Supporting Information

Hexadecyltrimethylammonium bromide (CTAB) Surfactant Supported Silica Material for the Effective Adsorption of Metanil Yellow Dye

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Adsorption Isotherm Models

**Langmuir adsorption isotherm equation**

Langmuir adsorption isotherm is used to predict the adsorption of dye molecules at specific homogeneous sites within the adsorbent and their monolayer-type of adsorption. In addition, this model is also used to calculate the maximum adsorption of adsorbent at various concentrations of dye molecules. Furthermore, from the regression coefficient ($R^2$) value the model suggests the favorable or unfavorable adsorption behavior from the linear graph obtained from the plot.

\[
\frac{C_e}{q_e} = \frac{1}{K_L} + \left(\frac{a_L}{K_L}\right)C_e
\]

(1)

where $C_e$ and $q_e$ are the adsorbate concentration at equilibrium (mg L$^{-1}$) and amount of My adsorption at equilibrium (mg g$^{-1}$), respectively. $K_L$ (L g$^{-1}$) and $a_L$ (L mg$^{-1}$) are Langmuir constants.

**Freundlich adsorption isotherm equation**

Freundlich adsorption isotherm suggests the non-ideal sorption on heterogeneous surface and also used to predict the multi-layer adsorption behavior of the materials.

\[
q_e = K_F C_e^{1/n}
\]

(2)

\[
\log(q_e) = \log(K_F) + \left(\frac{1}{n}\right) \log(C_e)
\]

(3)

where $C_e$ and $q_e$ are the adsorbate concentration at equilibrium (mg L$^{-1}$) and amount of My adsorption at equilibrium (mg g$^{-1}$), respectively. $K_F$ (mg g$^{-1}$ (L mg$^{-1}$)$^{1/n}$) is the Freundlich constants and $n$ is the adsorption intensity.

**Temkin adsorption isotherm equation**

Temkin model suggests the role and interaction of the adsorbing dye molecules with the adsorbent.

\[
q_e = B \ln A + B \ln C_e
\]

(4)

where $q_e$ is the amount of My adsorption at equilibrium (mg g$^{-1}$). $A$ is equilibrium binding constant (L g$^{-1}$) and $B$ is a constant related to the heat of adsorption ($B = RT/b$), where, $R$, $T$, and $b$ are the universal gas constant (8.314 J mol$^{-1}$ K$^{-1}$), absolute temperature (K), and Temkin constant (J mol$^{-1}$), respectively. $A$ and $B$ values can be obtained from slope and intercept of the graph of $q_e$ Vs ln$C_e$. 

S2
Adsorption kinetics study:
The kinetic study of an adsorbent is carried out generally by three type of models such as pseudo first-order, pseudo second-order, and intra-particle diffusion model because these models can give an idea about the chemical or physical adsorption behavior of the dye molecules by the adsorbent from their linear graph obtained from the pseudo first-order and the pseudo second-order models and their regression coefficient ($R^2$) values. The $R^2$ value that is close to 1 in the pseudo first-order model suggests that the physisorption occurs in the material, whereas if the $R^2$ value is close to 1, the chemisorption is favorable in the pseudo second-order model. Intra-particle diffusion model illustrates the diffusion of dye molecules in the adsorbent. The $R^2$ value that is close to 1 in this model suggests the excellent diffusion of the dye molecules. However, other factors may also play roles in the determination of rate-limiting steps in addition to the intra particle diffusion.

**Pseudo first-order model**
The pseudo first-order model is expressed by the Lagergren equation,

$$
\left( \frac{dq_t}{dt} \right) = k_1 \left( q_e - q_t \right) \tag{5}
$$

where $q_c$ and $q_t$ are the amount of dye molecules adsorbed on an adsorbent (mg g$^{-1}$) at equilibrium and at time $t$, respectively, and $K_1$ is the rate constant of the first order adsorption (min$^{-1}$). The integration of eq. (5) with initial condition of $q_t = 0$ at $t = 0$ gives the linear form of the equation.

$$
\log \left( q_e - q_t \right) = \log q_e - \left( \frac{k_1 t}{2.303} \right) \tag{6}
$$

By plotting a graph of $\log \left( q_e - q_t \right)$ vs $t$, the constant $k_1$ value can be determined from the slope and intercept.

**Pseudo-second-order model**

The pseudo-second-order kinetic model can be expressed by the following equation.

$$
\left( \frac{t}{q_t} \right) = \left( \frac{1}{k_2 q_e^2} \right) + \left( \frac{t}{q_e} \right) \tag{7}
$$

where $k_2$ is the pseudo-second-order rate constant (g mg$^{-1}$ min$^{-1}$) and $q_e$ (mg g$^{-1}$) can be obtained from the slope and intercept of $t/q_t$ vs $t$.

**Intra-particle diffusion model:**
The equation for intra-Particle diffusion model can be expressed as

$$
q_t = k_1 t^{1/2} + C \tag{8}
$$
where $q_t$ is the adsorption capacity at any time $t$ and $k_{id}$ (mg g$^{-1}$ min$^{-1/2}$) is the intra-particle diffusion rate constant and $C$ (mg g$^{-1}$) is the intra-particle diffusion constant relating to the thickness of the boundary layer.

**Thermodynamic study**

Thermodynamic study is used to investigate the effect of temperature on the adsorption of dye molecules by the adsorbent. This model is also used to predict the enthalpy ($\Delta H^o$), entropy ($\Delta S^o$) changes, and Gibbs free energy ($\Delta G^o$) values of the adsorbent by using the following equations.$^{37}$

The enthalpy ($\Delta H^o$), entropy ($\Delta S^o$) change, and Gibbs free energy ($\Delta G^o$) values were first obtained from equations (9 and 10) to set the thermodynamic parameters,

$$\log \left( \frac{q_e}{q_t} \right) = \left( \frac{-\Delta H^o}{2.303 \, RT} \right) + \left( \frac{\Delta S^o}{2.303 \, RT} \right) \quad (9)$$

$$\Delta G^o = \Delta H^o - T \Delta S^o \quad (10)$$

where $K_e = (q_e/q_t)$ from the graph of $\log K_e$ vs 1/T, the ($\Delta H^o$), entropy ($\Delta S^o$) values are determined from the slope and intercept values. In addition, the activation energy (Ea) and sticking probability ($S^*$) were depicted from the following equation:

$$S^* = (1 - \theta) \, e^{-Ea/RT} \quad (11)$$

The value of $\Theta$ was calculated from the equation,

$$(\theta) = \left( 1 - \frac{C_e}{C_0} \right) \quad (12)$$

The Ea value is calculated from the slope of ln (1-$\Theta$) vs. 1/T. The Ea values can indicate whether physisorption or chemisorption of the dye molecules by the adsorbent had occurred. Physisorption generally occurs when the Ea value is in the range of 5-40 kJ mol$^{-1}$, whereas chemisorption takes place when the Ea value is in the range of 40-800 kJ mol$^{-1}$. 
**Figure S1.** Chemical structures of metanil yellow (My), methylene blue (Mb), and rhodamin b (Rb).

**Figure S2.** (A) FTIR spectra and (B) XRD patterns of (a-c) MCM-41 after removal of the surfactant by 1, 2, 3-times of chemical etching (MCM-41-ACE$_1$, MCM-41-ACE$_2$, MCM-41-ACE$_3$, respectively).
Figure S3. Nitrogen adsorption and desorption (A) and pore size distribution (B) of (a) as-synthesized MCM-41 (MCM-41\textsubscript{6}-BCE) and (b and c) MCM-41 after the removal of surfactant by 1-time chemical etching (MCM-41\textsubscript{6}-ACE\textsubscript{1}) and calcination at 540 °C (MCM-41\textsubscript{6}-AC), respectively.

Figure S4. TGA curves of (a) as-synthesized MCM-41 (MCM-41\textsubscript{6}-BCE) and (b and c) after removal of the surfactant by 1-time chemical etching (MCM-41\textsubscript{6}-ACE\textsubscript{1}) and calcination at 540 °C (MCM-41\textsubscript{6}-AC).
**Figure S5.** TEM images of (A) as-synthesized MCM-41 (MCM-41₆-BCE) and (B and C) after removal of the surfactant by 1-time chemical etching (MCM-41₆-ACE₁) and calcination at 540 °C (MCM-41₆-AC).

**Figure S6.** DLS histograms of (A) as-synthesized MCM-41 (MCM-41₆-BCE) before (in black) and after My adsorption (in red), (B and C) MCM-41₆-ACE₁ and MCM-41₆-AC before (in black) and after My adsorption (in red), respectively, and (D) MCM-41₆-BCE after Mb (in black) and Rb (in red) adsorption, respectively (Adsorption time: 360 min).
Figure S7. FESEM images of (a) as-synthesized MCM-41 (MCM-41$_2$-BCE) and (b) after the removal of surfactant by 1-time chemical etching (MCM-41$_2$-ACE$_1$).

Figure S8. (A) My dye removal percentages of CTAB, MCM-41$_2$-BCE, MCM-41$_2$-ACE$_1$, MCM-41$_6$-BCE, and MCM-41$_6$-ACE$_1$ (adsorption time: 120 min, sample weight: 20 mg, shaking speed: 180 rpm, and bath temperature: 25 °C). (B) My Dye removal percentages of MCM-41$_6$-BCE, MCM-41$_6$-ACE$_1$, MCM-41$_6$-ACE$_2$, MCM-41$_6$-ACE$_3$, MCM-41$_6$-AC, SiNPs, and SiNPs-AC ((ACE$_2$ and ACE$_3$ represent the surfactant removal by 2 and 3-times of chemical etching, SiNPs and SiNPs-AC are the commercial silica nanoparticles before and after calcination, respectively. adsorption time: 360 min, sample weight: 20 mg, shaking speed: 180 rpm, and bath temperature: 25 °C).
Figure S9. (A) The dye removal percentages of MCM-41\textsubscript{6}-BCE (a) and MCM-41\textsubscript{6}-ACE\textsubscript{1} (b) at various adsorbent weight (10, 20, 30, 40, 50 mg) (concentration (100 mg L\textsuperscript{-1}) and shaking time 360 min). (B) Effect of CTAB leaching by the MCM-41\textsubscript{6}-BCE at different times (2, 4, and 6 h).

Figure S10. Intra-particle diffusion kinetics of My adsorption by MCM-41\textsubscript{6}-BCE (A) and MCM-41\textsubscript{6}-ACE\textsubscript{1} (B).
Figure S11. Langmuir (A, C, E) and Freundlich adsorption isotherms (B, D, F) of My by MCM-416-ACE\textsubscript{1} at various adsorption temperatures (25 °C, 30 °C, and 35 °C).
Figure S12. Temkin adsorption isotherms of My by MCM-41₆-BCE (A, C, E) and MCM-41₆-ACE₁ (B, D, F) at various adsorption temperatures (25 °C, 30 °C, and 35 °C).
Figure S13. (A and B) The standard free energy changes of adsorption with respect to temperature and (C and D) activation energy for the adsorption of My by the MCM-41_{6}-BCE (A, C) and MCM-41_{6}-ACE_{1} (B, D), respectively.
**Table S1.** Langmuir and Freundlich isotherm model constants for the adsorption of My onto MCM-41$_6$-ACE$_1$ at 25 °C, 30 °C, and 35 °C.

| Parameters       | 25 °C  | 30 °C  | 35 °C  | Parameters       | 25 °C  | 30 °C  | 35 °C  |
|------------------|--------|--------|--------|------------------|--------|--------|--------|
| Intercept        | 0.0443 | 0.0419 | 0.0298 | Inter.           | 1.4923 | 1.5373 | 1.6090 |
| Slope            | 0.0208 | 0.0173 | 0.0165 | Slope            | 0.0927 | 0.1117 | 0.0815 |
| R$^2$            | 0.9903 | 0.9809 | 0.971  | R$^2$            | 0.3898 | 0.7787 | 0.3850 |
| K$_L$ (L g$^{-1}$) | 22.573 | 23.866 | 33.557 | n                | 10.788 | 8.953  | 12.270 |
| a$_L$ (L mg$^{-1}$) | 0.4695 | 0.4129 | 0.5537 | K$_F$ (mg g$^{-1}$ (1 mg$^{-1}$)$^n$) | 31.067 | 34.459 | 40.644 |
| Q$_0$ (mg g$^{-1}$) | 48     | 58     | 61     | -                | -      | -      | -      |

Note: R$^2$-regression coefficient, K$_L$ (L g$^{-1}$) and a$_L$ (L mg$^{-1}$) are the Langmuir constants. Q$_0$-maximum adsorption capacity. K$_F$ and n are the Freundlich constants.

**Table S2.** Thermodynamic parameter values for the adsorption of My onto MCM-41$_6$-BCE and MCM-41$_6$-ACE$_1$ at various concentrations.

| Parameters       | Concentrations (mg L$^{-1}$) | 50  | 100 | 150  | 200  | 250  |
|------------------|------------------------------|-----|-----|------|------|------|
| **MCM-41$_6$-BCE** |                             |     |     |      |      |      |
| ΔH$^\circ$ (kJ mol$^{-1}$) |                         | 67.46 | 75.25 | 144.64 | 109.69 | 90.60 |
| ΔS$^\circ$ (J mol$^{-1}$ K$^{-1}$) |                   | 256.79 | 279.85 | 499.36 | 374.69 | 306.19 |
| ΔG$^\circ$ (kJ mol$^{-1}$) (298K) |                   | -76.46 | -83.32 | -148.64 | -111.55 | -91.15 |
| (303K)            |                             | -77.74 | -84.72 | -151.16 | -113.42 | -92.68 |
| (308K)            |                             | -79.02 | -86.12 | -153.66 | -115.30 | -94.22 |
| R$^2$             |                             | 0.9162 | 0.6522 | 0.9213 | 0.9456 | 0.9977 |
| **MCM-41$_6$-ACE$_1$** |                          |     |     |      |      |      |
| ΔH$^\circ$ (kJ mol$^{-1}$) |                     | 67.74 | 128.10 | 29.17 | 14.39 | 20.80 |
| ΔS$^\circ$ (J mol$^{-1}$ K$^{-1}$) |                  | 260.75 | 453.27 | 96.94 | 41.47 | 61.80 |
| ΔG$^\circ$ (kJ mol$^{-1}$) (298K) |                  | -77.64 | -134.95 | -28.86 | -12.34 | -18.39 |
| (303 K)           |                             | -78.93 | -137.21 | -29.34 | -12.55 | -18.70 |
| (308K)            |                             | -80.24 | -139.48 | -29.83 | -12.76 | -19.01 |
| R$^2$             |                             | 0.5000 | 0.6536 | 0.9655 | 0.7325 | 0.8805 |
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