Effective adsorption of methyl orange on organo silica nanoparticles functionalized by a multi-hydroxyl-containing gemini surfactant: A joint experimental and theoretical study

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Figure S1 The TG-DTG curves of $G_{16}$

Figure S2 The nitrogen adsorption/desorption isotherms of SiNPs (a) and $G_{16}$-SiNPs (b).
Figure S3 UV-Vis spectra of MO solution before and after adsorption on G16-SiNPs

Figure S4 The spectra of MO and adsorbed G16-SiNPs

Table S1 The surface area, total pore volume, and average pore diameter value of SiNPs and G16-SiNPs.

| Sample     | \( S_{\text{BET}} \) (m²/g) | \( V_{\text{tp}} \) (cm³/g) | \( D_p \) (nm) |
|------------|-----------------------------|-----------------------------|--------------|
| SiNPs      | 62                          | 1.00                        | 16.3         |
| G16-SiNPs  | 134                         | 0.95                        | 16.0         |

\( S_{\text{BET}} \)-surface area, \( V_{\text{tp}} \)-total pore volume, and \( D_p \)-average pore diameter
Table S2 Vibrational analysis of optimized structures.

| G16 Frequency (1/cm) | Intensity (km/mol) | MO Frequency (1/cm) | Intensity (km/mol) |
|---------------------|-------------------|---------------------|-------------------|
| 22.27               | 0.08              | 4.65                | 4.48              |
| 25.68               | 0.31              | 5.44                | 0.04              |
| 38.73               | 0.15              | 10.16               | 5.71              |
| 43.4                | 0.41              | 11.94               | 0.95              |
| 60.78               | 3.06              | 18.23               | 0.15              |
| 67.26               | 0.28              | 23.14               | 1.59              |
| 120.51              | 0.52              | 27.88               | 0.13              |
| 124.66              | 4.27              | 32.89               | 0.01              |
| 146.22              | 23.39             | 33.41               | 0.05              |
| 155.77              | 2.07              | 40.63               | 0.16              |
| 162.35              | 0.47              | 42.12               | 0.64              |
| 188.85              | 2.76              | 48.19               | 0.03              |
| 226.67              | 11.94             | 50.42               | 0.3               |
| 238.84              | 2.31              | 53.49               | 0.02              |
| 242.33              | 10.33             | 55.17               | 0.24              |

1. Characterization

The structural characters of SiNPs and G16-SiNPs were characterized by Fourier transformed infrared spectroscopy (FT-IR, Nicolet IS10 FT-IR spectrometer in the range of 4000-400 cm⁻¹, with resolution of 4 cm⁻¹) and X-ray diffractometer (XRD, in the 2θ range from 1º to 10º, at the scanning rate of 1º min⁻¹). Thermogravimetric analysis (TG-DTG, NETZSCH STA 449 F5/F3 Jupiter, from 30 to 800 ºC at 10 ºC min⁻¹, nitrogen atmosphere) alternated with elemental analysis (EA, Vario EL cube) is applied to measure the sample thermal stability and modifier loading. Scanning electron microscope (SEM, SU8010, Japan) was adopted for a visual observation of SASs and organo-SASs.
The values of zeta potential were recorded on Zetasizer Nano ZS90 at pH of 3, 5, 7 and 9. All samples were all dried at 60 °C overnight before characterization.

2. The adsorption kinetics, isotherms and thermodynamics

The equations of pseudo-first- (S1), pseudo-second order (S2) and intra particle diffusion (S3) models, the Langumir (S4), Freundlich (S5) and Redlich-Peterson (S6), as well as thermodynamic parameters (S7 and S8) are expressed as follows:¹ ²

\[
\begin{align*}
\log(q_e - q_t) &= \log q_e - \frac{k_1}{2.303} t \\
\frac{t}{q_t} &= \frac{1}{k_2 q_e} + \frac{1}{q_e} \\
q_t &= k_i t^{1/2} + C
\end{align*}
\]

where \(k_1\) (min⁻¹) and \(k_2\) (g (mg min)⁻¹) were the pseudo-first-order and pesudo-second-order rate constants. \(q_e\) (mg g⁻¹) and \(q_t\) (mg g⁻¹) were the adsorption capacities at equilibrium and at time \(t\) (min), which represents contact time. All these unknown parameters can be determined from plots of \(\log (q_e - q_t)\) against \(t\) and \(t/q_t\) against \(t\). \(k_{id}\) (mg g⁻¹ min⁻¹/2) is the rate constant of the intra-particle diffusion kinetic model, the values of \(C\) and \(k_{id}\) can be determined from the intercept and slope of the linear plotted of \(q_t\) against \(t^{1/2}\), respectively.

The Langmuir, Freundlich and Redlich-Peterson isotherms were expressed as follows:³

\[
\begin{align*}
q_e &= \frac{Q_m K_f C_e}{1 + K_f C_e} \\
q_e &= K_f C_e^{1/n} \\
q_e &= \frac{A C_e}{1 + BC_e^n}
\end{align*}
\]

where \(q_e\) (mg/g) is the adsorption capacity onto per unit mass of adsorbent at equilibrium, \(C_e\) is the solute equilibrium concentration (mg/L), \(q_m\) (mg/g) is maximum adsorbed amount in the theoretical. \(k_l\) (L/mg), \(k_i\) (mg/g) and \(n\) represent the constants of Langmuir and Freundlich, respectively. \(A\) (L/g)
and $B (\text{L/mg})$ are the Redlich–Peterson model constant. $g$ fluctuated between 0 and 1 with two limiting behaviors: Langmuir form for $g = 1$ and Henry’s law form for $g = 0$.

Thermodynamic parameters could be calculated using the following equations:

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$  \hspace{1cm} (S7)

$$\Delta G^\circ = -RT \ln K_L$$  \hspace{1cm} (S8)

where $K_L$ is the Langmuir constant, $q_e$ and $C_e$ have the same definitions with above equations. $R$ is the universal gas constant (8.3145 J/(mol K)) and $T$ represents the absolute temperature in Kelvin. The values of $\Delta H^\circ$ and $\Delta S^\circ$ can be extrapolated from intercept and slope of $\ln K_L$ versus $1/T$.

Reference

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