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1	Functionalization of MCM-41 with titanium oxynitride deposited via
2	PECVD for enhanced removal of methylene blue
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14 Abstract

15 TiON and TiO₂ were grafted onto the surfaces of mesoporous silica MCM-41 by plasma 16 enhanced chemical vapour deposition (PECVD). The results of small-angle X-ray diffraction 17 (SAXRD), X-ray diffraction, X-ray photoelectron spectroscopy, transmission electron 18 microscopy, and nitrogen physisorption revealed that the mesoporous structure of MCM-41 19 was retained and the pore size reduced from 2.46 nm to 2.19 nm and 2.18 nm after grafting of 20 amorphous TiO_2 and TiON, respectively. In consequence, the pore volume and BET surface 21 area decreased. These results indicate the deposition of TiO₂ and TiON particles on the surface 22 of MCM-41, leading to partial blockage of its pores. The grafted materials were found to be 23 effective adsorbents for methylene blue dye. The results of batch adsorption experiments at pH 24 7 demonstrated that TiON@mSiO₂ nanocomposite showed the highest adsorption capacity in 25 comparison with MCM-41 and TiO₂@mSiO₂, which is due to its highly negative zeta potential 26 at neutral conditions. The equilibrium adsorption process fits well with the Langmuir isotherm 27 model and the calculated maximum adsorbed quantity q_{max} was found to be 129 mg/g. The 28 pseudo-second order model best represents the adsorption kinetics data. Accordingly, the 29 TiON@mSiO₂ nanocomposite can be used for the purification of wastewater from toxic 30 organic dyes such as methylene blue.

Keywords: PECVD, MCM-41, Dye adsorption, Water purification, mesoporous
 nanocomposite.

- 1 Title Page Footnote:
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4 **1. Introduction:**

5 The remediation of wastewater from dyes is a recurring challenge. Textile dyes and other 6 industrial dyestuffs coming from the paper, leather, cosmetic and printing industries are of 7 environmental concern due to the release of toxic and potential carcinogenic materials into 8 water [1-6]. Wastewater produced by the dye industry, which contains harmful organic 9 pollutants, is often discharged directly into natural bodies of water, such as rivers, or are 10 percolated into groundwater [7-9]. The removal of these organic pollutants has recently 11 attracted considerable attention due to their public health damage and environmental toxicity 12 [10]. Accordingly, much attention has been paid to the development of adsorption techniques through which molecules can be rapidly removed at low cost [11-14]. 13

14 Mesoporous materials, which show high adsorption affinity towards several organic and 15 inorganic pollutants, are applicable in many industrial processes [15-18]. Among them, 16 mesoporous silica, exhibiting high specific surface area, tunable pore size, low density, and 17 hydrophilic surfaces, is a very promising candidate for oil refining, gas sensors, catalyst support 18 and waste treatment [18-22]. Moreover, mesoporous silica can be easily dispersed in several 19 solvents as well as functionalized by several hydrophilic groups/materials due to the presence 20 of surface hydroxyl groups [23-25]. For example, the catalytic and adsorptive properties of 21 mesoporous silica, in particular Mobil Composition of Matter (MCM) and Santa Barbara 22 Amorphous type materials (SBA), can be enhanced by grafting with transition metal oxides 23 such as TiO₂, Fe₂O₃ and SnO₂ [26-28].

24 Two common approaches for functionalizing surfaces of mesoporous silica are: (i) post-25 grafting (post modification) procedures [23-25] and (ii) direct-grafting (direct co-26 condensation) through the co-polymerization of a silica precursor [21, 29]. Despite the fact that 27 direct-grafting is fast and takes place in one step, materials produced by this method exhibit a 28 less ordered mesoporous structure and low specific surface area in comparison with those 29 produced by the post-grafting method. Additionally, the pore structure as well as the specific 30 surface area can be well controlled in the post-grafting method which is usually used to 31 functionalize the surface of mesoporous silica with organic materials via the reaction with – 32 OH groups on their surface. Up to now, tremendous efforts have been devoted to apply the

post-grafting method in the synthesis of multifunctional mesoporous silica composites with
 improved catalytic and adsorption properties for effective wastewater treatment [23-25].

3 In this study, the composites TiO₂@mSiO₂ and TiON@mSiO₂ were prepared by grafting 4 MCM-41 with TiO₂ and TiON, respectively, by plasma enhanced chemical vapour deposition 5 (PECVD). The adsorptive properties of the obtained composites were investigated and 6 compared to the unfunctionalized MCM-41 silica. PECVD technique has been recently applied 7 for the preparation of TiO₂/MCM-41 composites [30] in several steps by coating the MCM-41 8 powder first on silica wafer as substrate before the deposition of TiO_2 by PECVD at 500°C. 9 The obtained composites were further annealed at 700°C. On the other hand, no reports about 10 using PECVD technique for grafting mesoporous silica with TiON. TiN/MCM-41 composites 11 were previously prepared by heat-treatment under ammonia gas at $T \ge 600^{\circ}C$ for very long 12 time (i.e. 24 hrs) [31]. However, these high preparation temperatures are energy consuming 13 and might result in the collapse of the hexagonal pore structure of MCM-41 and reduction in 14 its surface area, which may reduce its adsorptive properties. Accordingly, the main goal of this 15 work to modify the set-up of PECVD technique to deposit TiO₂ and TiON directly on MCM-16 41 powders at much lower temperatures (i.e. 150 °C) relative to those used in the previous 17 works [30, 31].

18

19 2. Experimental:

20 **2.1.** Chemicals

Cetyltrimethylammonium bromide (CTAB, 99%, Sigma-Aldrich), titanium tetra-isopropoxide
(TTIP, 97%, Sigma-Aldrich), ammonia solution in water (~30%, Sigma-Aldrich),
tetraethoxysilane (TEOS, 99.99%, Sigma-Aldrich), ethanol (absolute, Honeywell) and
methylene blue (Sigma-Aldrich) were used without further purification.

25 **2.2.** Synthesis of MCM-41

MCM-41 was synthesized by a modified heterogeneous system [32] as follows: 2.5 g of CTAB as templating agent was dissolved in 50 mL of deionized water at 30 °C, followed by the addition of 22 mL of aqueous ammonia hydroxide solution (30% NH₄OH) and 60 mL of absolute ethanol under continuous stirring. The dropwise addition of 5 mL of tetraethoxysilane to the surfactant solution resulted in the formation of a gel that turned into a white precipitate after stirring for a further two hours. The obtained white precipitate was filtered and washed with deionized water and ethanol. After drying at room temperature, the sample was heated to
550 °C with heating rate 1 °C/min in air and kept at this temperature for 5 h to remove the
template.

4

5 2.3. Preparation of TiO₂@mSiO₂ and TiON@mSiO₂

6 The grafting of TiO₂ and TiON at MCM-41 surface was performed by the PECVD technique 7 (Figure 1) according to the following procedure: (i) the deposition chamber was first evacuated 8 to 1 Pa using a vacuum pump; (ii) 1 g of MCM-41 powders were inserted into stainless steel 9 dish to act as deposition substrate (i.e. bottom electrode) and heated to 150°C by using a heating 10 device (Eurotherm); (iii) the Ti-based precursor was introduced into the deposition chamber by passing Ar as carrier gas through hot titanium (IV) isopropoxide solution at 80°C in an oil 11 12 bath, while the carrying line was heated at 100 °C in order to avoid any condensation of the 13 precursor; (iv) oxygen gas was simultaneously introduced as an oxidant during the deposition 14 process; (v) the plasma was generated inside the deposition chamber using an R.F. power generator (CESARTM 136) coupled with a matching box (RF Navio, Advanced Energy) that is 15 16 connected to an inner electrode (diameter 10 cm) on top of the chamber, while the bottom 17 electrode (diameter 10 cm) and body of the chamber were grounded; (vi) the non-reactive species were retained during the deposition process by a cold trap placed between the 18 deposition chamber and the vacuum pump. All deposition experiments were performed using 19 20 discharge power of 50 W for 60 min (the powder was mixed in the dish every 20 min to insure 21 better homogeneity of the deposit on the particles) at constant partial pressure of oxygen gas 22 P_{O2} and TTIP + Ar mixture ($P_{Ar + TTIP}$) of 10 Pa and 30 Pa, respectively, while the distance 23 between both electrodes (d_P) was 3.0 cm. TiON@m-SiO₂ was prepared by applying ammonia 24 gas with constant partial pressure of 10 Pa in addition to oxygen and TTIP + Ar mixture gases. 25 Then the prepared samples were calcined at 350 °C with rate 1 °C/min for 4 hours in air.



Figure 1. Schematic drawing of PECVD technique used for preparing TiO₂@mSiO₂ and
TiON@mSiO₂ samples.

4

5 2.4. Characterization

6 The prepared MCM-41 as well as TiO₂@mSiO₂ and TiON@mSiO₂ samples were 7 characterized using small-angle X-ray diffraction (SAXRD) using a Bruker AXS D8 8 ADVANCE with a Lynx Eye 1D detector (Bruker, Germany). Measurements were performed 9 in a Bragg–Brentano geometry using a CuK $_{\alpha 1}$ radiation wavelength of 0.154 nm at 35 kV and 10 40 mA. All the patterns were collected using a step time of 1 s/0.0003°. The crystalline phase of the materials was analysed by wide-angle X-ray diffraction (WAXRD) using a PANAlytical 11 12 Xpert-PRO diffractometer (PANalytical, Netherlands) equipped with an Xcelerator detector 13 and Ni-filtered CuK_{α 1} ($\lambda = 0.154$ nm) radiation. The scan step size was fixed at 0.0167°/step 14 and the time per step was 0.55 sec/step. The elemental composition and oxidation environment 15 of Ti on the prepared samples were investigated by X-ray photoelectron spectroscopy (XPS) on an Escalab 250 (Thermo Fisher Scientific, USA) using a monochromatic Al K Alpha 16 17 (1486.6 eV) at 2kV and 1 μ A. 400 μ m of the surface diameter was analysed with acquisition times of 1203.5 s. The XPS spectra were calibrated to C1s at 284.8 eV. Energy-dispersive X-18 ray spectroscopy analysis (EDX) was performed with a Zeiss EVO HD15 microscope (Zeiss, 19 20 Germany) coupled with an Oxford X-MaxN EDX detector. The morphology of all samples 21 was studied via transmission electron microscopy (TEM) on JEOL JEM 2100 (JEOL, Japan) 22 at an accelerating voltage of 200 kV. The samples were prepared by dispersing a small amount 23 of the powder in ethanol by ultrasonic treatment for 30 minutes. A drop of the suspension was 24 applied to a copper grid covered with a holey carbon film. The pore size and specific surface

1 area were studied with nitrogen sorption analysis. Nitrogen adsorption-desorption isotherms 2 were recorded at 77 K on a NOVA 3200 apparatus (Quanta-chrome Corporation, USA) after 3 degassing for 10 h at 200 °C under vacuum. Surface area was determined using the Brunauer, 4 Emmet and Teller (BET) method and was calculated from multi-point at relative pressure 5 (P/Po) range from 0.05 to 0.30. The pore size distribution was obtained from the Barrett, Joyner 6 and Halenda (BJH) method using the adsorption points of the isotherm. Zeta potential 7 measurements were carried out on Zetasizer Nano ZS (Malvern Instruments, Malvern, UK), 8 where all samples were dispersed in water at room temperature (i.e. 25° C). The FT-IR spectra 9 of the samples dispersed in KBr pellets were recorded by using the 670 FT-IR spectrometer (Varian) in the range 400 - 4000 cm^{-1} with the resolution 4 cm^{-1} . 10

11

12 **2.5.** Adsorption experiments

13 **2.5.1. Batch equilibrium studies**

14 An aqueous stock solution with a concentration 1000 mg/L of methylene blue (MB) dye was 15 first prepared by dissolving 1g of the dye in 1 L distilled water. The solutions were further 16 diluted to different concentrations in 1L flasks. Adsorption experiments were carried out in 100 17 mL flasks in which 25 mL of aqueous dye solutions with different concentrations (100-500 18 mg/L) were placed in the dark in order to avoid MB degradation by direct photolysis or by 19 photocatalysis. The adsorbent dosages of the three samples (MCM-41, TiO₂@mSiO₂ and 20 TiON@mSiO₂) were varied from 0.8 g/L to 2.4 g/L, while the pH of the solutions were 21 carefully controlled between 3 and 11 by using 0.1 M HCl and 0.1 M NH₄OH solutions. The 22 contact times were controlled in the range of 20 to 180 min. The stirring speed of 400 rpm at 23 room temperature was maintained for all experiments. The adsorbent was separated from the 24 dye solution after each adsorption experiment by centrifugation at 5000 rpm for 10 min. Then, 25 the concentrations of methylene blue (MB) dye were determined from their UV-Vis absorbance 26 according to the calibration method. A UV/VIS/NIR spectrometer (Perkin Elmer Lambda 9) 27 was used at $\lambda = 664$ nm. The percentage of the dye that was removed (% removal) and the 28 equilibrium adsorption capacity q_e (mg/g) were calculated as follows:

$$\% removal = \frac{(C_i - C_e)}{C_i} \times 100$$
⁽¹⁾

$$q_e = \frac{(C_i - C_e)V}{m} \tag{2} 1$$

4 where C_i and C_e refer to the initial and equilibrium concentration (mg/L), respectively, of the 5 dyes solutions, *m* is the weight of adsorbent (g) and *V* is the volume of dyes solutions (L).

6

2.5.2. Adsorption isotherms

7 The adsorption isotherms of MB dye onto TiON@SiO₂ sample were simulated using different 8 models, namely, Langmuir, Freundlich and Tempkin isotherms. The nonlinear form of 9 Langmuir isotherm model [33] is described in the Eq. S1 (ESI). The nonlinear form of 10 Freundlich model [34] is given by the Eq. S2 (ESI), while Tempkin model [35] and Dubinin– 11 Radushkevich model [36] are represented by the Eq. S3 and Eq. S4 (ESI), respectively.

12 2

2.5.1. Adsorption thermodynamics

13 Thermodynamic analysis of MB dye adsorption onto TiON@SiO₂ sample was conducted by 14 performing the adsorption experiments at different temperatures (298–338 K). The 15 corresponding thermodynamic parameters such as the adsorption Gibbs free energy change 16 (ΔG^0 , kJ/mol), the adsorption enthalpy change (ΔH^0 , kJ/mole), and the adsorption entropy 17 change (ΔS^0 , kJ/mole) were calculated according the eq. S6-S7 (ESI) [37].

18 **2.5.2.**

5.2. Adsorption kinetics

Experiments to determine the kinetics of MB dye adsorption onto TiON@SiO2 samples were 19 20 carried out by adding 40 mg of the TiON@SiO₂ powder into 25 mL of MB dye solution with 21 an initial concentration $C_i = 100 \text{ mg/L}$. The aqueous solutions were separated at different 22 contact times by centrifuging for UV-Vis absorbance measurements. The adsorption quantity 23 q_t (mg/g) of the dye onto the TiON@SiO₂ sample at time t was calculated according to Eq. S8 24 (ESI) and adsorption kinetic data was analyzed using the nonlinear form of pseudo-first-order 25 [38], pseudo-second-order [39], and Elovich kinetic [40] models according the Eq. S9-S11 26 (ESI).

1 **3. Results and discussion**

3.1. Structure, composition and porosity characteristics of MCM-41, TiO₂@mSiO₂ and TiON@mSiO₂ samples

4 Small angle X-ray diffraction (SAXRD) was initially used to characterize the effect of TiO₂ 5 and TiON deposition on the structure of the MCM-41 matrix. Figure 2 a shows the SAXRD patterns of MCM-41, TiO₂@mSiO₂ and TiON@mSiO₂ samples. SAXRD pattern of MCM-41 6 revealed three reflections at $2\theta_{100} = 2.423^\circ$, $2\theta_{110} = 4.203^\circ$ and $2\theta_{200} = 4.980^\circ$, which satisfy the 7 8 relation for *p6mm* hexagonal symmetry of the ordered mesoporous MCM-41 [41]. The SAXRD 9 patterns of TiO₂@SiO₂ and TiON@SiO₂ materials exhibit a (100) reflection, which suggests the hexagonal pore structure of MCM-41 is retained after the TiO₂ and TiON deposition. 10 11 However, in comparison with MCM-41, the relative intensity of the (110) and (200) reflections 12 are decreased compared to the (100) reflection after depositing TiO₂ and TiON, indicating the 13 decrease in the long-range order of the pores. This could be attributed to the deposition of TiO₂ 14 and TiON on the surface of MCM-41, leading to partial blockage of its pores. Moreover, with depositing TiO₂ and TiON on the surface of MCM-41, a small shift of (100) reflection to higher 15 16 2θ values was observed, which indicates a decrease in the interplanar distance d_{100} and the hexagonal unit cell parameter (a_0) . The lattice parameter a_0 of the samples were calculated 17 according to the formula $a_0=2d_{100}/\sqrt{3}$. The wall area (W) of the pores was also calculated using 18 the formula $W = \frac{a_0^2 \sqrt{3}}{4} - \frac{\pi D^2}{8}$ (see supporting information Figure S1), where *D* is the average pore 19 20 diameter determined from N₂ adsorption analysis. The results (see Table 1) revealed an 21 increase of the wall area of TiO₂@mSiO₂ and TiON@mSiO₂ in comparison with MCM-41 22 sample, which confirms the deposition of TiO₂ and TiON particles on the surface of MCM-41, 23 leading to partial blockage of its pores.

Wide-angle X-ray diffraction (WAXRD) patterns (Figure 2 b) of the three samples exhibited a broad reflection between $2\theta = 10^{\circ}$ and 20° , which indicates the amorphous structure of MCM-41 support as well as the deposited TiO₂ and TiON materials.



Figure 2: SAXRD (a) and WAXRD (b) patterns of MCM-41, TiO₂@mSiO₂ and TiON@mSiO₂
samples

1

5 The nitrogen adsorption-desorption isotherms and BJH pore size distributions (insets) of MCM-41, TiO₂@mSiO₂ and TiON@mSiO₂ samples are shown in Figure 3. The isotherms of 6 7 the three samples can be classified as a type IV isotherms, commonly related to mesoporous 8 materials, as established by the international Union of Pure and Applied Chemistry (IUPAC) 9 [42]. Nevertheless, some differences were observed between the sorption curves of 10 $TiO_2@mSiO_2$ and $TiON@mSiO_2$ in comparison with that of MCM-41 sample. The isotherm 11 of MCM-41 exhibits a type H1 hysteresis loop with a well-defined inflection at relative low 12 pressures $(p/p_0 = 0.2-0.4)$, which associated with well-ordered mesoporous materials with 13 narrow distributions of relatively uniform (cylindrical-like) pores. The inflection in the isotherm corresponds to the capillary condensation nitrogen inside the primary mesoporous 14 15 and its sharpness indicates a uniform pore size distributions [22]. On the other hand, N₂-16 physisorption isotherms of TiO₂@mSiO₂ and TiON@mSiO₂ exhibit two regions of hysteresis 17 between the adsorption and desorption traces, from relative pressures (p/p_0) of 0.2–0.35 and 18 0.40–0.60 (Fig. 8 b-c). The hysteresis at (p/p_0) of 0.2–0.35 is attributed to well-ordered 19 mesoporous structure of MCM-41, indicating that the deposition of TiO₂ and TiON did not 20 destroy the integrity of the mesoporous MCM-41 support. However, the inflection in their 21 isotherms exhibits a gentle slope, suggesting the decrease in the long-range order of the pores 22 with TiO₂ and TiON loading, which is also consistent with SAXRD results. The hysteresis loop 23 at the relative pressure range of 0.40–0.60 shows a type H4 characteristic, which is associated 24 with narrow slit-like pores in materials containing both micropores and mesopores [42, 43].

1 These results suggest the existence of the void defects in the framework of MCM-41 due to the deposition of TiO₂ and TiON particles on the surface. The BET surface area, average pore 2 3 diameter and pore wall area were calculated and listed in Table 1. As shown in Table 1, the 4 deposition of TiO₂ and TiON particles on MCM-41 surface resulted in a decrease in the pore 5 size from ~2.5 nm to ~2.2 nm, while an increase in the wall thickness between the pores was 6 observed. These results reveal pore blocking due to deposition of TiO₂ and TiON particles on 7 the surface of the MCM-41 particles. Accordingly, pore volumes and BET surface area 8 decrease significantly for TiO₂@mSiO₂ and TiON@mSiO₂ samples. However, the pore size 9 diameter in TiO₂@mSiO₂ and TiON@mSiO₂ is still higher than 2 nm, which indicates that the 10 mesoporosity is retained after the TiO₂ and TiON deposition.



Figure 3: Nitrogen adsorption-desorption isotherms and BJH pore size distribution profiles
(inset) of (a) MCM-41, (b) TiO₂@mSiO₂ and (c) TiON@mSiO₂ samples.

14

15 **Table 1**: Textural properties of MCM-41, TiO₂@mSiO₂ and TiON@mSiO₂ samples obtained

16	from SAXRD	and N ₂	physisorption	characterizations.
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Samples	<i>d</i> ₁₀₀ (nm)	<i>a</i> ₀ (nm)	S _{BET} (m ² /g)	Pore volume (cm ³ /g)	BJH Pore Diameter (nm)	Pore wall area (nm ²)
MCM-41	3.634	4.196	1268	0.92	2.5	5.240
TiO ₂ @mSiO ₂	3.535	4.082	869	0.57	2.2	5.331
TiON@mSiO ₂	3.593	4.149	801	0.55	2.2	5.591

¹⁷

18 To study the chemical composition on the surface of the obtained samples after PECVD

19 treatment, the three samples were investigated by X-ray photoelectron spectroscopy (XPS). As

20 observed in Figure 4 a, the fully scanned spectra demonstrated that Si, O and C existed in pure

21 MCM-41. The C in pure MCM-41 could have originated from the CTAB surfactant used as a

1 pore template. In addition to the previous elements, Ti was observed in TiO₂@mSiO₂ sample, 2 while Ti and N were detected in the surface of the TiON@mSiO₂ sample. Subsequently, the 3 O1s high-resolution XPS spectra of the MCM-41, TiO₂@mSiO₂ and TiON@mSiO₂ were 4 analyzed in Figure 4 b. The O1s spectrum of pure MCM-41 exhibits an asymmetric band that 5 consists of two peaks. The main peak at 533.2 eV can be assigned to oxygen from Si-O-Si 6 bonds, while the other low intensity peak at 534.7 eV can be attributed to the surface silanol 7 Si-OH groups. These two peaks are slightly shifted to lower binding energies for 8 theTiO₂@mSiO₂ and TiON@mSiO₂ samples, which could be due to the formation of Si-O-Ti 9 bonds [22]. Furthermore, an additional peak was observed at about 529.8 eV, which can be 10 ascribed to oxygen lattice in anatase (TiO₂). Next, the deposition of TiO₂ on the surface of 11 MCM-41 was confirmed from the Ti2p spectra of TiO₂@mSiO₂ and TiON@mSiO₂ (Figure 4 12 c). In the Ti2p spectrum of TiO₂@mSiO₂, the doublet peak Ti2p_{3/2} and Ti2p_{1/2} appear at 458.3 13 and 464.1 eV, respectively, arises from spin orbit-splitting. These two peaks correspond to Ti⁴⁺ 14 in the TiO₂ lattice [44]. Additionally, the shoulders Ti2 $p_{3/2}$ at 460.2 eV and Ti2 $p_{1/2}$ at 465.8 eV are consistent with Ti³⁺ cross-linked in the silica network [22]. These peaks were slighted 15 16 shifted by about 0.2 eV to higher binding energies for the TiON@mSiO₂ sample. Moreover, 17 the intensities of the shoulders Ti2p_{3/2} slightly decreased, which suggests the incorporation of 18 N in the TiO₂ lattice during the deposition process. The observed peak at 397.6 eV in the N1s 19 spectrum of TiON@mSiO₂ (Figure 4 d) further confirms the formation of titanium oxynitride 20 on the surface of MCM-41 [45]. The Ti/Si mole ratios measured from XPS spectra are 0.06 21 and 0.11% in the TiO₂@mSiO₂ and TiON@mSiO₂ samples, respectively. However, EDX 22 analysis reveals Ti/Si mole ratios of 0.08 and 0.09 in TiO₂@mSiO₂ and TiON@mSiO₂, 23 respectively.



1

Figure 4: XPS survey spectra (a) and high-resolution XPS spectra of O1s (b), Ti2p (c), and N1s
(d) for MCM-41, TiO₂@mSiO₂ and TiON@mSiO₂ samples.

4 Transmission electron microscopy (TEM) characterization was used to examine the pore 5 structure and morphology of all samples. Figure 5 shows the TEM images of MCM-41, 6 TiO₂@mSiO₂ and TiON@mSiO₂ samples. As shown in Figure S2 and Figure 5 a, MCM-41 7 exhibits long-range pore ordering. Uniform black spots are observed in the TEM images of 8 TiO₂@mSiO₂ and TiON@mSiO₂ (Figure 5 b and c), which correspond to deposited TiO₂ and 9 TiON particles on the surface of MCM-41. The average size of TiO₂ and TiON particles are 10 15 ± 1 and 18 ± 1 nm, respectively. As shown in Figure S2 and Figure 5 b and c, the porous 11 structure was maintained after the deposition of TiON on the surface of MCM-41, which is 12 consistent with SAXRD results.



Figure 5: TEM images of (a) MCM-41, (b) TiO₂@mSiO₂ and (c) TiON@mSiO₂ samples.

3

The deposition of TiO₂ and TiON on the surface of MCM-41 was also confirmed by pH-4 5 dependent zeta potential measurements. Figure 6 shows the surface zeta potential as function 6 of pH for MCM-41, TiO₂@mSiO₂ and TiON@mSiO₂ samples. The isoelectric point (IEP) of 7 unmodified MCM-41 was observed at pH 3.2, which is good agreement with previous reported 8 values (pH 3.1) [46]. IEPs of TiO₂@mSiO₂ and TiON@mSiO₂ have been shifted to slightly 9 higher values (pH 3.9 and 3.6 for TiO₂@mSiO₂ and TiON@mSiO₂, respectively) in comparison with that of MCM-41. This result is consistent with previous work, which reports 10 11 that oxides with highly electronegative ions (e.g. Si) show IEP at lower pH values in comparison with those with low electronegative ions (e.g. Ti) [47]. At pH lower than their 12 13 pH_{ZPC} values, the zeta potentials of three materials were positive, which may be due to the 14 protonation of the –OH groups on the surface of the mesoporous silica or TiO₂ particles in the 15 acidic solution. At high pH values, free hydroxide groups, which are prevalent in basic 16 solutions, can deprotonate the -OH groups on the surfaces of SiO₂ and TiO₂, resing in a negatively charged surface. However, TiO2@mSiO2 and TiON@mSiO2 samples exhibit 17 18 strongly positive zeta potentials at lower pH and strongly negative zeta potentials at higher pH 19 values in comparison to that of the unmodified MCM-41. These results can be explained by the 20 electronegativity of silicon and titanium ions, which can affect the strength of the O-H bonds 21 on SiO₂ and TiO₂. Additionally, the N-H bonding in TiON@mSiO₂ is weaker than the O-H 22 bonding as the electronegativity of nitrogen (3.0) is less than that of oxygen (3.5). Therefore, 23 TiON@mSiO₂ showed the highest negative zeta potential in the basic solutions because N-H 24 sites act as acidic sites. This result is also in good agreement with recent studies which show 25 that the surface zeta potential of TiO₂ becomes more negative as the amount of nitrogen doping 26 increases [48].





Figure 6: Zeta potential of MCM-41, TiO₂@mSiO₂ and TiON@mSiO₂ samples as function of
pH.

5

6 **3.2.** Adsorption of methylene blue

7 To study the effect of TiO₂ and TiON on the adsorption capacity q_e (mg/g) of MCM-41, batch 8 adsorption experiments of methylene blue dye from aqueous solutions were conducted on 9 MCM-41, TiO₂@mSiO₂ and TiON@mSiO₂ samples. Figure 7 shows the equilibrium 10 concentration of MB remaining in the water after 2 h of adsorption experiments using MCM-11 41, TiO₂@mSiO₂ and TiON@mSiO₂ samples with dosage of 1.6 g/L at pH value of 7.0 at room 12 temperature. As shown in Figure 7, the remaining concentration of MB dyes in the water are 13 very low when TiON@mSiO₂ and TiO₂@mSiO₂ are used as adsorbents. Accordingly, 14 TiON@mSiO₂ and TiO₂@mSiO₂ samples show higher equilibrium adsorption capacities q_e of 15 60 and 37 mg/g, respectively, than that of MCM-41 sample (19 mg/g). These results can be 16 explained by changing the surface charge of MCM-41 due to the deposition of TiO₂ and TiON 17 on the surface. As shown in Figure 6, the surface charges of TiON@mSiO₂ and TiO₂@mSiO₂ 18 are more negative than that of MCM-41, therefore, the positively charged groups $(=N(CH_3)_2)^+$ 19 of MB dye could be easily electrostatically attracted by TiO₂ and TiON particles on the surface 20 of MCM-41. Since TiON@mSiO₂ sample shows the highest adsorption capacity of the three 21 samples, this sample was chosen for further adsorption experiments.



Figure 7: Equilibrium concentration C_e of MB after adsorption experiments using (a) MCM-41, (b) TiO₂@mSiO₂ and (c) TiON@mSiO₂ samples with dosage of 1.6 g/L at equilibrium time of 2 h and pH value of 7 at room temperature. The blank sample refers to the initial concentration of the dye (100 mg/L).

6

7 3.3. Effect of adsorbent dose and solution pH on MB dye adsorption

8 The influence of the amount of TiON@mSiO₂ on the adsorption and removal of MB dye with 9 an initial dye-solution concentration of 100 mg/L, pH 7 and contact time of 2 h, are displayed in Figure 8 a. The removal percentage of MB significantly increased from 50% to ~97% with 10 11 an increase in adsorbent dose from 0.8 to 1.6 g/L, which is due to the increase in the number of active adsorption sites as the amount of adsorbent increased [49]. The constant removal 12 13 efficiency at doses more than 1.6 g/L indicates that the number of active adsorption sites no longer increases at these higher doses of adsorbent, which may be attributed to the partial 14 15 aggregation of adsorbent particles at higher adsorbent doses [50]. On the other side, the equilibrium adsorption capacity remarkably decreased from 60 to 22 mg/g with an increase in 16 17 adsorbent dose from 0.8 to 1.6 g/L, which is due to the limited concentration of dyes molecules 18 needed to saturate all the active adsorption sites at these high doses of adsorbent [51]. However, 19 the adsorbent dose of 1.6 g/L was chosen for further experiments because of the high removal 20 efficiency as well as adsorption capacity at this adsorbent dose.

As shown in Figure 6, the surface charge of TiON@mSiO2 was drastically changed with 1 2 varying the pH values of the solution. Additionally, the degree of ionization and the chemical 3 nature of MB dyes could be also affected by the pH of the solution. Therefore, the influence of 4 pH on adsorption capacity and removal of cationic MB dye with initial dye-solution 5 concentration of 100 mg/L onto TiON@mSiO₂ sample at dosage of 1.6 g/L and contact time 6 of 2 h was studied (Figure 8 b). It can be seen that an increase in the solution pH from 3 to 7 7 resulted in a remarkable increase in the adsorption capacity of MB dye from 22 to 60 mg/g as 8 well as removal efficiency from 35.3% to 96.6%. However, the adsorption capacity and 9 removal efficiency did not change significantly with a further increase in the solution pH above 10 7. These results can be explained by the variation of surface charges of adsorbent and MB dye 11 with solution pH. As shown in Figure 6, the surface charge of TiON@mSiO₂ is positive at low 12 pH (pH = 2) and becomes highly negative by increasing the pH to 7 [48]. Therefore, the 13 adsorption capacity of cationic dye MB onto TiON@mSiO₂ increased with increasing pH 14 values due to the increase in the electrostatic attraction between the positively charged groups $(=N(CH_3)_2)^+$ of the dyes and the adsorbent surface. No significant change in the surface charge 15 of TiON@mSiO₂ was observed with further increase in the solution pH above 7, thus, the 16 17 adsorption of cationic MB dye did not change significantly at higher pH, this result matched 18 with previous studies [52-55]. Accordingly, by taking in account environmental aspects, a 19 solution pH of 7 was chosen for the further kinetic and isotherm experiments.





Figure 8: Effect of adsorbent dose at pH 7 (a) and solution pH at dosage of 1.6 g/L (b) on the adsorption capacity (solid circles) and removal (solid triangles) of MB dye onto TiON@mSiO₂ sample at room temperature and contact time of 2 h.

1 **3.4.** Adsorption isotherms

Four adsorption isotherms of MB dye adsorbed onto the TiON@mSiO₂ sample at equilibrium, namely, Langmuir, Freundlich, Dubinin–Radushkevich (D–R) and Tempkin isotherms were used to fit the experimental data by nonlinear regression analysis as shown in Figure 9. The constants and adsorption parameters calculated for four isotherm models according to Eq. (S1-S4, ESI) as well as the determination coefficients (R^2) values of the fitting are listed in

Table 2. The Langmuir model, which assumes that a monolayer adsorption process occurs on the homogeneous surface of an adsorbent without considering the interaction between adsorbate molecules, results in the best fit with a high determination coefficient R^2 of 0.999. On the other hand, the Freundlich model (Figure 9), which assumes a multilayer adsorption process on a heterogeneous surface [34], gives lower R^2 (0.862) value in comparison with that of Langmuir isotherms (

Table 2). In order to determine the type of adsorption process (i.e. chemical or physical process) of MB dye onto TiON@mSiO₂, the Dubinin–Radushkevich (D–R) isotherm [56] was also applied. This model is frequently used to distinguish the physical and chemical adsorption of an adsorbate with its mean adsorption free energy, which can be calculated according to Eq. (S4, ESI). Moreover, the maximum adsorbed quantity of MB dye onto TiON@mSiO₂ sample can be also determined by using Eq. (S4, ESI). As shown in Figure 9 and

19 Table 2, the fitting of experimental data using the D-R model resulted in a good determination 20 coefficient $R^2 = 0.95$ and low value of mean adsorption free energy, E = 0.53 KJ/mol, 21 suggesting a physisorption process. Finally, the Tempkin isotherm is also used to study the 22 adsorbent-adsorbate interactions during the adsorption process. This model assumes a linear 23 decrease in the heat of adsorption for all molecules in the layer with coverage, which is 24 attributed to adsorbate–adsorbent interactions. The adsorption heat $b = -\Delta H$ of the adsorbates (dves) molecules and Tempkin isotherm equilibrium binding constant K_T (L/mg) 25 26 corresponding to the maximum binding energy can be calculated from this model according to 27 Eq. (S3, ESI). As shown in Figure 9 and

Table 2, the experimental adsorption data does not fit well with the Tempkin isotherm model and the $R^2 = 0.915$ is less than those of Langmuir and Dubinin–Radushkevich models. However, the positive value of adsorption heat *b* calculated from this model indicates that the adsorption process is exothermic [51].

- 1 The Langmuir isotherm model best describes the equilibrium adsorption process of MB dye
- 2 onto TiON@mSiO₂ sample by comparing the values of R^2 for four isotherm models (
- 3 Table 2). The calculated maximum adsorbed quantity q_{max} of MB is 129 mg/g, which is much
- 4 higher than that of the other adsorbents (Table 3). Therefore, TiON@mSiO₂ can be an effective
- 5 adsorbent for organic dyes such as MB.



Figure 9: Nonlinear Langmuir, Freundlich, Tempkin and Dubinin–Radushkevich isotherm models for adsorption of MB dye onto TiON@mSiO₂ sample (pH = 7, C_i = 100-500 mg/L,

9 Dosage = 1.6 g/L, t = 2 h). The lines represent the nonlinear fitting of the experimental data.

10

11 **Table 2.** The adsorption isotherm parameters for the adsorption of MB dye onto TiON@mSiO₂

12 sample according to nonlinear Langmuir, Freundlich, D-R model, and Temkin models.

Isotherm models	Parameters	Value of parameters
Langmuir	$q_{max} (\mathrm{mg/g})$	129
	k_L (L/mg)	0.252
	R^2	0.999
Freundlich	$k_F\left((\mathrm{mg/g})(\mathrm{L/mg})^{1/\mathrm{n}}\right)$	61.2
	n	7.2
	R^2	0.862
Temkin	k_T (L/mg)	26.87
	<i>b</i> (kJ/mol)	0.165

	R^2	0.915
D-R	$q_m (\mathrm{mg/g})$	122
	$k_D (mol^2/kJ^2)$	1.78 x 10 ⁻⁶
	E (kJ/mol)	0.53
	R^2	0.95

- 2 Table 3. Comparison of adsorption capabilities of TiON@mSiO₂ at room temperature with
- 3 other adsorbents for MB.

Adsorbent	q_{max} (mg/g)	Ref
MCM-41	74	[26]
TiO ₂ /MCM-41	54	[26]
Tungstophosphoric acid/TiO ₂	50	[26]
Tungstophosphoric acid@TiO2 /MCM-41	62	[26]
Beta-cyclodextrin silica nano hallow sphere	92	[57]
Fe ₃ O ₄ @metal-organic frameworks (MIL-100)	49	[27]
Chitosan and sepiolite clay composite	41	[58]
Reed biochar – hydroxyapatite	21	[59]
SnO2 quantum dots decorated silica nanoparticles	73	[28]
Co ₃ O ₄ /SiO ₂ nanocomposite	54	[60]
Polyvinyl alcohol (PVA)	123	[61]
TiON@mSiO ₂	129	This work

4

5 **3.5.** Thermodynamic studies

In order to study the influence of temperature on the adsorption process of MB dye onto TiON@mSiO₂ as well as to determine whether this adsorption process is exothermic or endothermic in nature, thermodynamic studies were performed. The Gibbs free energy (ΔG^0) was calculated according to the eq. S6 (ESI), while, the enthalpy (ΔH^0) and entropy (ΔS^0) were calculated by plotting Ln*K*_d as function of 1/T according to the van't Hoff equation eq. S7 (ESI) [37]. The linear fitting yielded a high regression coefficient ($R^2 = 0.995$) and the obtained values are listed in Table 4.

13 As shown in Table 4, the obtained values of Gibbs free energy change ΔG^0 are negative and 14 increase with temperature, which indicates that the adsorption of MB dye molecules onto 1 TiON@mSiO₂ is spontaneous in nature and becomes less favourable with increasing 2 temperature. Moreover, the negative values of enthalpy (ΔH^0) and entropy (ΔS^0) confirm the 3 exothermic nature of this adsorption process as revealed from Tempkin isotherm analysis. This 4 exothermic adsorption process was also observed in the removal of MB by SnO₂ quantum dots 5 decorated silica nanoparticles [28].

6 **Table 4.** Thermodynamic parameters calculated for the removal of MB dye by the 7 TiON@mSiO₂ ($C_0 = 100 \text{ mg/L}$, dosage = 1.6 g/L)

Thermodynamic parameters							
ΔG^0 (kJ mol ⁻¹) at different T (K)					$\Delta S^0 (\text{Jmol}^{-1} \text{ K}^{-1})$	ΔH^0 (kJ mol ⁻¹)	
298	308	318	328	338			
-7.1	-6.5	-5.4	-4.4	-3.6	-91	-34	

8

9 **3.6.** Adsorption kinetics

The influence of contact time on the adsorption capacity of MB dye onto TiON@mSiO₂ at room temperature is displayed in Figure S3. The removal efficiency of MB from the aqueous solution reached 84.9% with corresponding adsorption capacities of 53.05 mg/g in the first 20 min. The adsorption process reached equilibrium with removal efficiency of 96.6% within 120 min. The equilibrium adsorption capacities of MB dye onto TiON@mSiO₂ was 60.4 mg/g at a contact time of 120 min.

16 The adsorption mechanism of MB dye onto TiON@mSiO₂ was further analyzed using three 17 different kinetic models, namely, pseudo-first-order, pseudo-second-order, the Elovich model 18 as shown in Figure 10. The kinetic constants calculated for the three kinetic models according 19 to the Eq. S9-S11 (ESI) and the determination coefficient (\mathbb{R}^2) values of the fitting are listed in 20 Table 5. As shown in Figure 10 and Table 5, the experimental kinetic data are better fitted with 21 the nonlinear form of pseudo-second-order model (R^2 >0.9998) in comparison with those of the pseudo-first-order (R^2 >0.9972) and the Elovich kinetic models (R^2 >0.9991). Furthermore, the 22 calculated value of adsorption capacity (q_e (cal) = 62 mg/g) at equilibrium according to the 23 24 pseudo-second-order model was found to be in good agreement with the experimental values 25 (see Figure S3). Accordingly, the adsorption of MB dye onto TiON@mSiO₂ can be kinetically

- 1 well represented by a pseudo-second-order model in which a molecule of MB dye is adsorbed
- 2 onto two sites of the TiON@mSiO₂ surface, while the concentration of dye is constant [62].
- 3



Figure 10: Experimental kinetic data and nonlinear fitted curve with kinetic models of pseudofirst-order (solid line), pseudo-second-order (dashed line), Elovich model (dotted line) for adsorption of MB dye onto TiON@mSiO₂ sample at room temperature (pH = 7, $C_i = 100 \text{ mg/L}$, Dosage = 1.6 g/L).

9

10 Table 5. The adsorption kinetics parameters for the adsorption of MB dye onto TiON@mSiO₂

11 sample with pseudo-first-order, pseudo-second-order, Elovich model and intra-particle

12 diffusion models

Kinetics models	Parameters	Value of parameters
Pseudo-first-order	q_e (cal) (mg/g) k_1 (1/min) R^2	60 0.102 0.9972
Pseudo-second-order	q_e (cal) (mg/g) k_2 (g/(mg.min)) R^2	62 4.6 x 10 ⁻³ 0.9998

Elovich	α (mg/(g.min))	43.4 x 10 ⁴
	β (g/mg)	27.4 x 10 ⁻²
	R^2	0.9991

2 **3.7. FTIR** study of methylene blue adsorption

3 The FTIR spectra of TiON@mSiO₂, methylene blue and TiON@mSiO₂ after methylene blue 4 adsorption and pure methylene blue are shown in Figure 11. As shown in Figure 11 a, the 5 TiON@mSiO₂ sample exhibits similar vibrational band characteristic of mesoporous MCM-41 6 [63]. The absorption bands at 3450 and 1637 cm^{-1} corresponds to the stretching and bending 7 vibration of O-H group, respectively, which is due to the H₂O molecules on the surface. The peaks at 2978 and 1418 cm⁻¹ attributed to the stretching and bending modes of the C–H groups, 8 9 respectively, which originates from the residual organic precursor used in PECVD process. The absorption bands at 1235 and 1086 cm⁻¹ are due to the asymmetric stretching vibrations of 10 the Si–O–Si groups, while, the peaks at 798 and 578 cm⁻¹ are attributed to the symmetric 11 stretching modes of Si-O-Si groups. The absorption band at 969 corresponds to the silanol Si-12 OH group, whereas the peak at 467 cm^{-1} is due to the bending vibration of O–Si–O group. On 13 14 the other hand, the FTIR spectrum of MB dyes (Figure 11 c) reveals absorption bands corresponding to its main functional groups such as N-H and O-H stretching vibrations at about 15 3450-3410 cm⁻¹, C=N and C=C stretching vibrations at 1402-1605 cm⁻¹, C-H (methyl) 16 vibration at 1493 cm⁻¹, -CH₃ symmetric deformation at 1350 cm⁻¹, aromatic-nitrogen bond (Ar-17 N) at 1250 cm⁻¹, C-S vibration at 1142 cm⁻¹ and C-H (aromatic) vibration at 896 cm⁻¹ [64]. As 18 19 it can be seen from Figure 11 b, these characteristic bands of MB are observed in the spectrum 20 of TiON@mSiO₂ after methylene blue adsorption. Moreover, some absorption peaks 21 TiON@mSiO₂ adsorbent such as that corresponding to Si-OH are shifted to lower 22 wavenumber, which suggests the hydrogen bonding between MB and the mesoporous silica. 23 These findings point out that chemical adsorption might be involved in the adsorption process.



Figure 11: FTIR spectra of (a) TiON@mSiO₂, (b) TiON@mSiO₂ after methylene blue
adsorption and (c) pure methylene blue.

4 **4.** Conclusion

5 In this study, novel TiO₂@mSiO₂ and TiON@mSiO₂ nanocomposites with high surface area 6 were successfully manufactured by PECVD at low temperature (150 °C) and short production 7 time (1 h). The deposition of TiO₂ and TiON on the surface of the MCM pores was confirmed 8 by SAXRD, BET and Zeta-potential measurements. The mesoporous structure MCM-41 was 9 retained after the deposition TiO_2 and TiON on the surface, but the pore size, pore volume and 10 BET surface area decreased. The grafting of mSiO₂ by TiON was tested as an effective 11 adsorbent for methylene blue (MB) dye from aqueous solutions. The adsorption capacity 12 increased with increasing solution pH, and decreased with increasing adsorbent dose. The 13 adsorption equilibrium isotherm is well represented by the Langmuir model and the determined 14 maximum capacity q_{max} (129 mg/g) was much higher than that of the other silica adsorbents reported in previous studies. The negative values of ΔG^0 and ΔH^0 indicate that the adsorption 15 process is exothermic and more energetically favourable. This study shows that the 16 17 TiON@MCM-41 could be a promising adsorbent for the removal of toxic organic dyes in 18 wastewater.

19

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- 8

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