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Organic dye adsorption on mesoporous hybrid gels

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Abstract

Adsorption of two organic dyes (alizarin red S and phenol red) on mesoporous silica and hybrid gels is investigated. The mesoporous gels are derived from tetraethoxysilane (TEOS), methyltriethoxysilane (MTES), vinyltriethoxysilane (VTES), propyltriethoxysilane (PTES), and phenyltriethoxysilane (PhTES). The experimental results demonstrate that the adsorption capacity of the hybrid gels is much higher than that of the pure silica gel and increases as the gel surface becomes more hydrophobic. This suggests that the organic dye adsorption is governed mainly by the hydrophobic interaction between the organic dyes and the gel surface. Langmuir and Toth isotherm models are also tested against the experimental isotherm data.

Keywords: Adsorption; Organic dye; Mesoporous; Hybrid gel; Adsorption isotherm; Hydrophobic interaction

1. Introduction

Adsorption is one of the most widely used processes in industrial physicochemical operations such as separation and heterogeneous catalysis. An adsorbent with high adsorption capacity and good selectivity is very critical in adsorptive separation. Functionalized mesoporous oxides have been used as effective adsorbents [1–9] because of their high surface area and the functionalized pore channels of large diameter. The high surface area allows the binding of a large number of surface groups and the functionalized pore channels of large diameter allow an easy reaction with adsorbates.

The grafting of the functional groups to the pore walls of the mesoporous adsorbents can be fulfilled by the reaction between the hydrolyzable moieties and the surface silanol groups of the mesostructures. Although this method has been used for a design of new adsorbents and catalysts, it has two major shortcomings: (1) it is difficult to control the loading of the functional groups; (2) during surface modification or grafting unwanted polycondensation by-products can be easily formed. Direct incorporation of functional groups onto mesoporous silica adsorbents is an alternate route for the preparation of such materials, in which the templates could be removed by solvent extraction without damaging the silica frameworks. Unlike the grafting process, direct incorporation allows the functionalized mesoporous adsorbents to retain high surface area and pore volume, to have a uniform functional group distribution inside the pore channels, and to avoid the local clustering of the functional groups and the necking of the pore channels.

In order to describe the adsorption thermodynamics, and to predict and design the adsorption process, it is important to find suitable isotherm models of the experimental adsorption data. To date, the choice of an adsorption isotherm model for the adsorption in aqueous solutions has been reported mainly for the adsorption of activated carbons and their similar adsorbents [10–12]. Although the functionalized mesoporous oxides have been used for the adsorption of proteins [1], cytochrome c [2], nonylphenol [3], 4-chlorophenol [4], Taxol [5], heavy metal ions [6–8], and anions [9], little work has been done to study the adsorption mechanisms of these mesoporous adsorbents and to describe the adsorption of these adsorbents using different adsorption isotherm models. In this work, various organic groups such as methyl, vinyl, propyl, and phenyl groups are incorporated into mesoporous silica gels through a direct incorporation method. These mesoporous gels are used in adsorption of two different organic dyes in aqueous solutions to investigate the effect of different organic groups on adsorption. Two isotherm models are also used to describe the adsorption behaviors.

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Table 1
Compositions of the sols

No.	TEOS (ml)	MTES (ml)	VTES (ml)	PTES (ml)	PhTES (ml)	Ethanol (ml)	Water (ml)	HCl[a] (ml)	CTAB (g)	Ammonia[b] (ml)
1	88	0	0	0	0	300	22.4	3.2	7.2	2.4
2	69	16	0	0	0	300	22.4	3.2	7.2	2.4
3	69	0	16	0	0	300	22.4	3.2	7.2	2.4
4	69	0	0	18	0	300	22.4	3.2	7.2	2.4
5	69	0	0	0	19	300	22.4	3.2	7.2	2.4

The molar ratio was (TEOS + organosilane):water:ethanol:CTAB:HCl:NH_3 = 1:4:13:0.05:8 × 10^{-5} : 6 × 10^{-3} with TEOS : organosilane = 4 : 1.

[a] The concentration of HCl was 0.01 M.

[b] The concentration of ammonia was 1.0 M.

2. Experimental

2.1. Gel preparation and characterization

The gels were prepared through a two-step sol–gel process. TEOS, or TEOS and organosilane (MTES, VTES, PTES, or PhTES) (Aldrich), ethanol, H_2O, HCl and CTAB (Avocado) were mixed and stirred to get transparent sols. The sols were hydrolyzed in covered beakers for 3 days at room temperature before ammonia was added. After gelation, the gels were dried for 7 days at room temperature, followed by extraction with 200 ml of 2 M HCl in water/ethanol solution (the volume ratio between water and ethanol was 1:5) for three times at ca. 60 °C. The gels were then repeatedly soaked with water until the pH of the water after soaking was higher than 6. The soaked gels were dried at room temperature for 24 h, and finally dried at 50 °C for 2 days. The sol compositions and the final products are listed in Tables 1 and 2. BET surface area and pore size were determined by the Micromeritics ASAP 2010 apparatus using N_2 as a medium (Table 2).

2.2. Adsorption studies

Organic dyes, i.e. alizarin red S (ARS) and phenol red (PR) were used for the adsorption experiments. An amount of 0.10 g of gel was equilibrated with 10 ml dye solution at a desired concentration and 25 °C for 6 days. Initial solution pH was fixed at 2 with dilute HCl solution, and ionic strength of the solution was maintained at 0.25 M KNO_3. Dye concentration change was recorded on a UV-160A Shimadzu UV–vis spectrophotometer by measuring the solution absorbance at maximum absorption in suitable solutions: ARS at 420 nm in pH 2 solution; PR at 558 nm in pH 12 solution [13]. The amount of dye adsorbed onto the gels (q, in micromoles per kilogram of gel) was calculated by a mass balance relationship:

$$q = \frac{V(C_0 - C)}{W} \tag{1}$$

where C_0 and C are the dye concentrations (mmol L^{-1}) in solution before and after adsorption, and V and W are solution volume (L) and gel weight (kg).

3. Isotherm models

When the rate of adsorption is equal to the rate of desorption, adsorption reaches an equilibrium at which the adsorbate concentration in solutions remains constant. Adsorption isotherms can be obtained by plotting solid phase concentration against liquid phase concentration. For the adsorption onto liquid/solid interface, adsorption mechanisms are so complicated that no simple theory can adequately represent all experimental data. Thus, most of the isotherm models used to describe adsorption in solution are based on the empirical equations. In this paper, we choose the commonly used Langmuir and Toth isotherm models to treat our experimental isotherms.

3.1. Langmuir isotherm

The assumptions of the Langmuir isotherm are: (1) adsorption energy is constant over all sites; (2) adsorbed atoms or molecules are adsorbed at definite, localized sites; (3) each site can accommodate only one molecule or atom; (4) there is no interaction between adsorbates. At adsorption equilibrium, a saturation point is reached at which no further

Table 2
Textural properties of the final products

No.	Final products	BET surface area (m^2/g^{-1})	Average BJH adsorption pore size (nm)
1	TEOS gel	504	2.71
2	MTES/TEOS hybrid gel	671	2.63
3	VTES/TEOS hybrid gel	592	2.57
4	PTES/TEOS hybrid gel	580	3.01
5	PhTES/TEOS hybrid gel	47	2.79

Table 3
Adsorption isotherm constants and AREs

		Langmuir				Toth			
		K_L (mmol L^{-1})	a_L (mmol kg^{-1})	$a_L{}'$ ($\times 10^{-5}$ mmol/m^{-2})	ARE (%)	K_T	a_T	t	ARE (%)
Gel 1	ARS	6.57 ± 4.06	1.54 ± 0.43	0.31 ± 0.09	18.46	0.64	13.21	0.24	14.23
	PR	10.19 ± 1.58	16.21 ± 1.21	3.22 ± 0.24	11.98	0.17	19.65	0.79	9.74
Gel 2	ARS	4.97 ± 1.57	79.45 ± 6.99	11.84 ± 1.77	8.45	0.39	139.4	0.45	8.51
	PR	0.93 ± 0.18	105.1 ± 9.4	15.66 ± 2.33	4.68	1.07	98.64	1.10	4.58
Gel 3	ARS	1.32 ± 0.57	124.8 ± 25.6	21.08 ± 3.56	20.15	0.80	231.7	0.49	11.10
	PR	1.10 ± 0.33	75.12 ± 10.65	12.69 ± 2.14	7.97	0.81	67.91	1.08	5.66
Gel 4	ARS	2.18 ± 0.42	181.8 ± 13.4	31.34 ± 5.40	9.05	0.29	143.6	2.01	6.17
	PR	2.59 ± 0.79	122.3 ± 14.3	21.1 ± 3.6	10.04	0.45	140.9	0.80	9.82
Gel 5	ARS	9.06 ± 4.01	120.3 ± 14.5	256.0 ± 30.1	16.37	0.24	227.7	0.30	10.45
	PR	0.60 ± 0.17	89.72 ± 14.61	190.9 ± 31.1	9.74	1.67	52.19	2.42	8.13

adsorption can occur. Thus, the Langmuir isotherm reaches a plateau at the saturation point. The Langmuir isotherm can be represented by:

$$q = \frac{K_L a_L C}{1 + K_L C} \tag{2}$$

where a_L is the adsorption capacity and K_L the adsorption intensity or Langmuir coefficient. q and C are the equilibrium concentration of dye in adsorbent (mmol kg^{-1}) and in solution (mmol L^{-1}), respectively. The Langmuir equation is suitable for homogeneous adsorption and follows Henry's law at low concentrations [10].

3.2. Toth isotherm

For Toth isotherm a quasi-Gaussian energy distribution is assumed, and most sites are considered to have an adsorption energy lower than the maximum adsorption energy. The Toth isotherm is applicable for heterogeneous and multiplayer adsorption [14]. It is expressed as:

$$q = \frac{a_T C}{(K_T + C^t)^{1/t}} \tag{3}$$

where K_T and a_T are constants, and t is Toth isotherm exponent.

3.3. Data fitting and error evaluation

Nonlinear least square optimization technique has been applied to determine isotherm parameters. The average relative error (ARE) was used as a criterion for the quality of fitting:

$$\mathrm{ARE} = \frac{\sum |q - q_{\mathrm{cal}}| / q}{N} \times 100 \tag{4}$$

4. Results and discussion

For determination of the adsorption isotherms, the initial pH of the solutions is set to 2 because adsorption of ARS and PR on the similar gels is relatively high at this pH [13]. The experimental isotherm data and the isotherms predicted by the two isotherm models are shown in Fig. 1 and the corresponding isotherm constants and the AREs are listed in Table 3. To compare the quality of the fitting, the total average AREs and the average AREs based on the gel type are calculated in Table 4.

4.1. Effect of organosilane precursors on the adsorption

Use of different organosilane precursors changes the surface properties of the gels. The experimental results show that the adsorbed amount of dyes on the hybrid gels (Gels 2–5) is much higher than that on the pure silica gel (Gel 1).

Adsorption capacity of the gels is expected to increase as the gel surface becomes more hydrophobic. This is confirmed by the experimental results in which the adsorption capacity (a_L in Table 3) generally increases in the order of increasing hydrophobicity. However, the effect of organosilane precursors on the adsorption presents a complicated situation: although the mesoporous hybrid gel with phenyl group (Gel 5) may have the strongest hydrophobic interaction with the organic dyes, it does not show the highest adsorption capacity. This may be caused by its low surface area (Table 2)[1]. To account for the low surface area of the Gel 5, the adsorption capacity per unit surface area is calculated in Table 3 ($a_L{}'$), which confirms that the adsorption capacity increases as the surface becomes more hydrophobic.

4.2. Adsorption isotherm models

Fig. 1 demonstrates that both the Langmuir and Toth models describe the experimental isotherms reasonably well. A comparison of ARE values, though, suggests that the Toth

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[1] The quadrupole–quadrupole interaction between N_2 and phenyl groups on the surface of the Gel 5 may be responsible for the low surface area since it is known to interfere with the textural property determination using N_2 sorption method [15,16].

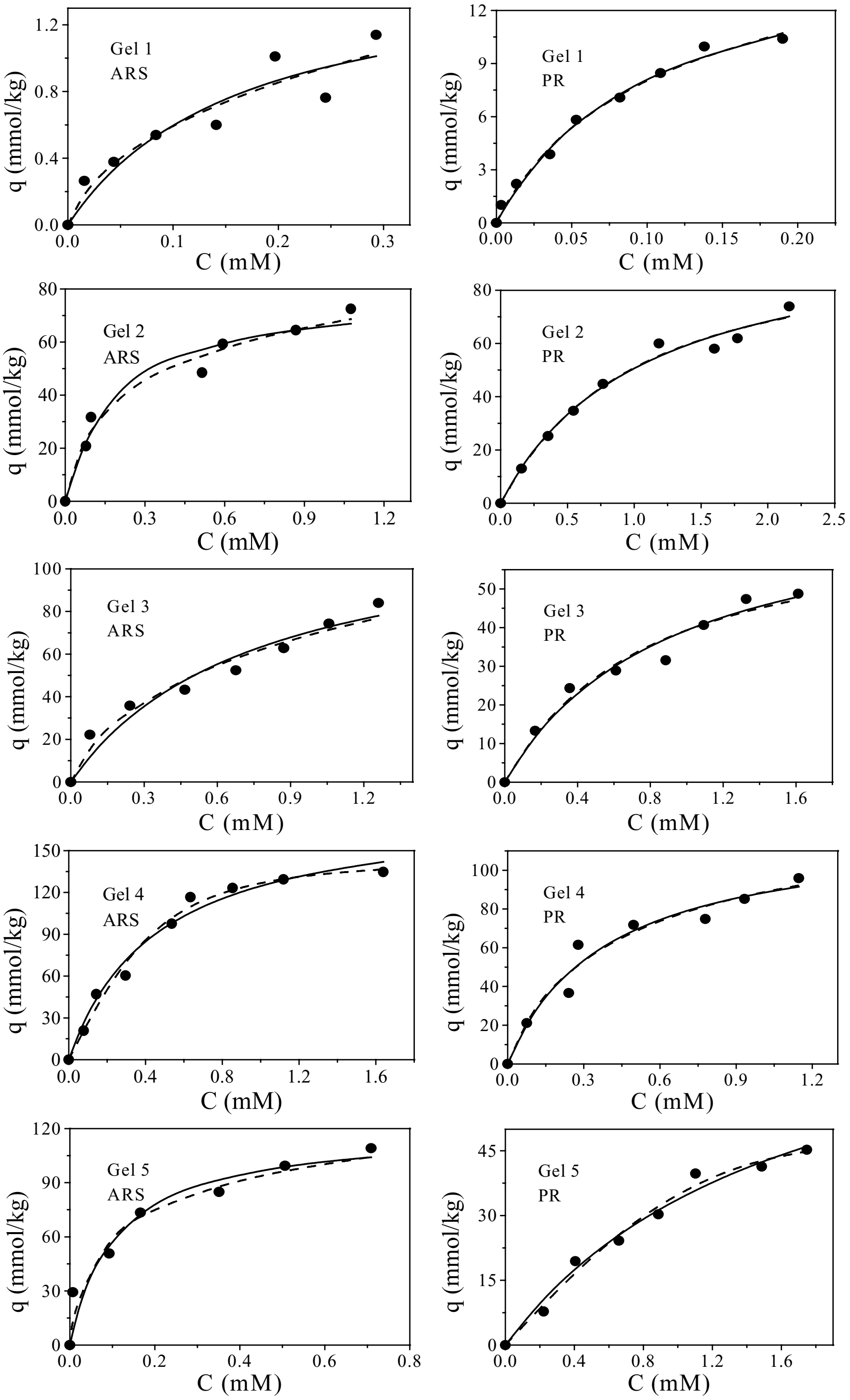

Fig. 1. Plots of the adsorption isotherms from experiments and models: (—) Langmuir isotherm; (- - -) Toth isotherm.

Table 4
A comparison of AREs

Isotherm	Total averageAREs (%)	Average AREs based on the gel type (%)				
		Gel 1	Gel 2	Gel 3	Gel 4	Gel 5
Langmuir	11.69	15.22	6.57	14.06	9.54	13.05
Toth	8.84	11.98	6.54	8.38	7.99	9.29

model describes the experimental data better than the Langmuir model (i.e. the AREs for the Toth model are lower than those for the Langmuir model in Tables 3 and 4). This is consistent with the adsorption of yellow and red dyes onto granular activated carbon, where the Toth isotherm was also found to best fit the adsorption data [11].

The role of heterogeneous surfaces has been an important topic of research in understanding the effect of heterogeneities on adsorption, either energetic heterogeneities or those derived from rough surface morphologies [17]. Furthermore, surface heterogeneities exert an important influence on many other physical and chemical processes, such as diffusion and reaction kinetics [18]. The Toth isotherm that considers the surface heterogeneity fits the experimental results better than the Langmuir isotherm that is based on homogeneous surface. The Toth isotherm also gives better fits for hybrid gels (Gels 2–5) than those for pure silica gel (Gel 1). The fitting results may provide insights on the heterogeneity of the gel surface.

The results from the adsorption models, however, must be taken with caution since most of the adsorption models are based on empirical equations and lack sufficient details to account for the complex nature of surface phenomena during adsorption in solution.

4.3. Adsorption mechanisms

Adsorption from solutions is a competitive process where equilibrium is determined by many factors resulting from adsorbent, adsorbate, and solvent properties. The porous structure of a solid, its energetic heterogeneity, and surface chemical properties (functional groups, surface charge, hydrophilic and hydrophobic nature) are the main factors influencing adsorption equilibria [19]. For a given adsorbent, the adsorption of different adsorbates is a function of solubility, polarity, structure, mass, and size of the molecules. The hydrophilic and hydrophobic nature of the adsorbates is also important for adsorption in aqueous solutions.

In the adsorption of ARS and PR, increasing the pore size was shown to enhance the adsorption of the dyes [13]. Since all the gels used in this study have similar average mesopore size (Table 2), it is reasonable to assume that pore size effect is negligible in adsorption compared to the interaction between the dye and the gel surface. There can be three types of interactions responsible for the dye adsorption: (1) electrostatic attraction; (2) hydrophobic interaction; (3) hydrogen bonding. The adsorption of ARS and PR on PTES/TEOS hybrid gel is schematically demonstrated in Fig. 2.

Usually there exist silanol groups on the silica gel surface. Gels prepared by two-step method have more silanol groups on their surface than the gels prepared by acid-catalyzed single-step method [20]. In aqueous solutions, the silanol groups on the gel surface can be protonated or deprotonated depending on the solution pH, which results in the corresponding changes of the silica surface charge. In the experimental conditions used in this study (pH ∼ 2), the silanol groups on the gel surface are protonated and the gel surface is positively charged. Thus, there is an electrostatic attraction between the dye anions and the gel surface. In the adsorption of ARS and PR on the silica and hybrid gels, increase in pH was found to decrease the adsorption capacity due to the electrostatic repulsion between the dyes and the gel surface [13].

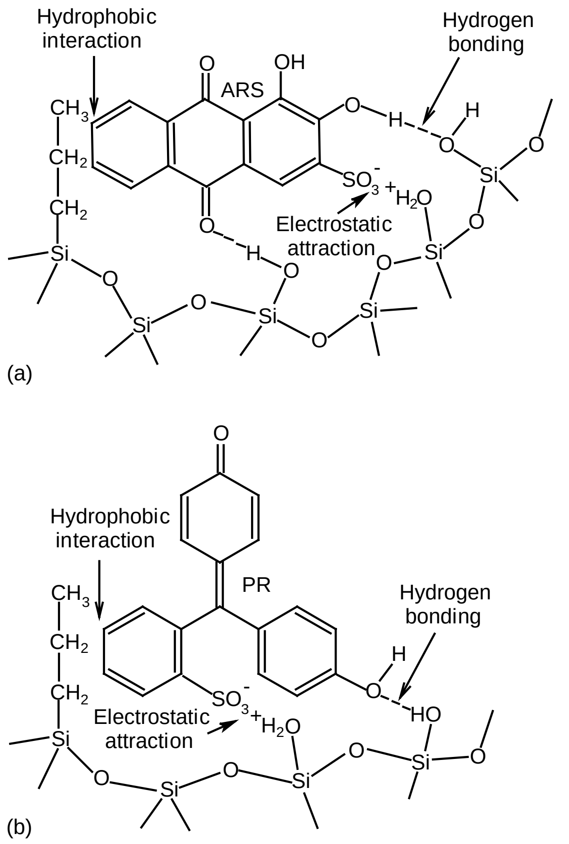

Fig. 2. Schematic diagrams for the adsorption of (a) ARS and (b) PR on the mesoporous PTES/TEOS hybrid gel in aqueous solution at pH 2.

In aqueous solutions, nonpolar molecules or groups have a tendency to associate. This tendency, governed mainly by entropy, is called hydrophobic interaction [21]. The adsorption capacity of the organic dyes on the hybrid gels (Gels 2–5) is much higher than that on the pure silica gel (Gel 1), suggesting that the hydrophobic interaction between the surface organic groups and the organic dyes plays an important role in adsorption.

For adsorption in aqueous solutions, hydrogen bonding is a more common interaction between the adsorbate and the adsorbent. As can be seen from Fig. 2, there is a hydrogen bonding between the organic dyes and the gel surface.

Pure silica gel (Gel 1) is expected to have the stronger hydrogen bonding and electrostatic interaction than the other gels because it should have more surface silanol groups. Thus, in the absence of hydrophobic interaction, the pure silica gel is expected to exhibit a maximum adsorption capacity. However, the experimental results demonstrate that the adsorption capacity is much higher for the hybrid gels (Gels

2–5) and generally increases as the gel surface becomes more hydrophobic. This suggests that the hydrophobic interaction plays a dominant role on adsorption capacity under the experimental conditions used in this study. This is consistent with the adsorption of ethyl(hydroxyethyl)cellulose onto silica surfaces of different hydrophobicity in which main driving force was also suggested to be hydrophobic attraction [22,23].

5. Summary

The equilibrium adsorption of alizarin red S and phenol red on the mesoporous silica and hybrid gels has been studied. The adsorption capacity of the hybrid gels is much higher than that of the pure silica gel and generally increases as the gel surface becomes more hydrophobic. This suggests that hydrophobic interaction between organic dyes and the organic groups on the hybrid gel surface plays a dominant role in the adsorption of the organic dyes. Two different adsorption isotherm models (Langmuir and Toth isotherm models) are also tested against the experimental data to show that both models can describe the experimental isotherms reasonably well.

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