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Adsorption Kinetics and Thermodynamics of Methylene Blue onto *p-tert*-Butyl-calix[4,6,8]arene-Bonded Silica Gel

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New-style adsorbents of *p-tert*-butyl-calix[4,6,8]arene-bonded silica gel—C*n*ABS (C4ABS, C6ABS, C8ABS)—were prepared by bonding *p-tert*-butyl-calix[4,6,8]arene to the silica gel surface through the coupling reagent, 3-glycidoxypropyltrimethoxysilane. The products were characterized by FTIR, thermogravimetry, elemental analysis, and scanning electron microscopy. The adsorption of methylene blue from aqueous solution by C*n*ABS was studied. Kinetic studies showed that the adsorption of the dye onto C*n*ABS fit a first-order kinetic model. The equilibrium adsorption data were interpreted using the Langmuir and Freundlich models. The adsorption of methylene blue onto C*n*ABS was better represented by the Langmuir equation. The saturation adsorption quantity monotonically increased with the number of phenolic units in the calixarene ring. The thermodynamic parameters for the adsorption reaction were calculated through a van't Hoff analysis. The whole adsorption process was endothermic, which resulted in an increase of the adsorption quantity with a temperature increase. The new-style adsorbent of C*n*ABS was regarded as a potential adsorbent to deal with dyes or organics in wastewaters.

Introduction

Azo dyes are important colorants having extensive application in the leather, textile, paper mill, additive, foodstuff, and cosmetic industries. However, approximately (10 to 15) % of the overall production of azo dyes is released into the environment, which is very dangerous because some of the azo dyes and their degradation products have a toxic, carcinogenic, or mutagenic influence on living organisms. Therefore, azo dye-containing wastewater should be treated before discharge.

In recent years, much attention has been paid to chemical separation techniques and the design and synthesis of new extraction reagents for ions and molecules. This attention results from environmental concerns and efforts to save energy and enhance recycling at the industrial level. In this respect, supramolecular chemistry has provided important avenues to prepare new types of adsorbents and extraction reagents. This was achieved with the development of macrocyclic receptors, such as crown ethers,[1] cyclodextrins,[2−10] and calixarenes.[11,12]

Calix[*n*]arenes are cyclic oligomers synthesized by condensation of a *p*-alkylated phenol and formaldehyde. Although all members of the series from $n = 4$ to 20 are known, even oligomers (tetramers, hexamers, octamers, etc.) are easier to synthesize than odd ones. Calixarenes have a particular configuration because of their cavity. They have the flexibility to adjust the cavity dimension and the ability to form inclusion compounds with a great variety of guests, from charged molecules such as anions and metallic cations to apolar compounds. This versatility makes the calixarene family the third major class of macrocyclic binding agents after crown-ethers and cyclodextrins.[13,14] Therefore, the use of calix[*n*]arenes in harnessing environment pollution has aroused the interest of environment researchers.

Nowadays, many researchers are interested in cross-linking calixarenes with suitable cross-linkers to form an insoluble resin which has specific adsorption based on inclusion complex formation.[11,12,15,16] In this article, silica gel has received considerable attention as a basic matrix for designing a new adsorbent. *p-tert*-Butyl-calix[4,6,8]arenes were bonded onto the surface of silica gel through the coupling reagent 3-glycidoxypropyltrimethoxysilane to prepare a new style of adsorbent—C*n*ABS (C4ABS, C6ABS, C8ABS). To research the adsorption capacity and mechanism of adsorption, methylene blue, a kind of cationic azo dye, was chosen as the adsorbate (the structure is shown in Figure 1(A)). The thiazine dye methylene blue has many applications in industry as a common textile dye. Methylene blue is a frequently used cellular stain and a redox indicator and is employed as a spectroscopic probe. In particular, its adsorption on all kinds of adsorbents attracts considerable research interest. We researched the adsorption behavior of methylene blue on C*n*ABS. The thermodynamic and kinetic parameters for the adsorption reaction were calculated through a static adsorption study. The adsorption mechanism of the adsorption reaction has been discussed. The new-style adsorbent of C*n*ABS was regarded as a potential sorbent to deal with dye or organic contaminated wastewater.

Experimental Section

Experiment Reagent. The *p-tert*-butyl-calix[*n*]arenes ($n = 4, 6, 8$) were synthesized according to references available in the literature.[17,18] Methylene blue (C.I. Basic Blue 9, C.I. Classification Number 52015) was purchased from the Shanghai Chemical Reagents Company and used without purification. 3-Glycidoxypropyltrimethoxysilane was obtained from Sigma-Aldrich and used without any purification. Activated silica gel was purchased from the Qingdao Silica gel desiccant factory. Highly pure water was obtained from a Millipore Milli-Q UV system.

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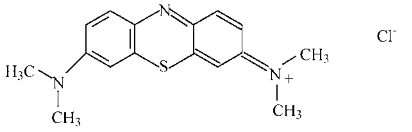
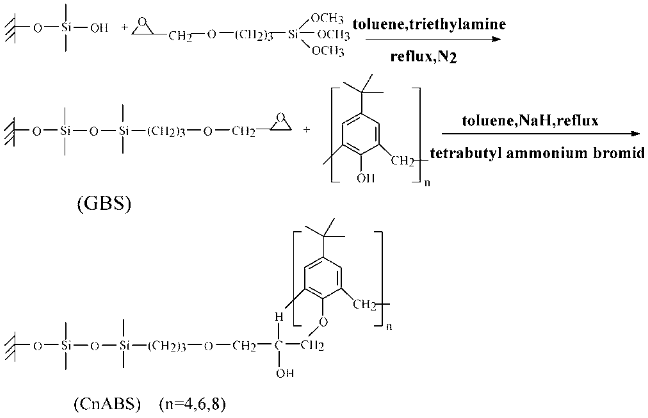


(A) Structure of Methylene blue (methylene blue)



(B) Schematic diagram of preparation CnABS

Figure 1. (A) Structure of methylene blue. (B) Preparation of *p-tert*-butyl-calix[4,6,8]arene-bonded silica gel (C*n*ABS).

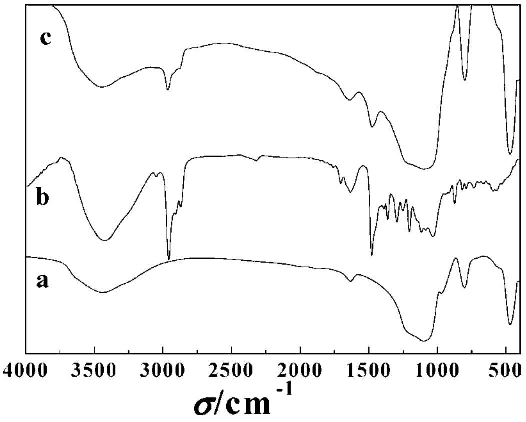


Figure 2. FT-IR spectra of (a) activated silica gel, (b) *p-tert*-butyl-calix[8]arene, and (c) C8ABS.

Instrument. FTIR spectra for the different samples were recorded on a Bruker TENSOR 27 FTIR spectrometer operated at a resolution of 4 cm^{-1}. Carefully weighed quantities of the different samples were subjected to thermogravimetry (TGA) on a STA409PC (NETZSCH) TGA instrument at a heating rate of 10 $°C \cdot min^{-1}$. Elemental analysis for the adsorbents was measured by using a SERIES Π 2400 (PerkinElmer) elemental analyzer. The morphology and size of the adsorbents were investigated by a Philips XL-30ESEM scanning electron microscope (SEM) instrument operated at an accelerating voltage of 20 kV. The UV−vis spectra were recorded on a UV-2550 (Shimazu, Japan) double-beam spectrophotometer equipped with a stoppered quartz cell with a 1.0 cm optical path length. Adsorption experiments were completed on a laboratory shaker HZ-9211K (Jiangsu, China).

Preparation of Adsorbent. The adsorbents of C*n*ABS were synthesized by the methods reported in the literature.[19−21] The preparation scheme of C*n*ABS is shown in Figure 1(B). The procedure is described briefly as follows: a mixture of 3-glycidoxypropyltrimethoxysilane and activated silica gel in dry toluene was stirred and heated at reflux under dry nitrogen gas with triethylamine as a catalyst for 6 h. 3-Glycidoxypropyl-bonded silica gel (GBS) was prepared. Subsequently, GBS and a small amount of the catalyst were added to the mixture of *p-tert*-butyl-calix[*n*]arene and NaH in dry toluene and refluxed under an inert atmosphere for 24 h. The mixture was filtered, washed, and dried, and the adsorbents (C*n*ABS) were obtained, which were characterized by FTIR, TGA, elemental analysis, and SEM.

Adsorption Experiment. To research the adsorption kinetic behavior of methylene blue onto C*n*ABS, batch adsorption experiments were done by agitating 50 mL of dye solution (20 $mg \cdot L^{-1}$, pH = 8) with fresh C*n*ABS (200 mg) in glass bottles using a laboratory shaker at 180 rpm and room temperature, (25 ± 1) °C. At different adsorption times, the dye solution was separated from the adsorbent by centrifugation at 8000 rpm for 5 min. The adsorption amount of methylene blue onto C*n*ABS at different adsorption times was estimated by monitoring the residual methylene blue in the solution at a wavelength of maximum absorption (663 nm) by using a UV−vis spectrophotometer. The equilibrium adsorption amount of C*n*ABS, q_e ($mg \cdot g^{-1}$), was calculated using the following relationship[22,23]

$$q_e = \frac{(c_0 - c_e)V}{W} \tag{1}$$

where c_0 was the initial concentration of methylene blue ($mg \cdot L^{-1}$), c_e the equilibrium concentration of dye ($mg \cdot L^{-1}$), V the volume of the solution (L), and W the mass of the C*n*ABS (g).

Adsorption isotherms were obtained by using a batch equilibration technique at different temperatures.

Results and Discussion

Characterization of Adsorbents. Because the structures of the three adsorbents were similar, the characterization results of C8ABS are only presented. The FTIR spectra of activated silica gel, *p-tert*-butyl-calix[8]arene, and C8ABS were measured by FTIR spectrometry with a KBr film and are shown in Figure 2. Figure 2(a) shows the FTIR spectrum of activated silica gel. The band observed at 3445 cm^{-1} was assigned to a −OH stretching vibration. The band observed at 1082 cm^{-1} was assigned to the asymmetrical stretching vibration of the silicon-oxy tetrahedron. The symmetrical stretching vibration and bending vibration of Si−O were 801 cm^{-1} and 468 cm^{-1}, respectively. For *p-tert*-butyl-calix[8]arene, the characteristic vibration peaks of OH at 3435 cm^{-1}, $-C(CH_3)_3$ stretching vibration at 2957 cm^{-1}, and phenyl plane bending vibrations at (1628 and 1474) cm^{-1} are clearly observed in Figure 2(b). In Figure 2(c), the band observed at 2957 cm^{-1} was assigned to the *p-tert*-butyl stretching vibration, which indicated that *p-tert*-butyl-calix[8]arene was immobilized on the surface of the activated silica gel.

TGA measurements of purified powders of activated silica gel, *p-tert*-butyl-calix[8]arene, and C8ABS were carried out from room temperature to 800 °C, and the data are shown in Figure 3. The weight loss of activated silica gel (curve a) was about 6 %, which was attributed to loss of water in the temperature interval of room temperature to 120 °C. Two main steps on thermal degradation curves for *p-tert*-butyl-calix[8]arene are shown in Figure 3(b). The first step ranging from (366 to 410) °C was assigned to the loss of the functional group of *p-tert*-butyl in calixarene. The weight loss was about 38 %, which was similar to the theoretic value. The second step ranging from (410 to 530) °C was attributed

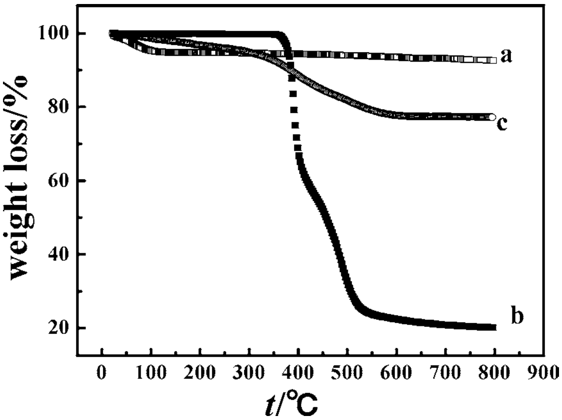


Figure 3. TG curves of (a) activated silica gel, (b) *p-tert*-butyl-calix[8]arene, and (c) C8ABS.

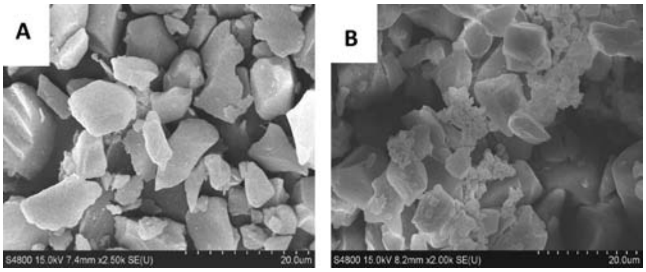


Figure 4. SEM micrograph of (A) activated silica gel and (B) C8ABS.

to the breakage of the ring of the calix[8]arene. The C8ABS (curve c) mainly displayed two weight losses in the temperature intervals of room temperature to 320 °C (6 % weight loss) and (320 to 570) °C (17 % weight loss). For C8ABS, the first step of weight loss was attributed to loss of water and desorption of *p-tert*-butyl-calix[8]arene from the solid, and on the basis of the result of curve b, the second step of weight loss was attributed to the decomposition of *p-tert*-butyl-calix[8]arene. The results of elemental analysis further confirmed the immobilization of *p-tert*-butyl-calix[8]arene on activated silica gel. Elemental analysis for GBS: C, 8.3 %, H, 1.4 %. The ratio of C:H was very close to the theoretical value of GBS. Elemental analysis for C8ABS: C, 15.3 %, H, 1.8 %. The ratio of C:H was also very close to the theoretical value of C8ABS. The results indicated that the *p-tert*-butyl-calix[8]arene was successfully immobilized to the silica gel. The bonded amount of *p-tert*-butyl-calix[8]arene onto silica gel was about 0.4 $\text{mmol}\cdot\text{g}^{-1}$. Figure 4 shows the SEM micrograph of activated silica gel (A) and C8ABS (B). It was clear that the morphology of activated silica gel was no change after *p-tert*-butyl-calix[8]arene immobilized on the surface of the carrier.

Influence of pH on the Adsorption Quantity. The value of pH is known as one of the most important factors affecting the adsorption quantity of adsorbents. Figure 5 shows the influence of the initial solution pH on the adsorption quantity of methylene blue onto C*n*ABS. From Figure 5, the adsorption quantity of methylene blue onto C*n*ABS increased with pH, while the value of pH changed from 2 to 10. Slight increases in the adsorption quantity are shown in Figure 5 at low acidity. There were significant changes in the adsorption quantity at high values of pH. Several investigations reported that the adsorption quantity of basic dyes usually increased as the pH increased.[24,25] Basically, at lower values of pH, positively charged surface sites on the adsorbent do not favor the adsorption of dye cations due to electrostatic repulsion. On the contrary, at high pH, OH^- on the surface of the adsorbent favors the adsorption of cationic dye molecules. However, the value of pH of dye solution was regulated to neutral in the application of dye or organic wastewater treatment. In addition, the methylene blue dye solution ranging from (10 to 1000) $\text{mg}\cdot\text{L}^{-1}$ did not precipitate at pH 8.0, as reported elsewhere.[26] Therefore, from the results of experiment and the point of view of application, pH = 8.0 was chosen as the appropriate value of the initial solution.

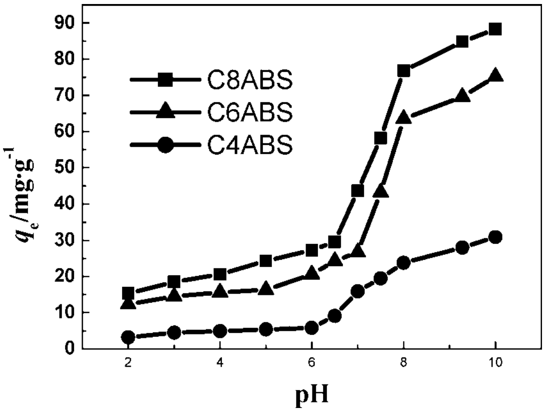


Figure 5. Adsorption quantity of methylene blue onto C*n*ABS at different pH at 25 °C.

Kinetic Behavior of Adsorption. From batch adsorption experiments at different temperatures, the adsorption quantities of methylene blue onto C4ABS, C6ABS, and C8ABS at different adsorption times are shown in Figure 6(A), (C), and (E), respectively. In Figure 6(A), it is clearly shown that the adsorption quantity of methylene blue was increased with the time during the first 60 min, and an adsorption equilibrium was reached after 100 min. When C6ABS was used as the adsorbent, the adsorption quantity of methylene blue increased rapidly with the time during the first 20 min, and an adsorption equilibrium was reached after 60 min (Figure 6(C)). If C8ABS was used, the adsorption reaction reached an equilibrium after only 3 min (Figure 6(E)). Assuming a pseudofirst-order adsorption kinetic model can be used to describe the adsorption of methylene blue onto CnABS,[27] the adsorption quantity of methylene blue at different times can be expressed as follows

$$-\ln(1 - q_t/q_e) = k_s t \qquad (2)$$

where k_s (min^{-1}) is the adsorption rate constant and q_e and q_t ($\text{mg}\cdot\text{g}^{-1}$) are adsorption quantity of dye adsorbed at any time and at equilibrium, respectively. Plots of $-\ln(1 - q_t/q_e)$ versus t at different temperatures are shown in Figure 6(B), (D), and (F). The linearity between $-\ln(1 - q_t/q_e)$ and t shows that the adsorption of methylene blue onto C*n*ABS was a pseudofirst-order reaction. From the slope of the straight lines, the pseudofirst-order rate constant k_s at different temperatures was evaluated and is listed in Table 1. From Table 1, with the increasing of temperature, the adsorption quantity at equilibrium, q_e, and adsorption rate constant, k_s, increased. At the same temperature, the value of the adsorption rate constant increased with the number of phenolic units in the calixarene ring of the adsorbents. When C8ABS was used as the adsorbent, the adsorption rate constant was larger than that of C4ABS or C6ABS, and the adsorption reaction was accomplished in 3 min.

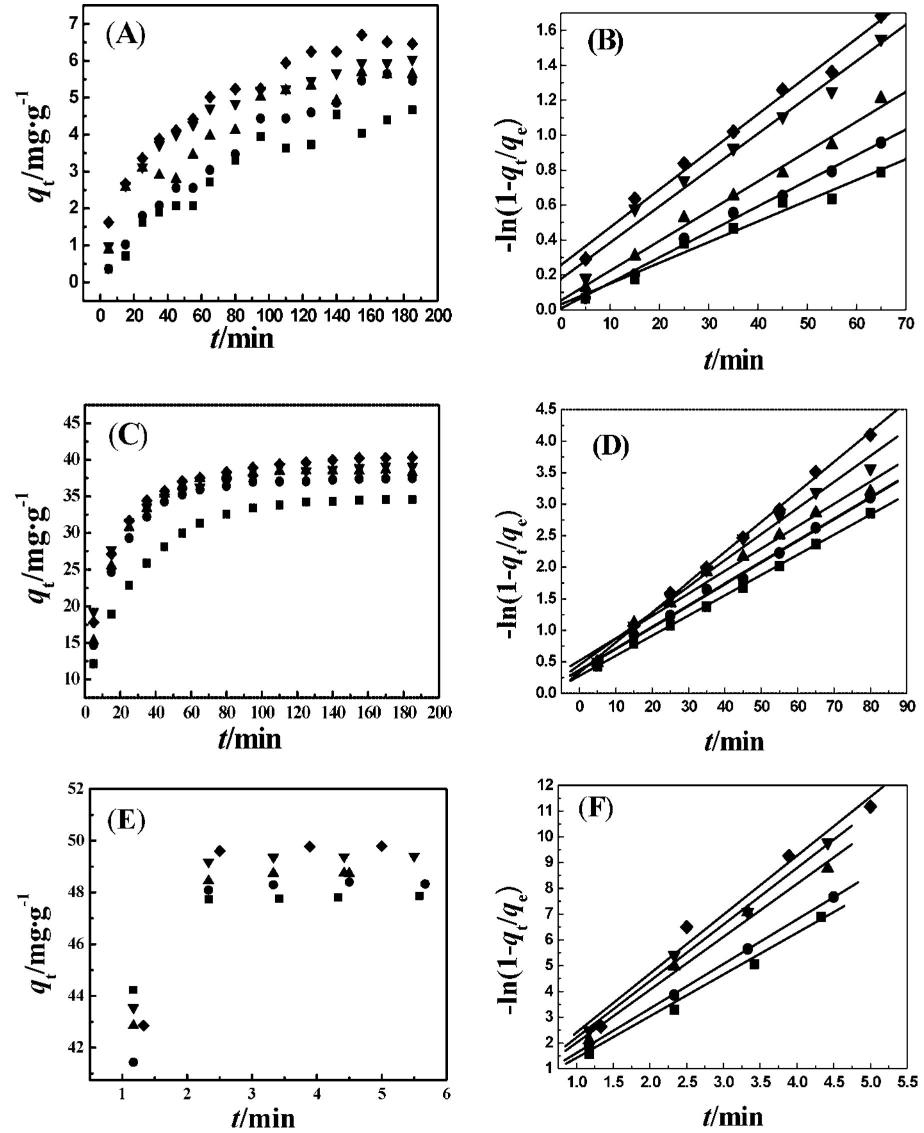


Figure 6. Relationship between q_t and t. (A) C4ABS, (C) C6ABS, and (E) C8ABS. The plot of $-\ln(1 - q_t/q_e)$ versus t. (B) C4ABS, (D) C6ABS, and (F) C8ABS. Temperature/°C: ■ 25; ●, 30; ▲, 35; ▼, 40; ◆, 45.

Table 1. Equilibrium Adsorption Quantity, q_e, the Pseudofirst-Order Rate Constant, k_s, and the Apparent Activation Energy, E_a, at Different Temperature

	C4ABS					C6ABS					C8ABS				
T/K	298	303	308	313	318	298	303	308	313	318	298	303	308	313	318
q_e/mg·g^{-1}	4.4	5.7	5.8	6.2	6.7	34.6	37.5	38.6	39.1	40.3	47.9	48.3	48.7	49.4	49.8
k_s/min^{-1}	0.029	0.032	0.043	0.048	0.054	0.097	0.11	0.12	0.13	0.14	2.05	2.20	2.33	2.40	2.47
E_a/kJ·mol^{-1}			26.5					10.7					7.2		

The relationship of the pseudofirst-order rate constant k_s with temperature T can be described by the Arrhenius equation shown as follows

$$\ln k_s = -\frac{E_a}{RT} + \ln A \tag{3}$$

where R is the gas constant; E_a is the apparent activation energy (kJ·mol^{-1}); and A is the apparent pre-exponential factor. Figure 7 shows the relationship between ln k_s and T^{-1}. The apparent activation energy, E_a, was estimated from the slope of the straight line, and the result is shown in Table 1. With the increase of the value of n in CnABS, the value of E_a decreased, which indicates that the adsorption reaction of methylene blue onto C8ABS was easier than that of C4ABS or C6ABS.

Adsorption Isotherms. The adsorption isotherms of methylene blue onto CnABS at different temperatures are shown in Figures 8(A), (D), and (G). Assuming the adsorption coincided with Langmuir's model,[28,29] the relationship between q_e and c_e can be described as follows

$$\frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{K_L q_m} \tag{4}$$

At equilibrium, c_e (mg·L^{-1}) and q_e (mg·g^{-1}) are the liquid phase concentration and solid phase concentration of adsorbent at equilibrium; q_m (mg·g^{-1}) is the saturation adsorption quantity;

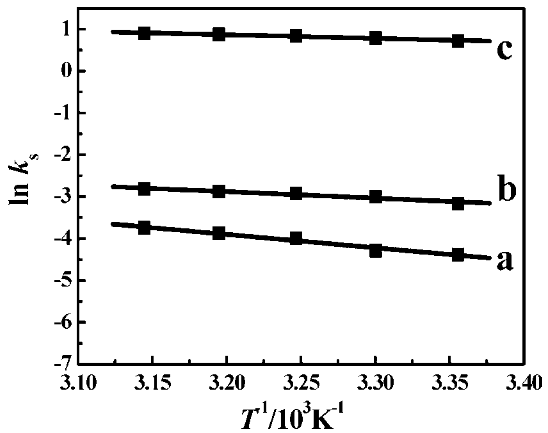


Figure 7. Relationship between ln k_s and T^{-1}. (a) C4ABS, (b) C6ABS, (c) C8ABS.

and K_L (L·mg^{-1}) is the Langmuir adsorption constant. Figures 8(B), (E), and (H) show the relationships between c_e/q_e and c_e at different temperatures. The linear relationship observed implies that adsorption of methylene blue onto C*n*ABS obeyed Langmuir's model. According to the slope and the intercept of the straight lines, q_m and K_L can both be evaluated. Table 2 lists the values of q_m and K_L at different temperatures. From Table 2, both q_m and K_L depend on the temperature. With increasing temperature, the values of q_m and K_L increase gradually, which indicates that the higher the temperature, the more advantageous for the adsorption of methylene blue onto C*n*ABS. Comparing the adsorption capacity of the three adsorbents at the same temperature, the saturation adsorption quantity monotonically increased with the number of phenolic units in the calixarene ring, which indicated that the cavity size of the host played an important role in the adsorption process. The larger the cavity size of calix[8]arene, the larger the formation constant between calix[8]arene and methylene blue was,[30] which resulted in the adsorption capacity of C8ABS being the largest.

For the Langmuir isotherm, the essential characteristics can be expressed in terms of a dimensionless factor called the separation factor (R_L)[31−33]

$$R_L = 1/(1 + K_L c_0) \tag{5}$$

where K_L is the Langmuir constant (L·mg^{-1}) and c_0 is the initial concentration (mg·L^{-1}). The value of R_L indicates the type of the isotherm to be either unfavorable, linear, favorable, or irreversible. If $R_L > 1$, it follows unfavorable adsorption; a value of 1.0 for R_L indicates linear; a value of R_L less than 1.0 indicates favorable; and a value of R_L equal to zero suggests irreversible adsorption. Table 2 shows R_L values between zero and one, which indicates favorable adsorption.

The value of the monolayer saturation quantity demonstrated that the C*n*ABS adsorbent exhibits interesting adsorption properties toward cationic dyes. Compared with some recent

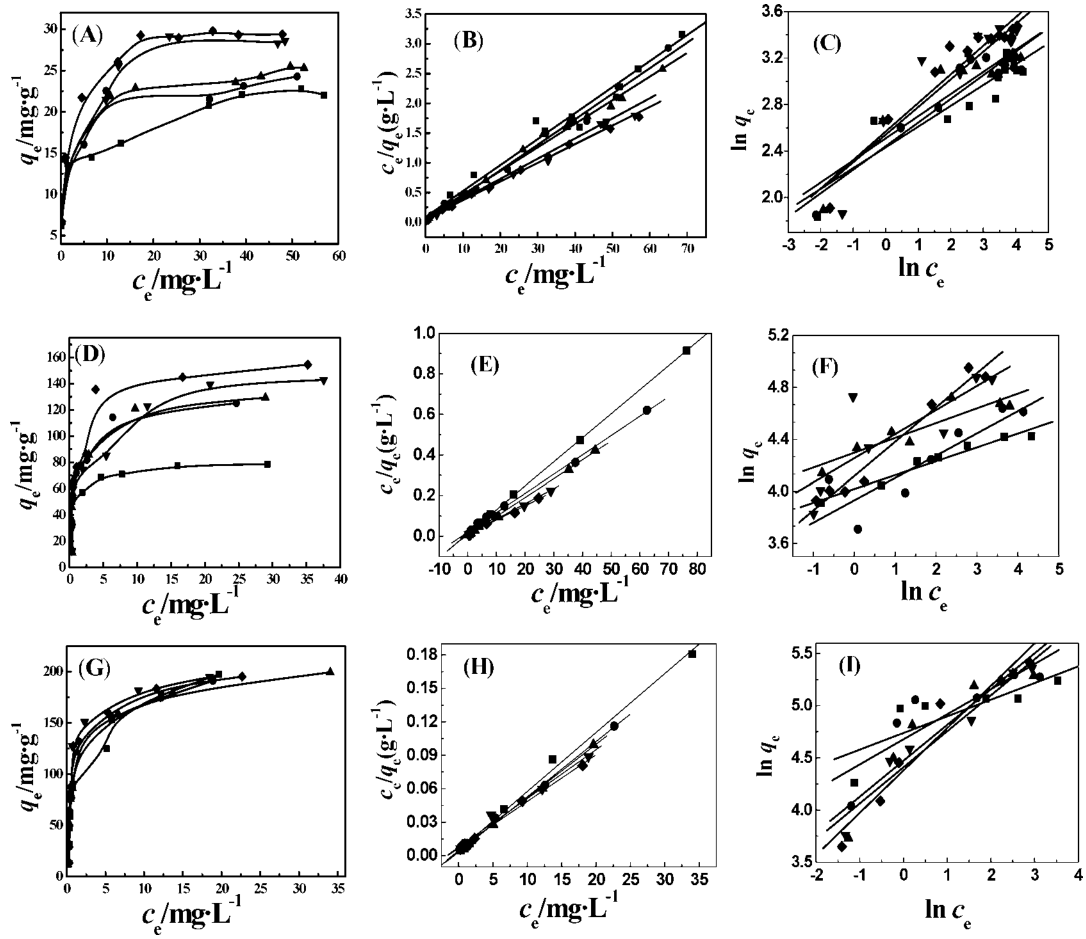


Figure 8. Adsorption isotherm for methylene blue onto C*n*ABS adsorbents. (A) C4ABS, (D) C6ABS, (G) C8ABS. Relationship between c_e/q_e and c_e at different temperatures. (B) C4ABS, (E) C6ABS, (H) C8ABS. Relationship between ln c_e and ln q_e at different temperatures. (C) C4ABS, (F) C6ABS, (I) C8ABS. Temperature/°C: ■, 25; ●, 30; ▲, 35; ▼, 40; ◆, 45.

Table 2. Saturation Adsorption Quantity, q_m, Adsorption Constant, K_L, and the Separation Factor, R_L, for the Langmuir Isotherm at Different Temperatures

	C4ABS					C6ABS					C8ABS				
T/K	298	303	308	313	318	298	303	308	313	318	298	303	308	313	318
q_m/mg·g^{-1}	23	24	26	29	30	87	138	139	151	161	188	196	203	207	209
K_L/L·mg^{-1}	0.50	0.57	0.59	0.66	0.67	0.33	0.42	0.50	0.62	0.68	0.67	0.85	0.93	1.02	1.13
R_L	0.17	0.15	0.14	0.13	0.12	0.24	0.19	0.17	0.14	0.13	0.13	0.11	0.10	0.09	0.08

Table 3. Saturation Adsorption Quantities (q_m/mg·g^{-1}) from the Literature for Methylene Blue Obtained on Nonconventional Low-Cost Adsorbents

adsorbents	q_m/mg·g^{-1}	reference
pinewood	556	Tseng et al., 2003[35]
clay	300	Freundlich, 1906[34]
C8ABS	188	this work
Coir pith	120.43	Choy et al., 1999[36]
sewage sludge	114.94	Otero et al., 2003[37]
C6ABS	87	this work
fly ash	75.52	Janos et al., 2003[38]
CD/CMC	56.5	Crini and Peindy, 2006[5]
silica	56.2	Tsai et al., 2004[39]
yellow passion fruit	44.7	Pavan et al., 2008[40]
hazelnut shell	41.3	Ferrero, 2007[41]
lemon peel	29.0	Kumar and Porkodi, 2006[42]
C4ABS	23	this work
orange peel	20.5	Annadurai et al., 2002[43]
dead biomass	18.54	Namasivayam et al., 2001[44]
date pits	17.3	Annadurai et al., 2002[43]
silica	11.21	Kannan and Sundaram, 2001[45]
rice husk	9.89	Sharma and Uma, 2010[46]
orange peel	5.87	Kavitha and Namasivayam, 2007[47]
marine seaweed	5.23	Cengiz and Cavas, 2008[48]
sawdust	4.89	Pekkuz et al., 2008[49]

Table 5. Thermodynamic Parameters for Adsorption of Methylene Blue on CnABS at 298.15 K

	C4ABS	C6ABS	C8ABS
ΔH^Θ/kJ·mol^{-1}	11.7	19.5	25.5
ΔS^Θ/J·K^{-1}·mol^{-1}	83.1	111.8	146.0
ΔG^Θ/kJ·mol^{-1}	−13.1	−13.8	−15.0

data in the literature (Table 3), the results also revealed the potential of the C*n*ABS material, especially C8ABS, to be an effective adsorbent for removing basic dyes.

It is well-known that the Freundlich isotherm is one of the earliest known relationships for describing adsorption.[34] This isotherm is an empirical equation employed to describe heterogeneous systems and is expressed by the following equation

$$\ln q_e = \ln K_F + \frac{1}{n}\ln c_e \tag{6}$$

where q_e is the equilibrium dye concentration onto the adsorbent (mg·g^{-1}); c_e is the equilibrium dye concentration in solution (mg·L^{-1}); K_F is the Freundlich constant; and $1/n$ is the heterogeneity factor. A plot of ln q_e versus ln c_e is shown in Figures 8(C), (F), and (I). Table 4 lists the values of K_F, n, and R^2 at different temperatures for the Freundlich isotherm. From the value of R^2, the linear relationship did not fit well for the adsorption system under the concentration range studied. Apparently, this plot demonstrated that equilibrium adsorption data of methylene blue were not described by the Freundlich isotherm.

Thermodynamics Parameters of Adsorption. To elucidate the thermodynamic origins of the adsorption reaction of methylene blue onto C*n*ABS, the thermodynamic parameters for the adsorption reaction were determined through a van't Hoff analysis. The relationship of the Langmuir adsorption constant K_L with temperature T can be described by the van't Hoff equation shown as follows

$$\ln K_L = -\frac{\Delta H^\Theta}{RT} + \frac{\Delta S^\Theta}{R} \tag{7}$$

where R is the gas constant; ΔH^Θ is the enthalpy change; and ΔS^Θ is the entropy change. ΔH^Θ (kJ·mol^{-1}) and ΔS^Θ (J·mol^{-1}·K^{-1}) were calculated from the slope and intercept of linear plots of ln K_L vs T^{-1} (the plots are not shown).

The Gibbs energy change, ΔG^Θ, was estimated from the following relationship

$$\Delta G^\Theta = \Delta H^\Theta - T\Delta S^\Theta \tag{8}$$

The thermodynamic parameters determined are shown in Table 5. It is interesting that the positive enthalpic changes of methylene blue onto C*n*ABS (Table 5) suggest an endothermic nature of adsorption. Generally speaking, it was expected that adsorption processes (either from gas or liquid phase) were exothermic due to the heat released after bond formation between solute and adsorbents, and the adsorption quantity always decreased with increasing temperature.[50−52] However, the endothermic adsorption of methylene blue on C*n*ABS appears to be an uncommon behavior. In this case, the positive enthalpic change of methylene blue onto C*n*ABS was attributed to a special adsorption mechanism. In the actual adsorption process, the release of high-energy water molecules from the cavity upon complexation leads to the endothermic reaction.[53] The adsorption of methylene blue onto C*n*ABS was an exothermic reaction. The heat of desorption of high-energy water molecules from the cavity of calixarene was larger than the heat of adsorption of methylene blue onto C*n*ABS. Therefore, the whole adsorption process was an endothermic reaction. This was also supported by the increase in the value of the adsorption capacity of all the adsorbents with a rise in temperature. On the other hand, the value of the entropy change (ΔS^Θ) was positive for methylene blue adsorption onto C*n*ABS. The adsorption of

Table 4. Adsorption Constants K_F and n and the Coefficients of Determination for the Freundlich Isotherm at Different Temperatures

	C4ABS					C6ABS					C8ABS				
T/K	298	303	308	313	318	298	303	308	313	318	298	303	308	313	318
K_F	11.4	11.5	12.3	12.7	13.4	56.3	51.2	73.4	71.8	62.2	112.6	107.6	88.2	80.0	82.5
n	0.18	0.20	0.19	0.24	0.25	0.11	0.17	0.11	0.19	0.26	0.16	0.24	0.34	0.35	0.45
R^2	0.787	0.891	0.865	0.799	0.910	0.854	0.765	0.841	0.660	0.868	0.669	0.741	0.863	0.946	0.935

methylene blue dye molecules on C*n*ABS was entirely driven by the entropic increase (Table 5). This was the typical case driven by the classical hydrophobic interaction in the inclusion complexation. The hydrophobic interaction seemed to be the main binding contribution in the calixarene—methylene blue complexation system. A reasonable explanation was the release of high-energy water molecules from the cavity upon complexation and the desolvation of methylene blue dye molecules.

Conclusions

New-style adsorbents of *p-tert*-butyl-calix[4,6,8]arene-bonded silica gel—C*n*ABS (C4ABS, C6ABS, and C8ABS)—were synthesized successfully. The adsorption of methylene blue onto C4ABS, C6ABS, and C8ABS fit a first-order kinetic model, and the apparent adsorption rate constants were (0.029, 0.097, and 2.05) min^{-1} at 25 °C, respectively. The adsorption behavior of methylene blue onto C*n*ABS obeyed Langmuir's model. The order of the saturation adsorption quantity at 25 °C was consistent with the size of the calixarene ring, i.e., C4ABS < C6ABS < C8ABS. The thermodynamic parameters for the adsorption reaction were calculated through a van't Hoff analysis. The adsorption of methylene blue dye molecules on C*n*ABS was entirely driven by the entropic increase, which was due to the release of high-energy water molecules from the cavity upon complexation and the desolvation of methylene blue dye molecules. Because the adsorption reaction was an endothermic process, a higher temperature was advantageous for the adsorption of methylene blue onto adsorbents. The new-style adsorbent of CnABS can be regarded as a potential adsorbent for the application in dye or organic wastewater treatment.

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