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 the synthesis of hybrid ordered mesoporous silica-carbon (Si/C) materials with moderate pore volume and surface area has been developed from the pre-calcinated MCM and the carbon precursor of Tectonagrandis (TG) dry leaves powder by the direct carbon loading method. The carbon precursor of pre-activated carbon (PAC) from the dry leaves powder of TG was prepared with the assistance of sulphuric acid by the partial chemical activation method. The controlled studies of the carbon loading method indicate that the PAC is a better precursor for the preparation of hybrid Si/C material than activated carbon from TG leaves. By this direct carbon loading strategy, the carbon content in the silica matrix is fixed up to 50 weight percentages with respect to silica and renders a novel and highly ordered mesoporous Si/C (OMSC) material. The synthesized hybrid Si/C materials are completely characterized by physico-chemical analyses. The observed 2θ values (2θ = 1.15°, 1.5°, 1.8°) of SAX’s analysis, XRD patterns and thermogravimetric analysis of hybrid Si/C materials indicate that the synthesized materials are considerably different from carbon coated Si/C materials. The OMSC hybrid material containing high surface area has been chosen for dye adsorption that exhibits excellent dye adsorption behavior with Methylene Blue (MB) dye up to 97% in a short span of time. The effects of material dosage, contact time and initial concentration of MB dye adsorption were discussed. Adsorption kinetics of the pseudo first order (PFO) and pseudo second order (PSO) model along with adsorption isotherms of Langmuir and Freundlich were verified for the adsorption of MB on OMSC\textsubscript{2}. The experimental result was best fitted to the pseudo second order kinetic models and Freundlich adsorption isotherm. The calculated maximum adsorption capacity (q\textsubscript{m}) (279 mg g\textsuperscript{-1}) is in good agreement with the experimentally observed value, which is higher than other silica-carbon materials.

Keywords Tectonagrandis · Ordered mesoporous material · Hybrid Si/C material · Partial activated carbon · Methylene blue · Adsorption

1 Introduction
The preparation of ordered mesoporous materials (OMM) has been attained an extensive research interest due to their applications in the field of gas separation, synthesis of biofuels, chromatography, drug delivery process, water purification, electrodes usage, electrochemical double layer capacitors and fuel cells [1–17]. For the synthesis of carbon based OMM’s, polymer blend/organic gels and carbonization of polymer aerogels have been used via hard and soft template methods [4, 18–27]. Among the methods, the mesoporous carbon materials have been efficiently obtained by the hard template co-condensation process [3]. Similarly, a vast number of highly ordered silica-based mesoporous materials are obtained via soft template assisted sol-gel and hydrothermal
processes [4, 18–27]. In the recent past, the hybrid silica/carbon OMMs have received industrial attention due to their enhanced rigidity, thermal and mechanical properties, chemical stability, extended pore volume, improved hydrophilic and hydrophobic nature. For instance, a functionalized hybrid Si/C material was explored for efficient catalytic esterification of maleic anhydride, succinic acid and oleic acid with ethanol [28]. However, a very limited strategy has been reported for the preparation of hybrid ordered Si/C materials. The ordered mesoporous Si/C composite materials were obtained from fine chemicals with tetraethyl orthosilicate (TEOS) by co-polymerization/co-condensation followed by the carbonization processes [29–36]. Similarly, sulfur and nitrogen functionalized mesoporous Si/C materials were obtained from thiophene and pyrrole by in-situ polymerization within the pores of SBA-15 and KIT-6 materials followed by the carbonization process [37]. From these methods, useful fine chemicals are used as a carbon precursor which is being carbonized within the silica matrix of the materials. However, a remarkable breakthrough was achieved using the agricultural waste materials such as rice husks containing silica-carbon sources that have been utilized for the synthesis of OMMs [38]. It is clear from these studies, the preparation of hybrid Si/C material either from the hard template or soft template methods, the carbon yielding precursor should interact with the template and retain its shape along with silica sources. Hence, we assume that the plant source as a carbon precursor has the ability to interact with an amphiphilic polymer template under hydrothermal conditions which could provide a hybrid Si/C OMM. For instance, a direct synthesis of mesoporous carbons with bicontinuous pore morphology from crude plant material was reported using the hydrothermal carbonization process [39]. In addition, the direct and desired carbon loading strategy from biogenic material for the synthesis of hybrid Si/C mesoporous materials has not yet been reported. Hence, it is necessary to develop a strategy for the synthesis of hybrid Si/C mesoporous materials from dry TG leaves as carbon precursor via the soft template assisted direct carbon loading strategy.

Organic synthetic dyes have been utilized in many industries like food, papers, pharmaceuticals, cosmetics, paints, plastics, leathers and textiles. The low biodegradability and the stability of dye stuff threaten the environment and real danger to living beings. Among the various dyes, cationic methylene blue (MB) dye is an essential colouring material for cotton, wood and leather industries and industrial effluents are a predominant source of water and soil pollutants [40, 41]. In addition, MB dye causes severe harmful effects on human beings such as nausea, vomiting, increased heart rate and skin/eye irritations [42, 43]. Aiming that, several methods such as adsorption, photocatalytic oxidation, coagulation has been employed for removing MB dye from the effluents [40, 41, 44, 45]. Owing to the simplicity of design, the generation of non-toxic compounds, low cost and high efficiency, the adsorption techniques have been used widely in waste water treatment for the removal of MB dye. The removal of industrial dye pollutants utilizing porous materials in the sense of environmentally benign is an important area of contemporary research. Herewith, we have reported the synthesis of highly ordered Si/C hybrid materials using TG leaves as a carbon precursor in the desired percentage by the direct carbon loading strategy. The high surface area containing synthesized material has been chosen and evaluated for the adsorption of MB dye. The OMSC material exhibits an excellent dye adsorption behavior with Methylene Blue (MB) dye up to 97% in 75 min.

2 Experimental section

2.1 Chemicals

The analytical grade of tetraethyl orthosilicate (TEOS), sulphuric acid (H$_2$SO$_4$), sodium carbonate (Na$_2$CO$_3$), triblock copolymer poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) (Pluronic P-123, Mw = 5800, EO$_{20}$PO$_{70}$EO$_{20}$) and methylene blue (MB) were purchased from Sigma-Aldrich chemicals and used as such without further purification.

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

Fresh Tectonagrandis (TG) leaves were collected from our college premises. The TG leaves were washed many times in running water and dried at room temperature for 7 days. The dry TG leaves were crushed as fine powder mechanically and the particle size was controlled up to 50 microns by the mesh filtration process. Pre-activated carbon was prepared by a partial chemical activation method [46–49]. Initially, 5 g of TG leaves powder was soaked in 15 ml of 50% H$_2$SO$_4$ for 24 h and then the resulting black slurry was stirred at room temperature for 12 h. The black mass was neutralized by 270 ml of 1 N Na$_2$CO$_3$ and filtered using whatman-40 filter paper. To remove the excess acid/base, the black solid was washed many times with distilled water and then dried for 12 h at 120 °C. The resulting material is pre-activated carbon (PAC). The batch process was repeated three times and the yields of PAC were noted. In each batch, 5 g of TG leaves powder yielded approximately 2.98 g of PAC (approx. 59% yield). The synthesized PAC was further subjected to mechanical mortar using Fisher Scientifics automatic mortar for 12 h. Similarly, the activated carbon was prepared from TG leaves powder (5 g) with 25 ml of conc. H$_2$SO$_4$ by refluxing for 24 h. The resulting black slurry was allowed to stir room temperature for 12 h and neutralized by 900 ml of 1 N Na$_2$CO$_3$. The neutralized black slurry was filtered through the funnel using whatman-40 filter paper and washed many times with distilled water to remove the excess acid and base. The black mass was
dried initially at 110 °C and then heated in a tubular furnace at 400 °C under a nitrogen atmosphere for 3 h. The resulting black mass was called activated carbon (AC). The batch process was repeated three times with 5 g of TG leaves powder, yielding approximately 2.55 g (approx. 51% of yield) of AC. The percentage of yield is calculated using the following Eq. 1

\[
\% \text{of yield} = \frac{W_f}{W_i} \times 100
\]  

(1)

Where, \(W_f\) is the mass of the activated carbon and \(W_i\) is the mass of the TG leaves powder.

### 2.3 Synthesis of hybrid ordered mesoporous silica/carbon (OMSC) materials from PAC

The hybrid OMSC materials were synthesized by a template controlled sol-gel process \[51, 52\]. The molar composition of the reaction mixture is 4g: 6.67: 0.12: 0.041 of P-123, \(H_2O\), \(H_2SO_4\) and TEOS/PAC (\(Si_1/X/C_X\)) respectively. Where, 0.041 mole of TEOS contains 2.46 g of silica which is considered as 100 weight percentage (wt%). The weight percentage of the carbon (PAC) in OMSC materials has been chosen as 25 (0.615 g), 50 (1.230 g) and 75 (1.845 g) wt% with respect to the wt% of Si (2.46 g). The ratio of the materials \(Si_{0.75}/C_{0.25}\), \(Si_{0.50}/C_{0.50}\), \(Si_{0.25}/C_{0.75}\) and are denoted as OMSC1, OMSC2 and OMSC3 with respectively. The typical synthetic procedure for OMSC1 (\(Si_{0.75}/C_{0.25}\)) is given as below: 4 g of non-ionic triblock copolymer Pluronic P-123 was dissolved in 120 ml of water and stirred until the solution become clear. When the solution became clear, 6.405 g of TEOS contains 1.845 g of SiO\(_2\) (75%), and 0.615 g of PAC (25%) was added. Subsequently, 6.39 ml of conc. \(H_2SO_4\) was added to the mixture. The reaction mixture was allowed to heat for 24 h at 60 °C. The precipitate was filtered, washed in water and dried at 110 °C for 3 h. The material is represented as pre-calcinated ordered mesoporous silica carbon material (POMSC1). POMSC is a pre-calcinated material with a P-123 template. POMSC1 was then heated at 90 °C in 40% \(H_2SO_4\) (120 ml) for 24 hours to remove the P-123 and carbonize the PAC \[45\]. Finally, the polymer template was completely removed from the POMSC materials by annealing them in a nitrogen atmosphere at 200 °C for 2 h. The calcinated whitish brown powder is represented as OMSC1. The same procedure is explored for the preparation of hybrid Si/C materials with different weight percentages containing (\(Si_{0.50}/C_{0.50}\), \(Si_{0.25}/C_{0.75}\)) OMSC materials by the direct carbon loading method.

### 2.4 Adsorption Studies of MB

A batch adsorption process was used to investigate the adsorption of methylene blue on OMSC2. The adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks which contain 100 ml of dye solution with different initial concentrations (30-150 mg L\(^{-1}\)) using 100 mg of OMSC2 material at 35 °C. The different dosages of OMSC2 (30-140 mg) were added to 100 mL of MB dye (30 mg L\(^{-1}\)) solution at room temperature and agitated in a mechanical shaker with 100 rotations per minute. The dye adsorption was calculated for various time intervals (1, 2, 3, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75 min). The adsorbents were filtered and the residual concentration of MB dye was analyzed using a JASCO-UV-530 spectrophotometer at absorbance maximum wavelength (\(\lambda_{max}\)) of 613 nm. The adsorption capacity of OMSC2 \([q_t \text{ (mg g}^{-1}\)]\) in each adsorption system was calculated at different time intervals using the following equation \[53\].

\[
q_t = \frac{(C_0 - C_t) \times V}{m}
\]  

(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).
2.5 Characterization details

The Fourier transform infra-red (FT-IR) spectrum was recorded using a JASCO 460 plus spectrometer and the spectral range is 4000-400 cm\(^{-1}\). Small-angle X-ray scattering measurements of synthesized materials were recorded in the Bruker D8 Advance powder X-ray diffractometer range of 0.5 to 10 (2\(\theta\) value). X-ray scattering studies were recorded using an X’ Pert Pro-Panalytic instrument (recorded 2\(\theta\) value range from 5 to 90) by Cu K\(\alpha\) radiation. 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) on an Oxford X-act tescan instrument. A high resolution transmission electron microscope (HRTEM) analyzer was used for analyzing the surface morphology of the materials through a 200 KV FEI-Technai G2 20 S-Twin high resolution transmission electron microscope (HR-TEM). Thermogravimetric analysis (TGA) was carried out from the temperature range of 30-800 °C under N\(_2\) flow with the heating rate at 10 °C min\(^{-1}\) using a Perkin Elmer-STA 600 model instrument. N\(_2\) sorption analysis was carried out using Micromeritics, Tristar (II) 3020, after degassing at 200 °C for 12 h in a vacuum (6.58×10\(^{-5}\) 1/ torr). Batch adsorption studies were analyzed by a UV-Vis spectrophotometer (JASCO UV-530 spectrophotometer).
3 Results and Discussion

3.1 FT-IR studies

The FT-IR spectrum of the synthesized OMSC$_{1-3}$ and POMSC$_1$ materials are shown in Fig. 1. The IR spectra of OMSC$_1$ and OMSC$_2$ are similar to each other, and their functional groups significantly resemble with the hybrid Si-C materials [27]. The polymeric template C-H stretching frequency was observed at 2964 cm$^{-1}$ in POMSC$_1$ material whereas it disappeared in the OMSC$_{1-3}$ materials. Interestingly, the characteristic Si-C band appeared at 1250 cm$^{-1}$ in the OMSC$_{1-2}$ material [54]. The asymmetric stretching vibration of the Si-O-Si band in OMSC$_{1-2}$ was observed at 1000-1300 cm$^{-1}$ and 800 cm$^{-1}$. In contrast to the inner wall carbon-coated SBA material, the broadening of the asymmetric stretching vibration of the Si-O-Si band (1000-1300 cm$^{-1}$) indicates that the
OMSC$_{1-2}$ materials consist of a C-Si bond or in composite nature [27]. However, the silyl functional group band has not appeared in OMSC$_3$ and their functional pattern of the FT-IR spectrum is closely similar to activated carbon as shown in Fig. 2. The absence of a silyl functional group band in the FT-IR spectrum of OMSC$_3$ indicates that the reaction contains more than 50 wt% of carbon content which prevents the precipitation of silica from TEOS. Thus, the concentration of carbon in the reaction plays a vital role in the synthesis of hybrid OMSC.

The synthesis of OMSC was attempted using activated carbon (AC) instead of PAC. However, the formation of OMSC has not been observed under controlled experimental conditions. It can be attributed to the fact that a significant difference is observed between the spectra of PAC and AC. The observed broad and flat IR band at 3100-3600 cm$^{-1}$ reveals that the PAC consists of carboxylic acid, alcohol, phenol, thiol, and amine functional groups, whereas AC contains the least such functional entities (Fig 2). When AC is used as a carbon precursor, the precipitation of polar TEOS along with hydrophobic AC on the polymer template P-123 is suppressed due to the absence of vast functional entities like PAC.$^1$

### 3.2 Small angle X-ray spectroscopic (SAXs) studies

The low angle X-ray diffraction studies of OMSC$_{1-2}$ and POMSC$_1$ are shown in Fig 3. From Fig. 3, the higher intensity reflection peak at 1.15° supports the presence of ordered porosity and mesophase structure of the OMSC$_{1-2}$ and POMSC$_1$ materials. In POMSC$_1$, the reflection peak is not clear due to the blocking of pores either by the PAC or the polymer template [55]. A pronounced reflection peak (2θ = 1.15°) along with mild two peaks is observed in the OMSC$_{1-2}$ and POMSC$_1$ materials like SBA-15 (2θ = 1.5°, 1.8°). However, the observed reflection peak positions of OMSC materials indicate that the synthesized materials are different from the direct carbonized hybrid Si/C materials [27, 56].

$^1$ 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, H$_2$O, H$_2$SO$_4$ 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. H$_2$SO$_4$ was added 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. H$_2$SO$_4$ 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 H$_2$SO$_4$ 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).

### 3.3 X-ray Diffraction (XRD) Studies

XRD analyses were examined for the study of the crystalline nature of the materials and are shown in Fig. 4. The observed broad single peak approximately at 25° (28 value) and non-smoothening pattern indicate that the POMSC$_1$, OMSC$_{1-2}$ materials are amorphous in nature. The crystallinity of the material depends on the position and nature of the dopant in the silica matrix. The observed amorphous nature of OMSC materials reveals that the carbon may persist in the core of the materials whereas the direct carbonized hybrid Si/C materials are crystalline in nature [27].

### 3.4 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) of OMSC$_{1-2}$ is shown in the Fig. 5. TGA was carried out in the temperature range from 30 °C to 800 °C with the rate of 10 °C min$^{-1}$ in N$_2$ atm. The first weight loss profile of OMSC$_{1-2}$ is 11% and 17% with respectively in the temperature range of 31-132 °C. This weight loss can be attributed due to the removal of adsorbed moisture/water content on the materials. Due to the higher carbon content and greater adsorption of water, OMSC$_2$ shows greater weight loss (17%) then OMSC$_1$ in the first TG weight loss profile. The second weight loss TG profile of OMSC$_{1-2}$ is 17% and 11% with respectively in the temperature range of 132-646 °C. The second region is associated with the removal of the residual carbon content of polymer/untreated PAC. Though OMSC$_2$ contains a higher carbon ratio, the TG weight loss profile of OMSC$_2$ is lower than OMSC$_1$ and also lesser than any reported hybrid Si/C materials [4, 18, 19, 23, 27]. The observed result reveals two important conclusions such as i. Sulphuric acid etching followed thermal calcinations (200 °C) effectively removed the template carbon under the reaction condition ii. Acid-assisted carbonization of PAC effectively transforms into activated carbons that are unavailable under the pyrolytic degradation (TGA). The broadening of Si-O-Si stretching frequency in the FT-IR spectrum (Fig. 1) and the weight loss profile of TGA (Fig. 5) together imply that the OMSC$_{1-2}$ containing carbon bind in the silica matrix rather than coated over the surface of the material.

### 3.5 Field Emission Scanning Electron Microscope analysis (FESEM)

FESEM images of the synthesized OMSC$_{1-2}$ are shown in Fig. 6. The porous nature was displayed by the materials of OMSC$_{1-2}$ whereas OMSC$_3$ has a smooth pattern like activated carbon [57]. From the SEM images, the pore size of OMSC$_{1-2}$ materials is calculated and the values are around 4.7 nm to 5.6 nm by the image j software analysis in threshold
Table 1: EDX analysis of synthesized OMSC materials

| Synthesized hybrid Si/C materials | Mass percentage          |
|----------------------------------|--------------------------|
|                                  | Carbon       | Oxygen       | Silica       |
| OMSC1                            | 11.39 (22.8)% | 50.10        | 38.51 (77.2)%|
| OMSC2                            | 17.82 (34.7)% | 48.77        | 33.41 (65.3)%|
| OMSC3                            | 55.93 (98.18)%| 40.45        | 3.65 (1.82)% |

*a Experimentally observed carbon and silica wt% of the OMSC1,3 materials.  
*b Theoretically added wt% of carbon content of OMSC1,3

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

Fig. 7 TEM images of (a) OMSC₁ and (b) OMSC₂
adjustment and the materials retain their mesoporous nature [58]. The calculated pore size values from SEM images were compared with the BET adsorption isotherm. The calculated SEM values and BET pore size values are in good agreement with each other and the observed small variations may be due to the aggregation of particles on the OMSC surface.

3.6 Transmission Electron Microscope analysis

The order of porosity of OMSC1-2 materials is primarily supported by SAXS analysis and further confirmed by TEM analysis as shown in Fig. 7. From the TEM images, a well-ordered hexagonal array structure was observed in OMSC1-2 materials. Inter planar spacing values (d spacing values) between the adjacent hexagonal layers of OMSC1-2 are calculated and the values are 8.2 nm and 8.6 nm, respectively. Disparate the template carbonized hybrid Si/C material, OMSC1-2 materials have not shown any reflection planes in the SAED pattern and support the amorphous nature along with XRD analysis. It is further supported that carbon is in the silica matrix of material rather than on the surface.

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, b, and c. The amount of carbon content in the silica matrix is supported from the EDX spectra and is given in Table 1. It is clear from Table 1, after excluding the content of oxygen from these materials, the ratio between the C:Si in the OMSC1-2 has existed as approximately 23:77 and 35:65, respectively. The observed ratio between C/Si of these materials further validates and supports the experimental procedure of this strategy. It is interesting to mention that the concentration of carbon content in the hybrid material can be controlled up to 50 wt% in a desired manner. The EDX spectrum of OMSC3 clearly reveals that the high concentration of PAC (> 50 wt%) prevents the precipitation of silica from TEOS under the controlled reaction condition (Fig. 8c).

3.8 BET Surface Area Analysis

The porosity of synthesized OMSC1-2 was established by nitrogen (N2) sorption studies and the images are shown in Fig. 9. The surface area and pore size distribution of OMSC1-2 were calculated by using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) method respectively. The calculated surface area of OMSC1-2 and pore size distribution has given in Table 2. The N2 sorption obtained for the materials can be exhibited type IV adsorption isotherm. Combined with SAXS and TEM analysis, the obtained pore size distribution support the well defined mesoporosity of the materials. From BET surface area calculation, the surface area of hybrid OMSC1-2 is 488.19 m² g⁻¹ and 559.04 m² g⁻¹, respectively. Among them, OMSC2 consists of high surface area, pore volume and slightly narrowing the pore diameter than OMSC1 (Table 2). The narrowing of pore diameter may be attributed that the high amount of carbon content in the silica framework may reduce the pore diameter and wall thickness during the calcination [27]. The synthesized OMSC1-2 contains a significantly high surface area than template carbonized hybrid Si/C material (388 m² g⁻¹). The drop of wall thickness may be responsible for

| Table 2 | Texture properties of the synthesized materials OMSC1-2 |
|---------|--------------------------------------------------------|
| Samples | 2θ (111) | d (nm) | a (nm) | \( S_{BET} \) (m² g⁻¹) | \( V_p \) (cm³ g⁻¹) | \( P_{PSD} \) (nm) | \( b \) (nm) |
| OMSC1   | 1.22     | 10.825 | 12.5 | 488.19 | 0.524 | 4.6 | 8.2 |
| OMSC2   | 1.20     | 10.825 | 12.5 | 559.04 | 0.583 | 3.9 | 8.6 |

a 2θ, main (111) peak position; d, XRD (111) interplanar spacing; a = 2d/1.732; \( S_{BET} \), the BET specific surface area; \( V_p \), primary mesopores volume; \( P_{PSD} \), the pore diameter calculated using the BJH method; \( b \), the thickness of wall, \( b = a-P_{PSD} \)
the high surface area of the materials. The interplanar spacing value (d-spacing value) of OMSC1 is calculated (5 nm) by TEM analysis Fig. 10. The calculated interplanar spacing value is in good agreement with the pore diameter value of OMSC1 (4.6 nm) in N2 sorption studies Fig. 11.

The pore size distribution of OMSC1-2 is calculated from the N2 desorption isotherm by the BJH method as shown in Fig. 11. The material OMSC2 exhibited high pore volume with a narrow pore distribution than OMSC1. The pore diameter and volume of synthesized materials are shown in Table 2.

3.9 Application of OMSC2 in the adsorption of Methylene Blue dye

3.9.1 Effect of OMSC2 dosage and contact time

The high surface area containing OMSC2 has been chosen for the adsorption studies of Methylene Blue (MB) dye. Various dosages of OMSC2 were studied (30 mg to 140 mg) against 100 ml of 30 mg L\(^{-1}\) of MB dye solution. The effect of the dosage of OMSC2 on the MB dye adsorption is shown in Fig. 12. The adsorption capacity of OMSC2 is gradually increased from 17% to 95% by increasing the dosage from 30-140 mg against the dye in 30 mg L\(^{-1}\) solution. The highest adsorption capacity is obtained with 100 mg of OMSC2 at 75 min. The result indicates that the OMSC2 material exhibits better adsorption of dye in a shorter duration than the reported hybrid Si/C material [59–62]. The adsorption efficiency of OMSC2 (100 mg) is further evaluated against 30 mg L\(^{-1}\) of MB in 100 ml solution by UV-Visible spectrophotometer as shown in Fig. 13. Fig. 13 clearly indicates that the adsorption of MB takes place completely by OMSC2 within 75 min of contact time.

3.9.2 Effect of the initial concentration of MB dye

The effect of initial concentration on the adsorption of MB dye by OMSC2 was studied with various concentrations such as 30 mg L\(^{-1}\), 50 mg L\(^{-1}\), 100 mg L\(^{-1}\) and 150 mg L\(^{-1}\) using 100 mg of OMSC2 at 35 °C. The adsorption capacity (q\(_e\)) of OMSC2 rapidly increases while increasing the concentration of MB at 75 min as shown in Fig. 14. It is clear from Table 3, the adsorption capacity (q\(_e\)) of OMSC2 increases from 43 mg g\(^{-1}\) to 175 mg g\(^{-1}\) of MB dye when increasing the dye concentration from 30 mg L\(^{-1}\) to 150 mg L\(^{-1}\). The observed high adsorption capacity can be rationalized due to the high
concentration of dye molecules that may cause effective interaction with active surface of the OMSC\textsubscript{2} material. In addition, the high initial concentration of dye molecules creates a concentration gradient for mass transfer into the pores that results in the pore deposition of dye molecules has been taken in OMSC\textsubscript{2} [63].

3.9.3 Adsorption Kinetics

The adsorption kinetics of OMSC\textsubscript{2} was studied with various concentrations of MB (30--150 mg L\textsuperscript{-1}) in 75 min of contact time at 35 °C. To study the adsorption kinetics of OMSC\textsubscript{2}, the pseudo-first order (PFO) model and pseudo-second order (PSO) model were employed. Initially, the kinetic equation of the PFO model is studied as given in Eq. 3 [64].

\[
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t
\]  \hspace{1cm} (3)

Where, \(q_t\) and \(q_e\) (mg g\textsuperscript{-1}) are the adsorption capacity of OMSC\textsubscript{2} at a specific time \(t\) and equilibrium time (min), respectively. \(k_1\) (min\textsuperscript{-1}) is the rate constant of the PFO model. As shown in Fig. 15a, the rate constant (\(k_1\)) and adsorption capacity at equilibrium (\(q_{e,cal}\)) are calculated from the linear plot of time (t) vs ln (\(q_e- q_t\)). The results are tabulated in Table 3. From Table 3, it is clear that the calculated adsorption capacity (\(q_{e,cal}\)) and experimental results (\(q_{e,exp}\)) are different from the PFO model. In addition, the linear regression coefficient (\(R^2\)) of the linear plot is relatively low in the adsorption of...
MB on OMSC$_2$. It reveals that the adsorption of MB on OMSC$_2$ does not obey the PFO [64].

The adsorption kinetics of MB on OMSC$_2$ was employed by the PSO model. The kinetic equation of the PSO model is given in Eq. 4 [64].

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

Where, \(K_2\) (g mg$^{-1}$ min$^{-1}$) donates the adsorption rate constant. \(K_2\) and \(q_{e,cal}\) were estimated by the intercept and slope of the PSO model, respectively (Fig. 15b). From the plot of time \((t)\) vs \(t/q_e\), the PSO model \(K_2\) and \(q_{e,cal}\) were estimated from intercept and slope, respectively (Fig. 15b). The results are shown in Table 3. The PSO model is in good agreement with the experimental value of adsorption capacity \((q_e)\) and the correlation coefficient \((R^2 = 0.997, 0.998, 0.992, 0.999)\) is best fitted for the adsorption of various concentrations (30, 50, 100, 150 mg L$^{-1}$) of MB on OMSC$_2$ than the PFO model [63].

The intra-particle diffusion model was used to predict the mode of adsorption of MB on OMSC$_2$. The Weber and Morris intra-particle diffusion equation has been used as given in Eq. 5 [63].

\[
q_t = K_d t^{1/2} + C
\]

Where, \(K_d\) is the intra-particle diffusion rate constant (mg g$^{-1}$ min$^{-1/2}$), \(C\) is the intercept. \(K_d\) was calculated from the plot between \(t^{1/2}\) vs \(q_t\) as shown in Fig. 15c. From Fig. 15c the observed two intercept linear lines indicate that the intra-particle diffusion is not the rate limiting step rather the multi-step process may control the adsorption kinetics of MB on OMSC$_2$ [65]. In addition, the surface adsorption mechanism dominates in the first 15 min of contact time of MB on OMSC$_2$, thereafter the diffusion mechanism takes place in the adsorption of MB. From Fig. 15c, the increase in the concentration of MB dye increases the linearity of the first stage of the plot, indicating that the concentration of MB plays a vital role in the adsorption process. It is further supported by the PSO model adsorption kinetics of MB on OMSC$_2$.

A plausible mechanism has been proposed based on the Weber and Morris intra-particle diffusion plot of the adsorption of MB on OMSC$_2$ as follows.

(i) The first step is a rapid adsorption of the MB dye molecules from the aqueous medium to the external surface of the OMSC$_2$ (stage I).

(ii) The intra-particle diffusion has taken place between the externally adsorbed MB molecules into the pore of the OMSC$_2$ and a fresh adsorption of MB on the surface of the OMSC is taking place simultaneously in the second step (stage II).

(iii) The equilibrium has been attained between the adsorption of MB and aqueous medium in the final step (stage III).

In addition, the cationic MB dye naturally interacts with the surface silica hydroxyls of the OMSC by Van der Waals interaction and hydrogen bonding [65].

![Fig. 15 Adsorption kinetic of MB on OMSC$_2$](image)

### Table 3 Kinetic parameters of PFO and PSO in different concentration of MB

| Parameters | Initial concentration of MB (mg L$^{-1}$) | 30 | 50 | 100 | 150 |
|------------|-----------------------------------------|----|----|-----|-----|
| \(q_{e,exp}\) (mg g$^{-1}$) | | 43 | 66 | 119 | 175 |
| Pseudo First Order | | | | | |
| \(q_{e,cal}\) (mg g$^{-1}$) | | 54 | 104 | 218 | 311 |
| \(k_1\) (min$^{-1}$) | | 0.123 | 0.093 | 0.105 | 0.161 |
| \(R^2\) | | 0.903 | 0.916 | 0.994 | 0.990 |
| Pseudo Second Order | | | | | |
| \(q_{e,cal}\) (mg g$^{-1}$) | | 45 | 68 | 129 | 188 |
| \(k_2\) (g mg$^{-1}$ min$^{-1}$) | | 0.0048 | 0.0022 | 0.0009 | 0.0010 |
| \(R^2\) | | 0.997 | 0.988 | 0.992 | 0.999 |
| Intra particle diffusion model | | | | | |
| \(K_d\) (mg g$^{-1}$ min$^{-1/2}$) | | 17.808 | 12.784 | 6.312 | 4.157 |
| \(R^2\) | | 0.881 | 0.966 | 0.896 | 0.760 |
3.9.4 Thermodynamic consideration

In order to determine the adsorption equilibrium between the OMSC 2 material and dye, theoretical models such as the Langmuir and Freundlich adsorption isotherm were used in these studies. The Langmuir adsorption isotherm describe a uniform monolayer adsorption process and the equation is given in 6 [66]. The Langmuir adsorption isotherm of MB dye on OMSC 2 was studied with various concentrations such as 30 mg L⁻¹, 50 mg L⁻¹, 100 mg L⁻¹ and 140 mg L⁻¹ using 100 mg of material at 35 °C. The experimental adsorption isotherm of MB on OMSC 2 is given in Fig. 16. From Fig. 16, the adsorption of MB on OMSC 2 does not obey the monolayer adsorption isotherm.

\[
\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} C_e
\]  

(6)

Where, \( K_L \) (L g⁻¹) donates the Langmuir adsorption constant. \( q_m \) (mg g⁻¹) is a maximum adsorption capacity of OMSC 2 and \( C_e \) is the dosage of OMSC 2. The maximum adsorption capacity of OMSC 2 (\( q_m \)) and Langmuir adsorption constant (\( K_L \)) is calculated from the slope and intercept of the Langmuir adsorption isotherm (Fig. 16) and the values are given in Table 4.

The experimental conditions mentioned above (Langmuir adsorption isotherm, Freundlich adsorption isotherm) were investigated. The Freundlich adsorption isotherm is expressed in the following Eq. 7 [66].

\[
\ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e
\]  

(7)

Where, \( K_F \) (mg⁻¹ L¹/n g⁻¹) and \( n_F \) are the Freundlich adsorption constant. \( C_e \) is the equilibrium concentration of OMSC 2 and \( q_e \) is the amount of adsorption of MB per unit mass of OMSC 2. \( K_F \) values are calculated from the intercept value of the Freundlich adsorption isotherm in Fig. 17. From Fig. 17, the maximum adsorption capacity (\( q_e \)) of MB on OMSC is calculated at 279 mg g⁻¹ as shown in Table 4. Among them, the Freundlich adsorption isotherm is best fitted for the adsorption of MB on OMSC 2. The observed Freundlich adsorption isotherm and \( N_F \) value (>1) support the multilayer adsorption of MB on OMSC 2 and the process is purely physisorption. The intra particle diffusion model further confirms the multilayer deposition of dye on OMSC 2. The adsorption capacity of OMSC 2 was compared with the list of mesoporous materials and the material shows good adsorption capacity (Table 5) [40, 41, 63, 67, 68]. In contrast to transition metals doped SBA/MCM materials, the OMSC material adopts the Freundlich adsorption isotherm and has a reasonably high adsorption capacity value that may be facilitated due to the multilayer adsorption of MB.

The thermodynamic parameters such as Gibbs free energy of adsorption (\( \Delta G_{ads} \)) are calculated to assign the nature of adsorption from the Eq. 8 [69].

\[
\Delta G = RT \ln K_d
\]  

(8)

Where, \( R \) is a gas constant, \( T \) is the temperature and \( K_d \) is the distribution coefficient. The distribution coefficient (\( K_d \)) can be calculated by using Eq. 9.

\[
K_d = \frac{q_e}{C_e}
\]  

(9)

Where \( q_e \) (mg g⁻¹) is the equilibrium concentration of dye molecules on OMSC 2 and \( C_e \) (mg L⁻¹) is the equilibrium concentration of dye molecules in the solution. The \( K_d \) value is 1.4 and the \( \Delta G_{ads} \) value is -8.75 KJ mol⁻¹ at 313 K. The negative value of \( \Delta G_{ads} \) indicates the feasibility of the adsorption and the

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

| Parameter | Value |
|-----------|-------|
| \( q_m \) (mg g⁻¹) | 769 |
| \( K_L \) (L g⁻¹) | 0.0019 |
| \( R^2 \) | 0.8887 |
| \( q_m \) (mg g⁻¹) | 279 |
| \( K_F \) (mg⁻¹ L¹/n g⁻¹) | 5.12 |
| \( n_F \) | 1.15 |
| \( R^2 \) | 0.9994 |
process is spontaneous in nature. The value of $\Delta G_{ads}$ is $\approx -10$ KJ mol$^{-1}$ since the type of adsorption is physisorption [67].

4 Summary

Hybrid OMSC materials have been successfully synthesized from biogenous material of plant TG leaves as a carbon precursor by the soft template method for the first time. The TG leaves have been converted 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 it along with silica in the structure directing group without perturbing the sol-gel mechanism. At present, the exact interaction mechanism between PAC and silica/polymer is not yet known. It assumes that the polar functional nature of PAC can interact with the polymer template under the reaction condition and generate a composite material. In the controlled studies, it is clear that in the absence of TEOS, either with AC or PAC and P-123, the reaction mixture did not provide the desired products under hydrothermal conditions. The 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 1000-1300 cm$^{-1}$ is exhibited in calcinated materials due to their composite nature. The composite nature of the materials is further supported by the poor TG weight loss profile and absence of a reflection plane in the SAED pattern. Similarly, the mesoporous nature has been supported by low angle XRD 2$\theta$ value, BET adsorption, FESEM 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 to Si in EDX analysis is further validated and supported by the experimental procedure of this direct carbon loading strategy. The carbon content can be controlled up to 50 wt% in the silica matrix by this strategy. OMSC$_2$ showed good adsorption efficiency with MB dye and agreement with the PSO model and Freundlich adsorption isotherm. The maximum adsorption capacity ($q_m$) of OMSC$_2$ was observed in 279 mg g$^{-1}$ 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.

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Declaration of interests

- The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
- The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Compete of interest The authors declare no conflict of interest.

Research involving human participants and animals Not applicable

Informed consent Not applicable

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Footnote 1: Similar attempt was made to prepare ordered mesoporous carbon from TG leaves, pre-activated carbon was treated with Pluronic-A123 (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-A123 (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 for 24 h. The resultant solid mass was washed and dried at 110 °C for 3 h. The resultant carbon material was subjected for spectroscopic characterization and represented as disordered carbon (DC).

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