dye adsorption which exhibits an excellent dye adsorption behavior with Methylene Blue (MB) dye up to 97% in short span of time.

Keywords: *Tectonagrandis*, Ordered mesoporous material, Si/C hybrid material, Partial activated carbon, Methylene blue, Adsorption.

1. Introduction:

Development of ordered mesoporous materials (OMM) is an extensive area of research, in particular, due to their applications in the area of gas separation, synthesis of biofuels, chromatography, drug delivery, water purification, electrodes usage, electrochemical double layer for capacitors and fuel cells [1-17]. A number of methods such as polymer blend/organic gels and carbonization of polymer aerogels by using hard as well as soft template methods have been developed for the synthesis of carbon based mesoporous materials [18-28]. The hard template method, is one of the best methods, for the synthesis of mesoporous carbon materials by the co-condensation process [3]. Similarly, a vast number of highly ordered silica and silica based mesoporous materials are reported *via* soft template assisted sol-gel and hydrothermal process. In the recent past, silica/carbon hybrid OMMs received an industrial importance due to their enhanced rigidity, thermal, mechanical properties, chemical stability, extended pore volume, improved hydrophilic, hydrophobic nature. For instance, four steps synthesis of a highly functionalized hybrid Si/C material was reported for the catalytic esterification of maleic anhydride, succinic acid and oleic acid in ethanol [29]. Similarly, mesoporous Si/C composite material was reported by co-polymerization /co-condensation of fine chemicals with tetraethyl orthosilicate (TEOS) and carbonization processes [30-37]. Sulfur and nitrogen functionalized Si/C mesoporous materials have also been explored from *in-situ* polymerization followed carbonization of thiophene and pyrrole within the pores of SBA-15 and KIT-6 materials [38]. From these methods, useful fine chemicals are used as a carbon precursor which is being carbonized within the silica matrix of the materials. A remarkable breakthrough was achieved by the utilization of rice husk, an agricultural waste material, as a silica-carbon source for the synthesis of OMMs [39]. Development of ordered mesoporous materials (OMM) is an extensive area of research, in particular, due to their applications in the area of gas separation, synthesis of biofuels, chromatography, drug delivery, water purification, electrodes usage, electrochemical double layer for capacitors and fuel cells [1-17]. A number of methods such as polymer blend/organic gels and carbonization of polymer aerogels by using hard as well as soft template methods have been developed for the synthesis of carbon based mesoporous materials [18-28]. The hard template method, is one of the best methods, for the synthesis of mesoporous carbon materials by co-condensation process [3]. Similarly, a vast number of highly ordered silica and silica based mesoporous materials are reported *via* soft template assisted sol-gel and hydrothermal process. In the recent past, silica/carbon hybrid OMMs

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2. Experimental section

2.1 Chemicals:

The analytical grade of tetraethylorthosilicate (TEOS), hydrochloric acid (HCl), triblock copolymer poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) (Pluronic P-123, Mw = 5800, EO₂₀PO₇₀EO₂₀) and methylene blue (MB) were purchased from Sigma-Aldrich chemicals and used as such without any further purification.

2.2 Synthesis of pre-activated carbon and activated carbon from TG leaves

Fresh *Tectonagrandis* (TG) leaves were collected from our college campus. The TG leaves were washed many times in running water and dried at room temperature for 7 days. To utilize TG leaves as carbon precursor, the dried leaves were crushed a fine powder mechanically and the particle size was controlled up to 50 microns by the mesh filtration process. Pre-activated carbon was synthesized by a partial chemical activation method [41-43]. Initially, 5 g of TG leaves powder was soaked in 15 ml of 50% H₂SO₄ for 24 h and then

the resulting black slurry was stirred at room temperature for 12 h. The black mass was filtered and neutralized by 270 ml of 1N Na₂CO₃. The neutralized black solid is washed many times in distilled water to remove the excess acid/base and dried at 120 °C for 12 h. The resulting material is pre-activated carbon (PAC). The batch operation was repeated three times and the yields were noted. Each batch, 5 g of TGL powder yielded approximately 2.98 g of PAC (approx. 59 % yields). The synthesized PAC was further subjected to mechanical mortar using Fisher scientific automatic mortar for 12 h. Similarly, the activated carbon was prepared from 5 g of TGL powder by refluxing with 25 ml of Conc. H₂SO₄ for 24 h. The resulting black slurry was allowed to stir at room temperature for 12 h and then filtered through a funnel. The filtered mass was neutralized by adding 900 ml 1N Na₂CO₃ and washed many times with distilled water to remove the excess acid. The black mass was dried initially at 110 °C and then heated in a tubular furnace at 400 °C under nitrogen atmosphere for 3 h. The resulting mass was called activated carbon (AC). The batch operation was repeated with 5 g of TGL powder for three times to get approximately 2.55 g (approx. 51% of yield). The percentage of yield is calculated using the following equation [44].

$$\% \text{ of Yield} = \frac{W_f}{W_i} \times 100 \quad (1)$$

Where, W_f is the mass of the activated carbon and W_i is the mass of the TG leaf powder.

2.3 Synthesis of carbon ratio controlled hybrid order mesoporous silica/carbon (OMSC) materials from PAC

The hybrid OMSC materials were synthesized by template controlled sol-gel process [45, 46]. The molar composition of the reaction mixture is 4g: 6.67: 0.12: 0.041 of P-123, H₂O, H₂SO₄ and TEOS/PAC (Si_{1-X}/C_X) respectively [Foot note 1]. To synthesize various carbon content OMSC materials, the weight percentage of carbon (X) can be chosen as 25, 50 and 75 w/w % with respect to SiO₂. The representative synthetic procedure of OMSC₁ (Si_{1-0.25}/C_{0.25}) is given as below: 4 g of nonionic triblock copolymer Pluronic P-123 was dissolved in 120 ml of water and stirred until the solution become clear. When the solution becomes clear, 6.405 g of TEOS contains 1.845 g of SiO₂ (75%), and 0.615 g of PAC (25%) was added. Subsequently, 6.39 ml of Con H₂SO₄ was added with the mixture [FOOT NOTE 2]. The reaction mixture was allowed for heating at 60 °C for 24 h. The precipitate was filtered, washed in water and dried at 110 °C for 3 h. The resulting precalcinated material was heated at 90 °C with 120 ml of 40% of H₂SO₄ for 24 h for the purpose of disconnecting the ether

linkage between the P-123 as well as complete carbonization of PAC [46]. Finally, the template was completely removed by annealing at 200 °C for 2 h in nitrogen atmosphere [46]. The calcinated material is whitish brown power and is represented as OMSC₁. Similarly, two other materials with different weight percentages Si/C (X= 0.50 and 0.75) were prepared based on the above strategy and are termed as OMSC₂ and OMSC₃ respectively.

2.3 Batch Adsorption Studies

Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks which contain 100 mg of OMSC₂ material and 100 ml of dye solution with different initial concentrations (30 mg/L, 50 mg/L, 100 mg/L and 150 mg/L). The flasks were placed in a mechanical shaker at a constant temperature (313K) in 100 rotations per minute. The adsorbents were filtered and the residual concentration of MB dye was analyzed using a JASCO UV-530 spectrophotometer at a wavelength corresponding to the maximum absorbance of MB. The amount of adsorbed dye q_t (mg/g) was calculated at different time intervals using the following equation [47].

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad (2)$$

Where, C_0 is the initial concentration of MB, C_t is the concentration of MB at time (t), V is the volume of the solution (L) and m is the weight of the adsorbent (g).

2.4 Characterization details

Small-angle X-ray scattering measurements of synthesized materials were recorded in the Bruker D8 Advance powder X-ray diffractometer. X-ray scattering was recorded using X'Pert Pro-Panalytic instrument. The surface morphology and elemental composition of the samples were measured using field emission scanning electron microscopy (FESEM) attached with energy dispersive X-ray spectroscopy (EDAX) in oxford X-act tescan instrument. High resolution transmission electron microscope (HRTEM) analyzer was used for analyzing surface morphology of the materials through 200 KV FEI-Tecnai G2 20 S-Twin high resolution transmission electron microscopes (HR-TEM).

3. Results and Discussion

3.1. FT-IR studies

Initially, the synthesized OMSC₁₋₃ and pre-calcinated POMSC₁ materials were subjected for FT-IR spectroscopy as shown in Fig. 1. The IR spectra of OMSC₁ and OMSC₂ are similar

to each other which resemble the reported hybrid Si-C materials [28]. The template polymeric *C-H* stretching band has appeared at 2964 cm^{-1} in POMSC₁ material which disappeared in the calcinated materials. Interestingly, a characteristic Si-C band appeared at 1250 cm^{-1} in the OMSC₁₋₂ material [48]. FT-IR spectral pattern of OMSC₃, however, did not exhibit any silyl functional band which has very similar to AC material as shown in Fig. 2. It is clear from the FT-IR spectra of OMSC₁₋₃ that the carbon content in the reaction is greater than 50 w/w % of silica from TEOS, the precipitation of silica from TEOS with surfactant is prevented. Thus, the concentration of carbon play a vital role in the synthesis of hybrid Si/C OMM's. In contrast to the reported work, the broadening of the band at $1000\text{-}1300\text{ cm}^{-1}$ and 800 cm^{-1} are exhibited in calcinated samples (OMSC₁ & ₂) which are corresponding to the asymmetric stretching vibration of Si-O-Si band [28]. The broadening of the Si-O-Si band can be attributed either in the formation of C-Si bond in the silica matrix or in the composite nature of OMSC_{1&2} materials.

Fig. 1 FT-IR spectrum of ordered mesoporous silica/carbon materials.

In the presence of AC, however, the formation of OMSC did not observe under the controlled experimental condition. It can be attributed to FT-IR spectra, a significant difference is observed between the spectra of PAC and AC. The broad and flat IR band at 3100-3600 cm^{-1} are exhibited the presence of carboxylic acid, alcohol, phenol and amine groups in PAC which is not observed in AC. The band may correspond to -NH, -OH, C=C, C=O, C-H and -S-H the functional groups of PAC. When AC subjected for preparation of OMSC materials under the hydrothermal process, the participation of hydrophobic AC along with polar TEOS on P-123 is suppressed due to the absence of functional entities like PAC [FOOT NOTE 3].

Fig. 2 FT-IR spectrum of chemically activated PAC and AC materials.

3.2 Small angle X-ray spectroscopic studies (SAXs)

To study the mesoporous nature of the materials, low angle X-ray diffraction study is performed for the OMSC₁₋₃ and POMSC₁ materials. From the Fig. 3, the order of porosity and mesoporous nature of the precalcinated and calcinated materials OMSC_{1&2} are exhibited the higher intensity reflection peak at approximately 1.15° plane. In POMSC₁, the reflection peak is not clear due to the blocking of pores either by the carbon source or by the template polymer [49]. A pronounced diffraction peak ($2\theta = 1.15^\circ$) along with mild two peaks is observed in the OMSC₁₋₂ and POMSC₁ material like SBA-15 ($2\theta = 0.9^\circ, 1.5^\circ, 1.8^\circ$) and the

direct carbonized hybrid Si/C materials. However, the appeared peak positions of synthesized materials are slightly different positions which indicate that the synthesized materials contain similar mesoporous nature with different material nature [50].

Fig. 3 Small angle XRD spectra of pre-calciniced and calciniced OMM's.

3.3 X-ray Diffraction Studies (XRD)

Wide angle X-ray spectroscopic study was carried out to examine the crystalline nature of the materials. The XRD spectra of synthesized compounds are shown in Fig. 4. POMSC₁, OMSC₁₋₂ materials were exhibited a similar types of non-smoothing pattern due to the amorphous nature of the materials. The crystalline nature of the material usually depends on the nature of dopant and the existing position in the silica matrix. The dopants can be persisted either in the core of the material or on the surface which produces amorphous and crystalline nature with respectively. The observed amorphous nature of OMSC materials reveals that the dopant carbon may persist in the core of the materials whereas SBA-15 and direct carbonized hybrid Si/C materials are crystalline nature [28].

Fig. 4 XRD spectrum of POMSC₁, OMSC₁ and OMSC₂.

3.4 Thermo Gravimetric Analysis (TGA)

TGA was carried out to the samples of OMSC₁₋₂ from the temperature of 30 °C to 800 °C under N₂ atmosphere (Fig. 5). The first weight loss profile of 11% and 17% are observed at the temperature range between 31-132 °C with OMSC₁₋₂ respectively. This weight loss can be attributed to the removal of adsorbed moisture/water content on the materials. Due to the good adsorption nature of carbon, OMSC₂ in higher carbon content showed greater weight loss (17%) in the first TG weight loss profile. The second weight loss TG profiles of OMSC₁₋₂ are 17% and 11% respectively in the temperature ranges from 132-646 °C which are assigned for the removal of the residual carbon content of polymer/ untreated PAC. OMSC₂ contains a higher carbon ratio, however, TG weight loss profile of OMSC₂ is less than OMSC₁ and also lesser than any reported hybrid Si/C materials. The observed result gives two important conclusions that i. Sulphuric acid etching followed thermal calcination (200 °C) effectively remove the template under this condition ii. Acid assisted carbonization of PAC effectively converts into activated carbon which is unavailable under pyrolytic degradation (TGA). From the Fig. 1 & 5, the broadening of Si-O-Si stretching in FT-IR spectrum and poor weight loss in TG profiles implies that carbon in the synthesized Si/C

materials may exist in the matrix of the silica framework rather than coated over the surface of the material.

Fig. 5 TGA weight loss profile of OMSC₁ and OMSC₂.

3.5. Field Emission Scanning Electron Microscope analysis (FESEM)

FESEM images of OMSC₁₋₃ are shown in Fig. 6. The images of OMSC_{1&2} displayed the porous nature whereas OMSC₃ did display a smooth pattern. By using the SEM analysis, the pore size of OMSC_{1&2} materials is calculated and compared with BET adsorption isotherm which is good agreement with each other and remains the mesoporous nature.

Fig. 6 SEM images of (a) OMSC₁ (b) OMSC₂ and (c) OMSC₃.

3.6. Transmission Electron Microscope analysis

The order of porosity of OMSC_{1&2} materials is primarily supported by SAXS analysis which is further confirmed by TEM analysis Fig. 7. From the TEM images, a well-ordered hexagonal array structure was observed both OMSC_{1&2}. The *d* spacing values between the adjacent hexagonal layers are 8.2 nm and 8.6 nm in OMSC_{1&2} respectively. Unlike template carbonized hybrid Si/C material, OMSC_{1&2} materials do not contain any reflection planes in SAED pattern and support the amorphous nature of materials along with wide angle XRD analysis. It is further supported that carbon in the materials should be in the silica matrix rather than on the surface.

Fig. 7 TEM images of (a) OMSC₁ and (b) OMSC₂.

3.7. Energy Dispersive X-ray Spectroscopy

The elemental composition of the synthesized OMSC₁₋₃ was analyzed by EDX analysis and the images are shown in Fig. 8a-c. The amount of carbon content and their existence in the silica matrix has supported from the EDX spectra and are given in Table 1. However, if we exclude the oxygen content of these materials, the ratio of C: Si in OMSC_{1&2} is approximately 23:77 and 35:65 respectively. The observed ratio of these materials with respect to C/Si is further validated and supported the experimental procedure of this strategy. It is clear from the EDX spectra, the concentration of carbon content in the hybrid material can be controlled in the desired manner. It is further supported that the PAC, a partially oxidized organic compound, can be participated during the formation of mesoporous material along with silica on polymer templates. EDX image of OMSC₃ has clearly revealed that the precipitation of silica from TEOS is prevented due to the high concentration of PAC Fig. 8c.

Fig. 8 EDX spectrum of synthesized hybrid Si/C compounds OMSC₁, OMSC₂ and OMSC₃.

Table 1. EDX analysis of synthesized OMSC materials

Synthesized hybrid Si/C materials	Mass percentage		
	Carbon	Oxygen	Silica
OMSC1	11.39 (22.8) ^a (25%) ^b	48.35	38.51 (77.2) ^a
OMSC2	17.82 (34.7) ^a (50%) ^b	48.77	33.41 (65.3) ^a
OMSC3	52.79 (--) (75%) ^b	37.15	3.65

^aActual percentage of carbon and silica in the synthesized OMSC materials

^bParentheses in the table are theoretical value of carbon content.

3.8. BET- analysis

The porosity of synthesized OMSC₁₋₂ was established by BET (Brunauer-Emmett-Teller) analysis and exhibited type IV isotherm. A well-developed mesoporosity of OMSC₁₋₂ was supported by nitrogen adsorption-desorption isotherms as shown in Fig. 10. By using the BET analysis, the texture properties of surface area and total pore volume of the materials were calculated and listed in Table 2. The observed N₂ adsorption/desorption in BET analysis indicates the high degree of well defined framework mesoporosity of the materials which is already concerted along with SAXS and TEM analysis. The surface areas of hybrid Si/C materials OMSC_{1&2} are calculated as 488.19 m²/g and 559.04 m²/g respectively. Among the materials, OMSC₂ is having high surface area and pore volume with slight contraction in pore diameter (Table 2). This is may be due to the greater amount of carbon present in the silica framework which reduces the pore diameter during the calcination. The ordered channel array of OMSC₁ is 5 nm in pore diameter in TEM analysis which is a good correlation with BET analysis (4.6 nm). Compared with template carbonized hybrid Si/C material (388 m²/g),

the OMSC₁ & 2 contain a high surface area of 488.19 m²/g and 559.04 m²/g with respectively. The high surface area of the materials is due to the decreases in the wall thickness of OMSC_{1&2} compared with template carbonized hybrid Si/C material [28].

Fig. 9 TEM image of inter planar d-spacing value.

The pore size distribution of OMSC_{1&2} is calculated from N₂ desorption isotherm by Barrett-Joyner-Halenda (BJH) method as shown in Fig. 11. The material OMSC₂ exhibited high pore volume with narrow pore distribution than OMSC₁. Due to the high concentration of carbon in OMSC₂, the wall thickness increases causes the reduction of the pore diameter. The pore diameter and volume of synthesized materials are shown in Table 2.

Fig. 10 N₂ Adsorption and desorption isotherm of OMSC₁ and OMSC₂.

Fig. 11 BJH pore distribution cure of OMSC₁ and OMSC₂.

Table 2. Texture properties of the synthesized materials OMSC1 & 2.

Sample	2 θ (111)	d (nm)	a (nm)	S _{BET} (m ² /g)	V _p (cm ³ /g)	P _{psd} (nm)	b (nm)
OMSC1	1.22	10.825	12.5	488.19	0.524	4.6	8.2
OMSC 2	1.20	10.825	12.5	559.04	0.583	3.9	8.6

3.9. Application of OMSC₂ in *Methylene Blue* (MB) dye adsorption

3.9.1 Effect of OMSC₂ dosage and contact time:

The OMSC₂ is chosen for the dye adsorption studies which contained a high surface area than OMSC₁. Various dosage of OMSC₂ has been studied (30 mg to 140 mg) against 100 ml of 0.030 g/L of MB solution. The effect of removal of MB by OMSC₂ is shown in Fig. 12. Removal of MB is increased from 17% to 95% by increasing the dosage of OMSC₂. In 100 mg of OMSC₂, the adsorption reached saturation in 0.030 g/L solution at 75 min. By comparing the reported hybrid Si/C material, the material exhibits better adsorption property in a shorter duration [51-54]. The adsorption efficiency of 100 mg OMSC₂ is further evaluated against 0.030 g/L of MB in 100 ml solution by UV-Visible spectrophotometer as

shown in Fig. 13. Under this condition, MB is completely adsorbed by 100 mg of OMSC₂ in 70 min contact time.

Fig. 12 Effect of OMSC₂ dosage after 75 min of 100 ml solution.

Fig. 13 UV-Visible spectra of MB solution with different contact time.

3.9.2 Effect of the initial concentration of MB dye

The adsorption capacity (q_t) of OMSC₂ increases rapidly from 43 mg/g to 175 mg/g at 75 min while increasing the concentration of MB from 30 mg/L to 150 mg/L as shown in Fig. 14. The concentration of MB is high, a rapid collision takes place between MB and OMSC₂ at the equilibrium which make pore deposition of MB in the surface of the material.

Fig. 14 Effect of concentration of MB dye and adsorption capacity of OMSC₂.

3.9.3 Adsorption Kinetics

To study the adsorption kinetics of the hybrid material with MB, pseudo-first order (PFO) model and pseudo-second order (PSO) model were employed. The PFO model kinetic equation is shown as follows [52].

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

Where, q_t and q_e (mg/g) are the adsorption capacity of OMSC₂ at specific time t and equilibrium time (min) with respectively. The k_1 (min⁻¹) is rate constant of the PFO model. Rate constant (k_1) and adsorption capacity at equilibrium ($q_{e,cal}$) are calculated from Fig.15a. The kinetic equation of the PSO model is given as follows [52].

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

Where, k_2 (g/mg.min) is adsorption rate constant. K_2 and $q_{e,cal}$ were estimated by intercept and slope of the PSO model respectively (Fig. 15b).

Fig. 15 Adsorption kinetic of MB on OMSC₂ (a) Pseudo first order (PFO) model.
(b) Pseudo second order (PSO) model.

The results of the PFO and the PSO are given in Table 3. Among them, the PSO model is in good agreement with experimental value adsorption capacity (q_e) and best fitted with correlation coefficient ($R^2=0.99$). From the Fig. 15b, the calculated $q_{e,cal}$ and $q_{e,exp}$ experimental results of the adsorption kinetic properties of MB on OMSC₂ are best fitted for the PSO model than the PFO model.

Table 3. Kinetic parameters of pseudo first order and pseudo second order in different concentration at 313 K.

Parameters	Initial concentration of MB (mg/L)			
	30	50	100	150
$q_{e.exp}$ (mg/g)	43	66	119	175
Pseudo First Order				
$q_{e.cal}$ (mg/g)	54	104	218	311
k_1 (min ⁻¹)	0.123	0.093	0.105	0.161
R^2	0.90	0.91	0.99	0.99
Pseudo Second Order				
$q_{e.cal}$ (mg/g)	45	68	129	188
k_2 (g/mg.min)	0.0048	0.0022	0.0009	0.0010
R^2	0.99	0.99	0.99	0.99

3.9.4. Thermodynamic consideration

In order to evaluate the adsorption layer distribution between the material and dye, Langmuir and Freundlich adsorption isotherm were applied in this study. The Langmuir adsorption isotherm described uniform monolayer adsorption process and the equation is shown as follows [52].

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} C_e \quad (5)$$

Where, K_L (L/g) is Langmuir adsorption constant. q_m (mg/g) is a maximum adsorption capacity of OMSC₂ and C_e is the dosage of OMSC₂. The maximum adsorption capacity of OMSC₂ (q_m) and Langmuir adsorption constant (K_L) is calculated from the slope and intercept of the Langmuir plot Fig. 16.

Fig. 16 Langmuir adsorption isotherm of MB on OMSC₂.

Table 4. Parameters of Langmuir and Freundlich adsorption isotherm at 313 K.

Langmuir parameters			Freundlich parameters			
$q_m(\text{mg/g})$	$K_L(\text{L/g})$	R^2	$q_m(\text{mg/g})$	K_F	N	R^2
			$(\text{mg/g (L/mg)}^{1/n})$			
769	0.0019	0.8887	279	5.12	1.15	0.9994

Freundlich adsorption isotherm explains the multi-layer deposition of MB on the surface of OMSC₂. Freundlich adsorption isotherm is expressed in the following equation 6 [52].

$$\ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e \quad (6)$$

Where, K_F ($\text{mg/g (L/mg)}^{1/n}$) and n_F are the Freundlich adsorption constant. C_e is the equilibrium concentration of OMSC₂ and q_e is the amount of adsorption of MB per unit mass of OMSC₂. K_F values are calculated from the intercept value of Freundlich adsorption plot in Fig. 17. From the Fig. 17, the maximum adsorption capacity (q_e) is obtained as 279 mg/g. Langmuir and Freundlich adsorption isotherm parameters are shown in Table 4. Among

them, Freundlich adsorption isotherm is best fitted for adsorption of MB on OMSC₂. The adsorption capacity of OMSC₂ was compared with the list of mesoporous materials; a high adsorption capacity is showed by OMSC₂ with MB (Table 5). Compare with transition metals doped SBA materials; the observed adsorption capacity can be reasonable due to the presence of carbon content in the mesoporous material.

Fig. 17 Freundlich adsorption isotherm of MB on OMSC₂.

In order to assign the nature of adsorption, Gibbs free energy of adsorption (ΔG_{ads}) is calculated from the equation 7 [55].

$$\Delta G = -RT \ln K_d \quad (7)$$

Where, R is a gas constant (8.314), T is temperature and K_d is the distribution coefficient. The distribution coefficient (K_d) can be calculated by using equation 8.

$$K_d = \frac{q_e}{C_e} \quad (8)$$

Where q_e (mg/g) is the equilibrium concentration of dye molecules on OMSC₂ and C_e (mg/L) is the equilibrium concentration of dye molecules in the solution. K_d value is obtained

1.4 and ΔG_{ads} value is $-8.75 \text{ KJ mol}^{-1}$ at 313 K. The value of ΔG_{ads} is $\approx -10 \text{ KJ mol}^{-1}$ and since the type of adsorption is physisorption [56].

Table 5. Comparison of adsorbing capacity of OMSC2 and other silica materials.

Material	BET surface area (m^2/g)	Adsorption capacity (mg/g)	References
Ni-MCM-41	931	189	[57]
Al-SBA-15	693	79	[58]
Ti-SBA-15	1031	208	[59]
OMSC2	559	279	This work

4. Summary

Hybrid OMSC materials have been successfully synthesized from biogenous material of plant TG leaves as a carbon precursor by soft template method in the first time. The TG leaves is been converted in to partially chemical activated carbon by sulphuric acid which contains better functional entities than activated carbon. The superior functional nature of PAC is accounted by FTIR analysis and fruitfully utilized as a carbon precursor to prepare ordered mesoporous materials. Under the hydrothermal condition, the PAC interacted either with silica or polymer template and reinforced along with silica on the structure directing group without perturbing the sol-gel mechanism. At present, the exact interaction mechanism between PAC and silica/polymer has not yet known. It assumes that the polar functional natures of PAC can interact with the polymer template under the reaction condition and generate composite material. In the controlled studies, it is clear that in the presence of TEOS with AC or PAC and P-123 in absence of TEOS, the reaction mixture did not provide the desired products under hydrothermal condition. FT-IR spectrum pattern of synthesized OMSC materials has good agreement with hybrid Si/C materials. The observed broadening of the IR spectral band at $1000\text{-}1300 \text{ cm}^{-1}$ are exhibited in calcinated materials due to the composite nature. The composite nature of the materials is further supported by poor TG weight loses profile and absence of reflection plane in SAED pattern. Similarly, the mesoporous nature has been supported by low angle XRD 2θ value; BET adsorption, SEM and HR-TEM analyses with their specific inferences. The amorphous nature of the materials is confirmed by a wide angle XRD non-smoothening pattern and SAED pattern of materials. It is clear from the EDX spectrum, the concentration of carbon content has been controlled in the desired manner by this strategy. The observed carbon ratio of these materials with respect

SiO₂ in EDX analysis is further validated and supported the experimental procedure of this strategy. The carbon content can be controlled up to 50 w/w % in the silica matrix by this strategy. OMSC₂ showed good adsorption efficiency with MB dye and agreement with the PSO model and Freundlich adsorption isotherm. The maximum adsorption capacity (q_m) of OMSC₂ was observed in 279 mg/g which has a good correlation with the experimental values. The kinetic and thermodynamic results are supported by the physisorption mode of adsorption along with experimental value. The observed maximum adsorption capacity (q_m) at 279 mg/g is a good agreement with experimental data.

Associated Content

Ethics approval and consent to participate

Not applicable in this manuscript

Consent for Publication

Not applicable in this manuscript

Availability of data and Materials

All the characterization results were given in the manuscript.

Compete of interest

The authors declare no conflict of interest.

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Foot note 1:

Where, the subscript (1-X) in Si is represented the SiO₂ content of TOES (8.54 g) and considered as 100 weight percentage of SiO₂ (2.46 g) while the subscript of X in C is zero.

Foot note 2:

Si/C ratio in OMSC could be controlled by choosing the appropriate weight of PAC based on the conversion PAC in to AC by batch studies. By adding the PAC with weight equivalent of AC, the various compositions of hybrid Si/C materials was prepared.

Foot note 3:

Similar attempt was made to prepare ordered mesoporous carbon from TG leaves, pre-activated carbon was treated with Pluronic-123 (P-123) under sol-gel process. The composition of the reaction mixture is 4g: 6.67: 0.024: 0.041 of P-123, H₂O, H₂SO₄ and PAC respectively. The molar composition of PAC was chosen instead of molar composition of tetraethylorthosilicate (TEOS) in the preparation of SBA-15 under sol-gel process. The synthetic procedure is given bellow: 4 g of Pluronic-123 (P-123) was dissolved in 120 ml of water and stirred until the solution becomes clear. Pre-activated carbon (PAC) (0.492 g) was added as carbon source in the solution. 1.27 ml of Conc. H₂SO₄ was added to convert PAC into the ordered mesoporous carbon. The reaction mixture was refluxed at 60 °C for 24 h. The resultant solid mass was filtered and washed with water and the mixture was dried at 110 °C for 3 h. The dried mass was refluxed at 90 °C with 40% of H₂SO₄ for 24 h for removing template and completing the carbonization of pre-activated carbon by chemical activation method. By this method, the ether linkage of the polymeric pluronic-123 has been disconnected and the material was washed and dried at 110 °C for 3 h. The resultant carbon material was subjected for calcination by annealing at 200 °C for 2 h in air atmosphere. The material was subjected for spectroscopic characterization and represented as disordered carbon (DC).