Controlling textural, surface and adsorption characteristics of MCM-48 via hydrothermal treatment

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ABSTRACT
Excluding the autoclaving step in the synthesis recipe of MCM-48 resulted in the formation of silica lacking the three-dimensional channel system, the cubic microstructure and the surface silanol groups. This sample has poor wettability that limits the diffusion rate in aqueous media. Adsorption of methylene blue, MB, on such solid is pH-independent, dispersion forces-controlled, practically reversible, endothermic, non-spontaneous, and follows the pseudo-first-order kinetics and Freundlich mode of adsorption. The adsorbed molecules, 15 mg/g, lay flat on the surface with the formation of a double layer. The usual MCM-48 formed after autoclaving possessed a high adsorption capacity of 480 mg/g obtained through the specific mode of adsorption that increased with pH and proceeded practically irreversibly, exothermically, spontaneously, following the pseudo-second-order kinetics and favorable according to Langmuir model. In case of both types of obtained silica the adsorption of MB resulted in a general decrease in the entropy function.

1. Introduction
Porous materials are characterized by lower density and higher surface area than dense/nonporous materials. For most industrial applications including separation, catalysis and bioreactors open pores (connect to the outside) can play a crucial rule. Dense materials are used mainly for thermal insulation and low density structural components [1]. Mobil scientists employed long chain organic surfactant molecules as the structure-directing agent (SDA) during the synthesis of highly ordered Mesoporous silica material [2]. The Mesoporous materials are obtained by subsequent removal of the surfactant (template) by extraction or calcination. A template acts as SDA in the synthesis of porous materials [3]. Hydrothermal condition is actually a sol–gel process comprising formation of surfactant self-assembly, hydrolysis under acidic or basic condition of precursor (alkoxide or inorganic) forming oligomers, and final precipitation in the form of gel. The gel is treated hydrothermally for further condensation, solidification and reorganization of the material to an ordered arrangement.

M41S materials possess especially large and uniform well-defined pores whose diameter can be varied in the range of approximately 1.5–10.0 nm. Among this M41S family, MCM-48 is a three-dimensional channel system that has severable advantages compared to other members of M41S family being more resistant to pore blocking [4]. The structural peculiarities of the MCM-48 make it a potentially very interesting and targeted candidate as catalyst/catalyst support, adsorbent, sensor and an excellent inorganic template for the synthesis of nanostructures [5–13]. Usually, mesoporous MCM-48 molecular sieves are synthesized by hydrothermal method in basic medium. The synthesis of MCM-48 required relatively long reaction time and rigorous conditions. It is important to understand the dynamic adsorption and desorption of organics on mesoporous materials for their application in aqueous systems. Thus, the purpose of this work was to describe comparative study on mesoporous MCM-48 silica, obtained by varying a major synthesis parameter, which is autoclaving, keeping all other parameters the same. The prepared samples were used in adsorption study of methylene blue, MB, to emphasize the role of synthesis procedure.

2. Experimental
2.1. Materials
Cetyl trimethyl ammonium bromide (CTAB), Tetraethyl orthosilicate (TEOS) and Sodium Hydroxide (NaOH) and methylene blue (MB) were purchased from Sigma.

2.2. Preparation of MCM-48
Synthesis method employed was developed by Xu et al. [14], based on the Molar Ratio: 1 SiO2:0.2 CTAB: 100 H2O.
2.2.1. MCM-48 autoclave
(1) 8.8 g CTAB dissolved under slight warming (35°C) in 80 ml distilled water (I).
(2) 10 ml of 2 M NaOH added to (I) to give (II).
(3) 10 ml of TEOS added drop wise to (II) under stirring for 30 min at room temperature (25°C ± 2).
(4) After stirring, the mixture was transferred to Teflon-lined autoclave and heated at 100°C for 72 h.
(5) The product was recovered by filtration, washed with at least 1 L distilled water and oven-dried overnight at 80°C.
(6) The SDA was removed by first heating at 300°C for 2 h, and then calcined in air at 550°C for 8 h.

2.2.2. MCM-48-NO autoclave
Same procedure as previous section but the autoclaving in step 4 was replaced by heating in a tightly covered glass container at 100°C for 72 h.

2.3. Characterisation
2.3.1. Infrared spectroscopy
The infrared spectra of prepared solid were determined using KBr disc technique on a SHIMADZU infrared spectrophotometer in the range 400–4000 cm⁻¹.

2.3.2. Thermogravimetric analysis
Thermograms of prepared solids were obtained using SDT Q 600 thermal analyzer by following the weight change due to heating at a rate of 10°C/min in the temperature range 25–1000°C under N₂ atmosphere.

2.3.3. Adsorption–desorption isotherms of N₂ at 77 K
Nitrogen adsorption–desorption isotherms were obtained at 77 K using an automated adsorption equipment ASAP 2020 V3.05 H. All samples were subjected to automatic degassing before measurement.

2.3.4. X-ray diffraction
The X-ray powder diffraction measurements of samples were carried out on a Rigaku D/Max-II X-ray diffractometer with CuKα radiation.

2.3.5. Point of zero charge
PZC, for the oxides were measured according to the mass titration method [15]. Different amounts of solid (0.1–4.0 g) were added to the convenient volume of distilled water of natural pH (6.6) to compose solid/liquid mass percentage in the range 0.01–20%. The aqueous suspensions containing different amounts of the solid were left to equilibrate while covered for 24 h under agitation (100 rpm) at 25°C. The pH of each solution was then measured using a digital pH meter (Mettler-Toledo AG 8603, Switzerland). The PZC was determined as the converging pH value from the pH vs. adsorbent mass curve.

2.3.6. Adsorption test
A stock solution of 1000 mg/L of MB was prepared by dissolving 1 g of MB into 1 L of deionized water. It was subsequently diluted to different concentrations and the pH of dye solutions were maintained as needed by adding 0.1 M HCl or 0.1 M NaOH. The experiments were carried out by taking 50 ml of MB solution and a required amount of adsorbent into 150 ml conical flasks and stirred using a magnetic stirrer at a speed of 200 rpm. The adsorption was monitored by determining the concentration of MB in solution by double beam UV–Visible spectrophotometer (Systronics-2203) at λmax = 665 nm. The quantity of MB adsorbed on adsorbent at the time of equilibrium (Qads) was calculated by Equation (1)

\[
Q_{\text{ads}} = \frac{(C_0 - C_e)V}{W},
\]

where \(C_0\) and \(C_e\) are the initial and the equilibrium concentrations (mg/L) of MB in solution, \(Q_{\text{ads}}\) is quantity of MB adsorbed on the adsorbent at the time of equilibrium (mg/g), \(V\) is volume (L) of solution and \(W\) is mass of adsorbent (g) taken for experiment. Batch experiments were carried out to determine the effects of pH, contact time and temperature by varying the parameter under study and keeping other parameters constant.

3. Results and discussion
3.1. Characterization of solids
3.1.1. X-ray diffraction
Figure 1 shows the XRD patterns of the calcined samples. For autoclaved sample (1-a), the XRD profile is similar to MCM-48, the cubic material, consisting of a peak at 2θ = 3° and several peaks that can be assigned to the Ia3d space group [16]. On the other hand, X-ray diffraction pattern of no-autoclave MCM-48 sample, Figure 1(b) shows the absence of any of the peaks observed in case of autoclave MCM-48 sample. This revealed that the no autoclave MCM-48 has no cubic characteristics and completely lacks of mesoporosity characterizing MCM-48.

3.1.2. Infrared spectroscopy
SiO₂ exhibits three characteristic infrared absorption bands, namely at 1200–1000, 808 and 470 cm⁻¹ attributed to asymmetric stretching due to oxygen, symmetric stretching due to the motion of silicon atoms and bending modes of bulk Si–O–Si, respectively [17]. A small sharp band at 960 cm⁻¹ is due to Si–OH stretching of surface silanol groups [18,19]. The high-frequency region shows the stretching vibrations of the isolated (noninteracting) surface
silanols [20], preceded by a tail in the range 3700–3500 cm$^{-1}$ due to hydrogen-bonded silanols. That the hydrogen-bonded groups result in no defined maxima has been interpreted in terms of H bonds of different strengths [20]. The spectrum of sample autoclaved MCM-48, Figure 2 showed all these bands suggesting a stoichiometric silicon dioxide structure exposing silanol groups on its surface. On the other hand, the spectrum of sample no autoclave MCM-48, showed the different modes of Si–O–Si in the region 400–1200 cm$^{-1}$ but lacks the Si–OH band at 960 cm$^{-1}$ implying that this sample is formed while its surface does not expose surface silanols (Figure 2). This is further supported by the absence of the band at 1630–1650 cm$^{-1}$ due to bending mode of physically adsorbed water, and the high-frequency band in the range 3500–3700 cm$^{-1}$. Thus it can be concluded that the autoclaving step is necessary for SiO$_2$ to be normally formed as bulk Si–O–Si that terminates with surface Si–OH groups.

3.1.3. Thermogravimetric analysis

The thermogravimetric curves of the two silica samples are presented in Figure 3. The sample prepared without autoclaving showed only 1.5% weight loss through a gradual weight change in the temperature range 25–1000°C. The absence of significant physically adsorbed water weight loss and the gradual loss due to dehydroxylation known in case of silica is consistent with the result of IR for this sample. The thermogram of the sample prepared via autoclaving showed an initial weight loss region up to 100°C amounting to 2.7% weight loss corresponding to physically adsorbed water. The temperature region 110–1000°C showed a gradual weight loss amounting to 2.2% weight loss due to dehydroxylation of formed silica. Therefore, autoclaving as a hydrothermal treatment has resulted in a usual silica matrix that terminated by surface silanol groups.
3.1.4. Nitrogen adsorption–desorption

The nitrogen isotherm of no-autoclave sample is Type II [25] showing very small uptake until near saturation pressure, where capillary condensation in the few large voids between formed solid grains started (Figure 4(a)). The condensation region is characterized by a prevailing hysteresis loop closing at $p/p_0 \sim 0.9$. The high condensation pressure implies the presence of large mean pore size.

The PSD of this sample, calculated from desorption branch using BJH method [25] (Figure 4(b)) displayed a broad distribution in the range 20–100 nm pore width with a maximum in the range 35–50 nm of pore width. Such pore structure is expected to have low surface area and total pore volume. Table 1 collects the pore structure characteristics of the two silica samples.

The Type IV isotherm [25] of the sample MCM-48-Autoclave (Figure 5(a)) is characteristic of the Mesoporous solids showing a swing in adsorption branch at $p/p_0$ range 0.2–0.3 followed by a semi-plateau in the $p/p_0$ range 0.3–0.9. The horizontal part of the isotherm is characterized by a hysteresis loop in the $p/p_0$ range 1.0–0.45. The up rise in the isotherm in the early $p/p_0$ range is indicating of condensation in mesopores of uniform and narrow width. The PSD (BJH) of this sample displayed a peak at 2.2 nm of pore width indicating a mono and narrow pore size range (Figure 5(b)). The values of BET specific surface area [25], the pore volume and average pore size are presented in Table 1. It is clear the role of autoclaving in determining the pore structure characteristics.

3.1.5. Point of zero charge

The pH, at which the net total particle charge is zero, is called the point of zero charge (pzc), which is one of the most important parameters used to describe variable-charge surfaces. The value of pH is used to describe pzc only for systems in which $H^{+}/OH^{-}$ are the potential-determining ions (which is the common case). The pzc is the same as the isoelectric point (iep) if there is no adsorption of other ions than the potential determining $H^{+}/OH^{-}$ at the surface. This is often the case for pure ("pristine surface") oxides in water. If the solution pH is not the same as the solid pzc, then the equilibrium pH after the addition of an oxide shifts towards the pH of point of zero charge [26]. According to this concept the data presented in Figure 6 implies that the pzc is 5.5 and 6.6 for autoclave and no-autoclave samples, respectively. The drift of the pH of the soaking distilled water in case of the autoclave sample is due to the hydrolytic properties of the existing surface hydroxyls, while the absence of these groups on the surface of no-autoclave sample caused the dispersion medium to retain its intrinsic pH.

3.2. Adsorption of methylene blue

3.2.1. Effect of contact time

To determine the adsorption equilibrium time a weight of 0.1 g of each solid was kept in contact with a volume of 50 ml of MB solution of concentration 1000 mg/L under continuous stirring at room temperature and neutral pH. Samples of solution were analysed at different time intervals and the results are presented in Figure 7. It is noted that the autoclave sample reaches equilibrium at shorter time than the no-autoclave one, and for both samples a contact time of 200 min is enough for adsorption to reach equilibrium.

3.2.2. Effect of pH

The effect of pH on the adsorption process was assessed by adding 0.1 g of each solid to 50 ml of MB solutions (1000 mg/L) adjusted to different pH values in the range 2–10, kept under stirring for 4 h at room temperature (Figure 8). The results indicated that adsorption of MB on no-autoclave sample is pH-independent in the examined range; while for autoclave sample the adsorption was found to increase continuously as the pH increases. For this sample, the observed low methylene blue adsorption capacities at pH ≤ 4

Table 1. Pore structure characteristics of MCM-48 samples.

| Sample     | $A_{BET}$ (m$^2$/g) | ExArea$^a$ (m$^2$/g) | $V_p$$^b$ (cm$^3$/g) | $W_c$ (nm) |
|------------|----------------------|-----------------------|-----------------------|------------|
| No autoclave | 12.4                 | 9.9                   | 0.0219                | 7.0        |
| Autoclave   | 827.8                | 911.5                 | 0.5472                | 2.64       |

$^a$-Plot external area.

$^b$Pore volume at $p/p_0 = 0.97$.

$^c$Average pore width ($4V_p/A_{BET}$).

Figure 4. (a) N$_2$ adsorption–desorption isotherm (77 K) and (b) pore size distribution of no-autoclave MCM-48 sample.
(pH_{solution} < \text{pzc}) was predicted. At pH = 4, the surface is positively charged due to the excessive protonation of the hydroxyl surface functional groups, the methylene blue exists in a triple protonated form [27]. Under these conditions, the dye uptake was limited by repulsive forces which occurred between dye cation and positively charged surface. The high methylene blue adsorption capacities at pH $\geq$ 5 (pH_{solution} > \text{pzc}) can be attributed to negatively charged sites born due to the dissociation of hydroxyl groups on the surface, besides that methylene blue dye existed in a single protonated form [28]. In this case, the methylene blue uptake is caused by the electrostatic and/or hydrogen bonding interactions between negatively charged anions on the MCM-48 surface and the dye cations. The pH-independent adsorption in case of no-autoclave sample implies that the adsorption is mainly controlled by dispersion forces.

### 3.2.3. Adsorption isotherms

In the present study, the equilibrium data were analysed using the Langmuir and Freundlich models. The obtained adsorption isotherms were obtained on both samples using 0.1 g in contact with 50 ml of MB solution of different concentrations at pH = 8, room temperature for 4 h. The working pH was selected to be far enough from the conditions at which any suspected dissolution of solids can take place. The isotherm of no-autoclave sample, Figure 9 showed a gradual uptake through the solution equilibrium concentration range 0–800 mg/L reaching an adsorption value of 7.5 mg/g. The latter was followed by enhanced adsorption through a narrow range of equilibrium concentration, and displayed a value of adsorption of 7.5 mg/g after which a plateau was displayed. Considering the dimensions of MB molecule that width = 1.43 nm, depth = 0.61 nm and thickness = 0.4 nm [29], and the $A_{BET}$ of the solid (12.4 m$^2$/g) (Table 1), we can safely conclude that the amount of adsorbed MB at the first plateau corresponds to a monolayer of MB with the molecule laid flat on the surface with its longer length facing the solid surface. Furthermore, the second plateau implies that the adsorption was continued to form another (second) layer laid parallel to the first adsorbed one. The formation of the second adsorbed layer within narrower equilibrium concentration than the first implies that the formation of the first layer induced the formation of the second on its surface. Such mode of adsorption agrees well with a suggested dispersion force-controlled process, and the asymptotic reaching to equilibrium (Figure 7), agrees also with this interpretation. Autoclave sample resulted in an isotherm characterized by initial enhanced adsorption that reached plateau of 480 mg/g at equilibrium solution concentration <100 mg/L (Figure 9). The affinity of MB to autoclave sample is very high which is reflected in the very short time of reaching equilibrium, and the distinguished high uptake at small equilibrium concentration.

The MB adsorption data on both samples were analysed using the linear forms of Langmuir and Freundlich equations. The different parameters obtainable on using these two models are collected in Table 2. The data of no-autoclave sample, in the region of monolayer, were perfectly fitted by Freundlich form, Equation (2) while Langmuir Equation (3) showed perfect fitting for the data of autoclave sample (Figure 10).

\[
\begin{align*}
\text{Ln}Q_e &= \text{Ln}K_f + \frac{1}{n_f} \text{Ln}C_e, \quad (2) \\
\frac{C_e}{Q_{ads}} &= \frac{1}{K_f} + \frac{a_0}{K_f} C_e. \quad (3)
\end{align*}
\]

The Freundlich isotherm assumes adsorption on heterogeneous surface sites and formation of multi-layer of the sorbate at saturation. The observed fit of the equilibrium data to the Freundlich isotherm in case of no-autoclave sample is in line with the suggested
mechanism of MB sorption that is via dispersion pore-filling, forming double layer at saturation. Table 2 shows low Freundlich k value for no-autoclave sample that agrees with the low adsorption capacity of this sample for MB and a value of $n > 1$ indicates favourable adsorption conditions according to Freundlich model. The essential characteristic of the Langmuir isotherm can be expressed in terms of the constant separation factor $R_L$, \[ R_L = \frac{1}{1 + a_L C_0} \] which is also shown in Table 2. The value of $R_L$ indicates that the shape of the isotherm is either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The value of $R_L$ for the autoclave sample was 0.0075 (between 0 and 1), which confirms that the adsorption of MB on this sample is a favourable process.

3.2.4. Desorption
To assess the strength of the adsorption of MB on the surface of the two MCM-48 samples, the samples loaded with the maximum amount of adsorbed MB were collected, left to dry naturally, and then soaked under stirring in distilled water (0.1 g/50 ml) of pH = 8. The amount of released MB was determined at different times up to 24 h, and the results are presented in Figure 11. After 24 h the no-autoclave sample released 72% of the 15.0 mg/g adsorbed at equilibrium, while the autoclave sample retained 94% of the 480 mg/g adsorbed at equilibrium. These values clearly reflect the difference in the mode of adsorption occurred on the two samples; the molecules that stick to the surface through dispersion forces are expected to detach from the surface more easily than those adsorbed via electrostatic/and or hydrogen bonding. Desorption curve of the no-autoclave sample hints that complete desorption could be achieved after longer contact time.

3.2.5. Adsorption kinetics
To study the mechanism of adsorption kinetics in depth, the adsorption data in the time range 0–160 min were used. It was found that the first-order model, Equation (4) fits the data on no-autoclave sample, while pseudo-second-order model, Equation (5) fits the data on autoclave sample (Figure 12). The values of the specific rate constant for both samples are included in Table 3.

\[
\ln (Q_e - Q_t) = \ln Q_e - k_1 t, \tag{4}
\]
\[
t/Q_t = 1/(k_2 Q_e^2) + t/Q_e. \tag{5}
\]

The best fit of the pseudo-second order model in case of autoclave sample suggests that a chemisorption mechanism was involved in the adsorption [30] which is supported by the thermodynamics data (see below) that proved that the interaction in this case is not physical. The non-specific mode of adsorption in case of no-autoclave sample agrees with the applicability of the first-order kinetics that does not depend on the initial concentration. The calculated $t_{1/2}$ values that 38 and 2.5 min for no-autoclave and autoclave samples, respectively, agree well with the velocity differences noted in reaching the equilibrium conditions.

To determine whether film diffusion or intra-particle diffusion is the rate-limiting step, the Weber–Morris [31] intra-particle diffusion model, Equation (6), was tested

\[
Q_t = k_i (t^{1/2}) + C, \tag{6}
\]

$k_i$ (mg/g/min$^{1/2}$) is the rate parameter of the intra-particle diffusion control stage, $C$ is a constant related to the thickness of the boundary layer: the larger is the value of $C$, the greater is the boundary layer effect. According to the model, the sorption mechanism is via intra-particle diffusion when a plot of $Q_t$ versus $t^{1/2}$ will be linear; furthermore, intra-particle diffusion is
the sole rate-limiting step when such a plot passes through the origin. When the sorption process is controlled by more than one mechanism, then a plot of \( Q_t \) versus \( t^{1/2} \) will be multi-linear.

For no-autoclave sample, the plot showed two portions: an initial linear but steep and rapid portion, and a later horizontal portion (Figure 13). Since the linear plot of \( Q_t \) versus \( t^{1/2} \) is linear at the initial sorption stages, \( R^2 = 0.998 \), intra-particle diffusion was the main sorption mechanism in this part of the plot. The second portion of the plot (not shown in Figure 13) is slow and controlled by equilibrium diffusion mechanism which occurred when the rate of the sorption and desorption are insignificant. The very small deviation of the straight line from the origin (Table 3), further supports the conclusion of intra-particle diffusion. Additionally, it is shown that this sample has poor wettability that limits the diffusion rate, which explains the low value of \( k_i \).

For autoclave sample, the higher deviation of the straight line from the origin (Table 3), indicating greater boundary layer effect is due to the instantaneous utilization of the active adsorbing sites on the adsorbent surface. The pores in this sample are interconnected, forming a better-developed transportation network and effective diffusion path, therefore the value of \( k_i \) is higher than in the case of no-autoclave sample (Table 3).

**3.2.6. Adsorption thermodynamics**

In order to obtain in-depth information on the inherent energetic changes that are associated with adsorption, the thermodynamic parameters were estimated. The changes in Gibbs energy \( (\Delta G^0) \), enthalpy \( (\Delta H^0) \) and entropy \( (\Delta S^0) \) can be calculated from the following equations:

\[
K_d = \frac{Q_e}{C_e}, \quad (7)
\]

\[
\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}, \quad (8)
\]

\[
\Delta G^0 = \Delta H^0 - T \Delta S^0, \quad (9)
\]

where \( K_d \) is the distribution coefficient, \( T \) (K) is the absolute temperature and \( R \) is the universal gas constant \((8.314 \text{ J/mol K})\). The values of \( \Delta H^0 \) (kJ/mol) and \( \Delta S^0 \) (J/K mol) can be calculated from the slope and intercept of a plot of \( \ln K_d \) versus \( 1/T \), as shown in Figure 14. The thermodynamic parameters \( (\Delta H^0, \Delta S^0 \text{ and } \Delta G^0) \) are shown in Table 4. The adsorption
isotherms were measured under the above conditions at three temperatures, mainly 298, 308 and 318 K.

For no-autoclave sample, using the data through the first layer, the value of $\Delta H^o$ is positive, which indicates that the adsorption process of MB on this sample is endothermic. When $5 < \Delta H^o < 10 \text{ kJ/mol}$, it denotes that the adsorption mechanism is physisorption; when $30 < \Delta H^o < 70 \text{ kJ/mol}$, the adsorption mechanism is chemisorptions [32]. The value of $\Delta H^o$ obtained in case of this sample is even lower that the range assigned to physisorption which agrees with the

![Figure 11. The release rate of adsorbed MB on MCM-48 samples.](image)

**Figure 11.** The release rate of adsorbed MB on MCM-48 samples.

| Sample          | $Q_e$ (Exp) (mg/L) | $Q_e$ (Cal) (mg/L) | $k_1$ (min$^{-1}$) | $R^2$ | $Q_e$ (Exp) (mg/L) | $Q_e$ (Cal) (mg/L) | $k_2$ (g/min mg) | $C$ (mg/g) | $R^2$ |
|-----------------|-------------------|-------------------|-------------------|------|-------------------|-------------------|-----------------|--------|------|
| No autoclave    | 14                | 12.9              | 0.018             | 0.995| –                 | –                 | –               | –          | –    |
| Autoclave       | –                 | –                 | –                 | –    | 140               | 158               | 0.0004         | 72.1     | –58.6| 0.993|

**Table 3.** Adsorption kinetic models and kinetic parameters for MB adsorption onto MCM-48 samples.

![Figure 12. (a) First-order and (b) second-order plots for MB adsorption on MCM-48 samples.](image)

**Figure 12.** (a) First-order and (b) second-order plots for MB adsorption on MCM-48 samples.

![Figure 13. Weber–Morris kinetic plots of MB adsorption at $T = 298 \text{ K}$ on MCM-48 samples.](image)

**Figure 13.** Weber–Morris kinetic plots of MB adsorption at $T = 298 \text{ K}$ on MCM-48 samples.

![Figure 14. The linear dependence of $\ln K_d$ on $1/T$ based on the adsorption thermodynamics.](image)

**Figure 14.** The linear dependence of $\ln K_d$ on $1/T$ based on the adsorption thermodynamics.
suggested dispersion force driven mode of adsorption. The value of $\Delta S^o$ is small and negative indicating that the adsorption process is accompanied by a little increase in order. The MB molecules possessed more ordered configuration when transferred from the solution medium into the solid surface. However, the process proceeded non-spontaneously as inferred from the positive value of $\Delta G^o$ that showed increase with increasing temperature indicating that the adsorption becomes less spontaneous as temperature increases.

The adsorption data on autoclave sample resulted in a negative value of $\Delta H^o$ implying that the adsorption process is exothermically driven, and its value is out the range assigned to physical adsorption, but still lower than the chemical adsorption range. This agrees with the suggested mode of adsorption of MB on this sample being electrostatic and/or hydrogen bonding. The negative value of $\Delta S^o$ indicates that the adsorption has resulted in a general decrease in the randomness due to localized adsorption expected from the suggested mode of adsorption. However, the negative natures of $\Delta H^o$ and $\Delta S^o$ have resulted in negative values of $\Delta G^o$ implying a spontaneous process. The values of $\Delta G^o$ hint that the adsorption of MB on this sample becomes less spontaneous as temperature increases.

| Sample        | $\Delta H^o$ (kJ/mol) | $\Delta S^o$ (J/K mol) | $\Delta G^o$ (kJ/mol) | $R^2$ |
|---------------|-----------------------|------------------------|------------------------|-------|
| No autoclave  | 3.26                  | -28.2                  | 11.66                  | 11.95 | 12.23 | 0.9999 |
| Autoclave     | -13.01                | -36.4                  | -2.16                  | -1.80 | -1.43 | 1.0000 |

Table 4. Thermodynamic parameters for MB adsorption on MCM-48 samples.

4. Conclusions

The autoclaving step in the process of MCM-48 formation via soft template controls the evolution of its microstructure. Replacing by a normal thermal treatment precludes the presence of surface silanol groups responsible for the adsorption activity of silica, and results in an open pore structure exposing low surface area. This sample has poor wettability that limits the diffusion rate in aqueous media. The solid of such characteristics possesses low affinity for methylene blue, with weak, slow, non-spontaneous and reversible mode of adsorption. While this makes it unfavourable adsorbent, yet it could be advantageous if the issue of repeated use and wettability are considered. The prevailing surface silanol groups, and the interconnected pore system in MCM-48 control the thermodynamic and the kinetics of the process of methylene blue adsorption making it spontaneous, fast and practically irreversible. The variance observed in case of samples prepared under different conditions of hydrothermal treatment merits checking on using other adsorbates.

Disclosure statement

No potential conflict of interest was reported by the authors.

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