

Elimination of Surfactants and Small Dyes from Water with Silica-supported Dendritic Amphiphiles

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Abstract Silica-supported branched polyethylenimine (Sil@PEI) is a conventional adsorbent and shows a limited affinity to anionic surfactants and small dyes ($K = 10^6$ – 10^7 L/mol). If the PEI is alkylated with cetyl groups (C16), the K of the resulting adsorbents (Sil@PEI@C16- x , where x is the fraction of PEI units being alkylated) is significantly improved. Optimization shows that Sil@PEI@C16-0.15 can best reduce aqueous surfactants to a residue around 10^{-10} mol/L; while Sil@PEI@C16-0.6 can reduce even small aqueous dyes to a residue below 10^{-10} mol/L, nearly 10^5 -fold lower than that by Sil@PEI. The adsorbents are well recyclable. It is believed that in the case of dyes, the dense cetyl shell can isolate the PEI from the bulky water and thus suppress the competitive binding by water; while in the case of surfactants, the semiclosed cetyl shell can simultaneously meet electrostatic complement and hydrophobic complement to the surfactants.

Keywords: Dendritic amphiphile; Water treatment; Adsorbent; Micropollutant; Support.

INTRODUCTION

Water remediation is a globular challenge^[1, 2]. Organic anions, such as surfactants, phenols and dyes, are ubiquitously found as pollutants in water. Surfactants have become one indispensable element of modern life. Toxicity of a surfactant alone may be limited, but it may solubilize toxic, carcinogenic and mutagenic compounds such as polycyclic aromatic hydrocarbons (PAHs)^[3–5]. For example, a polystyrene (PS)-containing covalent micelle can enhance the content of pyrene (a typical PAH) in water by 10^3 -fold^[5]. Meanwhile, organic dyes are produced and consumed in large scale worldwide every year, and constitute negative impact on water quality and the aquatic ecosystem. Many inorganic and inorganic-organic hybrids have been reported to effectively adsorb dyes in water^[6–12]. However, now more concerns are focused on micropollutants in water, and on small species which defy to be captured from water by a conventional adsorbent, but currently few adsorbents can deal with them.

Adsorption is supramolecular host-guest chemistry in nature. Understanding the host-guest complementary mechanism is critical to develop new efficient adsorbents for water cleaning. Traditionally, specific interactions are employed for highly effective guest entrapment^[13]. Such a strategy suffers from two drawbacks, one is that only those guest species either topologically or electronically featured can be well entrapped; the other is that the hosts have to be meticulously tailored to meet a key-lock like complement to a specified guest in terms of size, morphology and electronic motif, rendering the synthesis of a host tedious and challenging. In recent decades, encapsulation by unimolecular inverted micelles (UIMs) and their analogues have been extensively

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explored^[14–23]. Unlike those driven by specific host-guest complement, encapsulation is usually promoted by statistical interactions which are dynamic and random in nature, thus is less rigorous on the host architecture and widely available. It is found that the statistical interaction strength can be enhanced by tuning the interior electronic environment of a UIM^[15, 16]. With the advent of one-step available hyperbranched polymers, UIMs have become widely available, and usually with dense functional groups residing in the core. Regarding the role of the hydrophobic shell of a UIM, it is less discussed. Researchers found that a thick and dense hydrophobic shell is necessary for efficient encapsulation^[20, 21]. For a UIM, if the hydrophobic shell is too thin or sparse, it is labile to aggregation, which may result in poor encapsulating capacity. On the other hand, regardless of the fact that a UIM may highly efficiently capture certain pollutants, it is too small to be separated from water. Here, by chemical attaching the PEI on a support of silica (200–300 μm), aggregation will not occur upon introduction of sparse hydrophobic chains onto it. Such a feature provides us a chance to evaluate the role of the hydrophobic shell on guest encapsulation. Interestingly, structure-property optimization shows that the density of the hydrophobic shell is critical to the capture of trace pollutants in water, with the K values being able to be improved by 5 orders in magnitude. Such adsorbents are favorable to the production of quality drinking water.

EXPERIMENTAL

Materials

Sodium dodecyl benzene sulfonate (SDBS) and hexadecylpyridinium chloride (CPC) were purchased from Aladdin (China). Sodium dodecyl sulfate (SDS), methyl orange (MO), 1,2-epoxypropane, and Silica particle (300 μm) were purchased from Sinopharm Chemical Reagents Company (SCRC, China). The small-sized fraction of silica was removed by stirring and decant. Sodium lauryl ether sulphate (LES) was purchased from DEM Chem. Co. Ltd (Shanghai, China). Potassium cetyloxytri(ethylene oxide) phosphate (CTEP) was purchased from Haian Chem. Co. Ltd (Jiangsu, China). Branched polyethylenimine (PEI, $M_n = 1 \times 10^4$, $M_w/M_n = 2.5$, degree of branch = 60%) was purchased from Aldrich.

Synthesis of Sil@PEI

The synthesis of Sil@PEI (PEI makes up 8.3% of the material) was based on a literature^[24]. Briefly, a mixture of PEI (18.00 g, eq. 0.418 mol repeat units of $\text{CH}_2\text{CH}_2\text{NH}$) and glycidyoxypropyltrimethoxysilane (3.2 mL, 14.72 mmol) in ethanol (250 mL) was prepared and refluxed under nitrogen atmosphere. The mixture was monitored with dynamic laser scattering (DLS) and when the size reached 10 nm, silica (45.00 g, activated by refluxing in dilute aqueous HCl for 36 h before drying) was dropped in and the mixture was kept under refluxing and mild stirring for 72 h. The solid was separated by filtration, fully washed with absolute ethanol before dried in vacuum at 323 K. From elemental analysis, it was derived that the PEI on silica made up to 8.3 wt%.

Synthesis of Sil@PEI@C16-x (x Represents the Fraction of Amino Protons Being Alkylated by Cetyl Groups)

The synthesis is exemplified by the synthesis of Sil@PEI@C16-0.15. Cetyl glycidyl ether^[15] (0.86 g, 2.90 mmol) in chloroform (80 mL) was mixed with Sil@PEI (10 g, eq. 19.3 mmol of $\text{CH}_2\text{CH}_2\text{NH}$), and the mixture was stirred at room temperature for 5 days. The solid was separated by filtration and fully washed with chloroform before being dried in vacuum at 323 K, yielding a solid (10.81 g, 94.2% based on cetyl glycidyl ether). Element analysis, C: 10.62; H: 2.23; N: 2.49. The alkylated fraction of PEI on silica was derived from the equation: $(7\text{C}\% - 13\text{N}\%) / 114\text{N}\% = 14.89\%$, where C% and N% represent the mass content of the element carbon and nitrogen, respectively. Sil@PEI@C16-0.30 and Sil@PEI@C16-0.60 were synthesized similarly, with element analysis as: C: 15.53; H: 3.01; N: 2.31 and C: 23.30; H: 4.25; N: 2.02, respectively.

Sil@PEI-OH

For comparison, the reactant of cetyl glycidyl ether was replaced with epoxypropane (0.6 eq. of NH) and a quantitative reaction also occurs, as judged from elemental analysis (spectrum not shown).

Measurements

Elemental analysis was carried out with an Elementar-vario EL III microelemental analyzer. UV/Vis spectra

were recorded on a Mapada UV-6300 spectrophotometer (Shanghai Mapada Instruments Co. Ltd.). Ion chromatography (IC) analysis was carried out on a Metrohm MIC-7 system which included a Supp5 ion exchange chromatography column with a mobile phase at a flow rate of 0.7 mL/min. An elute composing of Na₂CO₃ in water and NaHCO₃ in water was adopted, and the whole IC system was equipped with an electrical conductivity detector. The fluorescence spectra of aqueous samples were recorded on an F-2700 (Hitachi) fluorescence spectrometer.

Adsorbing Capacity of Sil@PEI@C16-x against Surfactants and Dyes

Typically, to solution samples of SDBS (6 mL, 7.48×10^{-5} mol/L) in a PB buffer (pH = 7.4, 0.01 mol/L), different amounts of Sil@PEI@C16-0.15 (5–20 mg) were added to each sample, and the resulting mixtures were subjected to mild stirring. Aliquots were taken for UV/Vis measurements to monitor the adsorption equilibration, where a neat buffer was used as a reference.

Cleanup of Aqueous Surfactants and Dyes with Sil@PEI@C16-x

Typically, to an aqueous solution of SDBS (500 mL, 1.6×10^{-5} mol/L in a PB buffer (pH = 7.4, 0.01 mol/L)), Sil@PEI@C16-0.15 (850 mg) was added, and the resulting mixture was subjected to mild stirring. After sufficient equilibration (20 h, monitored with a UV/Vis spectrometer), the adsorbent was separated by filtration and washed with fresh buffer. The aqueous filtrate was subjected to complete evaporation under reduced pressure in several batches with a small glass container, or by freeze drying. Finally, 1 mL of deionized water was added to fully wash the glass container (the volume increased to 1.07 mL), and further subjected to UV/Vis measurements with a neat buffer (2 mol/L) as a reference. In case the surfactant was not featured in UV/Vis spectrum, IC was employed for detection.

Adsorption Isotherms of Anionic Surfactants by Sil@PEI@C16-x

Typically, the adsorption isotherm was carried out by set the amount of Sil@PEI@C16-0.15 (350 mg) in a PB buffer (pH = 7.4, 0.01 mol/L) while changing the relative amount of SDBS ($0.015\text{--}5.5 \times 10^{-5}$ mol/L). After sufficient equilibration, the residual concentration was detected after concentration in a manner mentioned above.

Determination of the Association Constant K

According to the definition, the association constant $K = [\text{adsorbent-guest}]/[\text{free guest}][\text{adsorbent}]$, where [free guest], [adsorbent-guest], and [adsorbent] represent the activity (or concentration) of the corresponding species at equilibrium. Since the activity of the solid adsorbent with or without captured guests should be regarded as one^[25], the equation is simplified as:

$$K = 1/[\text{free guest}] \quad (1)$$

The K can also be analyzed with Klotz equation^[26]:

$$1/r = (k/n)/[\text{free guest}] + 1/n \quad (2)$$

where r is the molar ratio of the bounded guest to PEI; n is the maximum possible number of bound guests per PEI; and k is an experimental constant relating to the properties of both the adsorbent and the guest and should be measured experimentally. Given no guest-guest interaction among the adsorbed guest, the association constant (K_i) of the adsorbent upon binding to the i th guest is solely determined by a statistical factor and the following relation stands:

$$K_i = (n-(i-1))/(ik) \quad (3)$$

Adsorption Kinetics

The adsorption kinetics of anionic surfactant was carried out as follows: typically, a vial was charged with SDBS (6 mL, 7.48×10^{-5} mol/L) in a PB buffer (pH = 7.4, 0.01 mol/L), then Sil@PEI@C16-0.15 (10 mg) was added. The resulting mixture was subjected to standing while the absorbance of aqueous phase was monitored with a UV/Vis spectrometer with a neat buffer as a reference every 2 h until equilibration. The data were analyzed by

the pseudo-first order equation (Lagergren model)^[27]:

$$dq_t/dt = k_1(q_e - q_t) \quad (4)$$

or pseudo-second order chemisorption kinetic:

$$dq_t/dt = k_1(q_e - q_t)^2 \quad (5)$$

where q_e and q_t are the sorption capacity (mg/g) at equilibrium and at time t , respectively, and k_1 is the rate constant of sorption.

RESULTS AND DISCUSSION

Synthesis of Adsorbents

Silica (200–300 μm) supported PEI (Sil@PEI) was synthesized as previously reported^[24], where the pores of the silica were blocked by the PEI because the surface area decreased from 437 m^2/g to 27.6 m^2/g . Meanwhile, it seems that the surface of silica is fully covered by PEI because the resulting Sil@PEI no longer shows any affinity to a cationic dye such as methylene blue or to a cationic surfactant such as CPC. Cetyl groups are further introduced onto the Sil@PEI by reacting with cetyl glycidyl ether (C16), leading to Sil@PEI@C16- x (Fig. 1, where $x = 0.15, 0.30$ and 0.60 , as determined by element analysis).

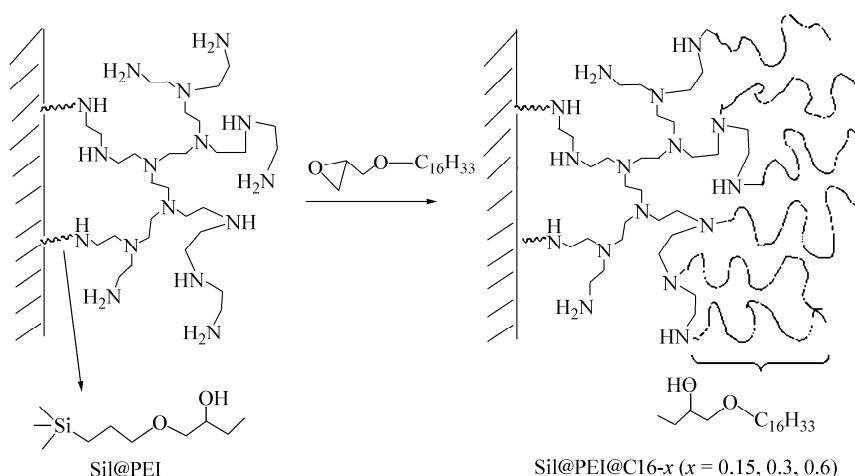
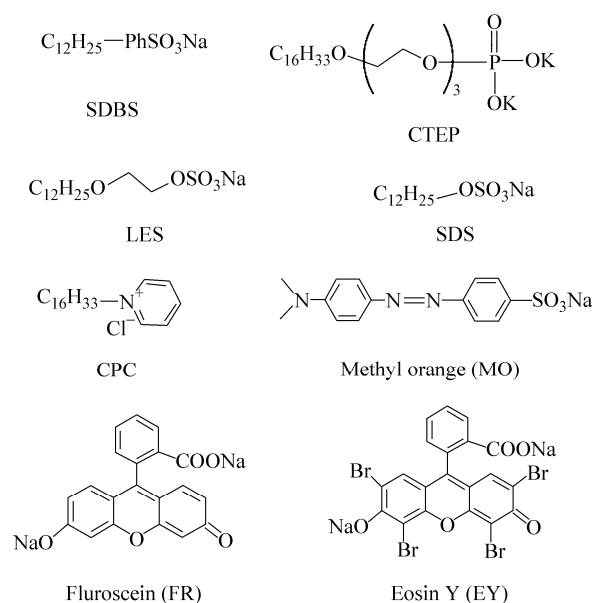
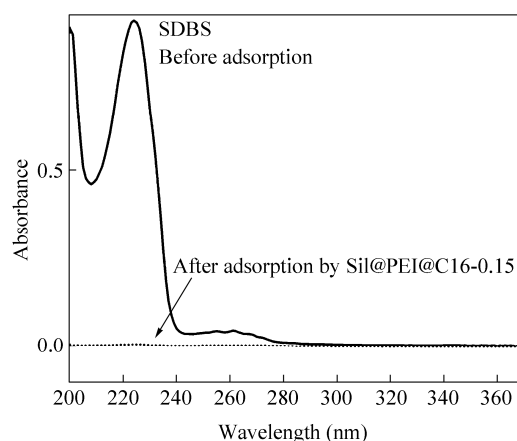


Fig. 1 Outline of the synthesis of adsorbents of Sil@PEI@C16- x (PEI has 232 repeat units on average but only several are shown here for clarity.)

Capture of Aqueous Anionic Surfactants

Since PEI usually exists as a cationic electrolyte in water unless $\text{pH} > 10$, effective adsorbing of anionic surfactants with Sil@PEI should be possible when $\text{pH} < 10$. When enough amount of solid Sil@PEI is dropped into an SDBS (Fig. 2)-containing water, the SDBS content decreases sharply within 20 h and is not UV/Vis detectable (Fig. 3) unless sufficient concentration. The residual concentration finally reaches 2.59×10^{-8} mol/L (entry 1, Table 1), as measured with a UV/Vis spectrometer after 500-fold concentration. Compared with typical adsorbents, the capacity of these adsorbents is moderate, but when considering the binding strength to the pollutant, these adsorbents are unique. For example, for an organoamine-functionalized mesoporous silica (the highest K values even for a relatively large dye are within 10^6 L/mol)^[6], and for Sil@PEI, it is 1.56×10^8 L/mol; while for Sil@PEI@C16-0.15, the K is 1.15×10^9 L/mol. One can notice that Sil@PEI is somewhat outstanding in binding a surfactant as compared with a typical organosilica. It is known that the macromolecular PEI is rather flexible as compared with small organic groups attached to silica, and thus can undergo larger conformational change to provide more statistical interacting sites to undergo complement with the anionic SDBS, which should be the reason for the higher affinity to the anionic surfactant.

**Fig. 2** Chemical structures of several surfactants and dyes**Fig. 3** UV/Vis spectra of SDBS before (solid line) and after (dot line) sufficient treatment with Sil@PEI@C16-0.15
Conditions: [SDBS]₀ = 7.48 × 10^{−5} mol/L; pH 7.4 (PB buffer 0.01 mol/L)**Table 1.** Adsorption data of Sil@PEI@C16-x against anionic SDBS and cationic CPC in water^a

Entry	Surfactants	Adsorbent	q_e^b (mg/g)	Residue ^c (10 ^{−9} mol/L)	K^d (L/mol)
1	SDBS	Sil@PEI	5.33	25.9	3.86×10^7
2	SDBS	Sil@PEI@C16-0.15	8.05	2.1	4.76×10^8
3	SDBS	Sil@PEI@C16-0.30	4.56	28.6	3.50×10^7
4	SDBS	Sil@PEI@C16-0.60	3.62	35.0	2.85×10^7
5	CPC	Sil@PEI	0	—	—
6	CPC	Sil@PEI@C16-0.60	3.03	8450	1.18×10^5
7	SDBS	Sil@PEI	—	6.42 ^e	1.56×10^8
8	SDBS	Sil@PEI@C16-0.15	—	0.87 ^f	1.15×10^9

^a Adsorption at pH 7.4 (PB buffer, 0.01 mol/L) within 30 h; the error of UV/Vis measurements is within 2%; ^b saturated adsorption capacity, determined by UV/Vis (SDBS: $\varepsilon_{224} = 1.24 \times 10^4$ L/mol/cm; CPC: $\varepsilon_{259} = 0.45 \times 10^4$ L/mol/cm);

^c Residual concentration of the substrate at equilibration, determined by UV/Vis of a concentrated sample and conversion to equivalent concentration; ^d Association constant (K) derived by Eq. (1); ^e In the absence of PB, pH 9.28;

^f in the absence of PB, pH 9.07

While for Sil@PEI@C16-0.15, the association constant is improved by another order in magnitude, and we suppose the additional hydrophobic complement between cetyl groups and SDBS should be responsible for the improvement. With further increase of the cetyl groups on PEI, the association constants decrease instead (entries 3 and 4, Table 1), being even lower than that of Sil@PEI, which implies that electrostatic complement is suppressed by the dense cetyl groups due to steric factors. To learn if hydrophobic complement exists, the cationic surfactant of CPC is used in place of the anionic SDBS. In the case of Sil@PEI, no CPC can be adsorbed (entry 5, Table 1) due to electrostatic repulsion, while in the case of Sil@PEI@C16-0.60, a considerable amount of CPC can be adsorbed (entry 6, Table 1), supporting that hydrophobic complement exists. In most experiments, the adsorption is carried out in a buffered medium for convenience of comparison, however, the phosphate in the buffer may compete for the cationic sites on PEI. Control experiments support this supposition, where an unbuffered medium favors a higher K value (entry 7, 8, Table 1). Other anionic surfactants are also tested with Sil@PEI@C16-0.15 (Table 2), and the residual concentrations are all decreased to a level of 10^{-9} mol/L in a PB buffer, and the cetyl groups improves the association constants by typically over one order of magnitude as well. These facts once again support that certain amount of hydrophobic chains on the cationic adsorbent favor the cleanup of anionic surfactant.

Table 2. Cleanup of several surfactants with two adsorbents ^a

Surfactants	q_e (mg/g)		Residue (10^{-9} mol/L)		K (L/mol)
	Sil@PEI	Sil@PEI@C16-0.15	Sil@PEI	Sil@PEI@C16-0.15	Sil@PEI@C16-0.15
SDS	5.30	8.32	32.7	2.84	3.52×10^8
AES	5.61	8.56	29.2	2.36	4.23×10^8
CPK	5.72	7.79	21.6	1.32	7.58×10^8

^a Adsorption at pH 7.4 (PB buffer, 0.01 mol/L) for 30 h, detected by IC after 500-fold concentration

To learn the adsorption mechanism, the adsorption isotherm is plotted (Fig. 4a). The adsorption isotherm can be divided into four regions. Such an isotherm pattern seems to be a typical case for the adsorption of ionic surfactants by one oppositely charged adsorbent^[7]. In region I (surfactant $< 8.8 \times 10^{-9}$ mol/L), the linear relationship implies a monolayer adsorption occurs and no guest-guest repulsion exists. The adsorption is mainly promoted by electrostatic complement between the anionic surfactant and the cationic adsorbent, but hydrophobic complement should also exist as judged from the higher K values upon comparison with that of Sil@PEI. With the increase of the surfactant in the system, multilayer adsorption occurs, leading to an enhanced adsorbing capacity (region II); but with the multilayer stacking of the surfactant along the surface of the adsorbent, surfactant-surfactant repulsion becomes important and the q_e is less sensitive to the residual surfactant in the liquid (region III); and finally the adsorption reaches an equilibrium where q_e remains almost intact with free guest in the liquid (region IV). This curve clearly shows that the binding strength (K) is not a constant along with the absorption process. However, it is also derived that up to 80% of the saturation adsorption, the K value is still larger 9.3×10^7 L/mol, as derived from the section of region II (1.88×10^{-8} mol/L).

The above conclusion is further supported by Klotz analysis (Fig. 4b). Klotz analysis can provide information on guest-guest interaction and guest-host binding strength^[26]. As shown in Fig. 4(b), when SDBS is below 8.3×10^{-9} mol/L, a linear relationship exists, implying no guest-guest interaction (corresponding to region I in Fig. 4a). The binding strength is $K_I = 7.4 \times 10^8$ L/mol, slightly larger than that derived from Eq. (1) ($K = 4.76 \times 10^8$ L/mol, Table 1, entry 2). This is reasonable because in Klotz equation K_I represents the association constant of the adsorbent upon binding the first guest, while in Eq. (1) the K represents the average association constants in region I. Upon entering region II ($8.3 \times 10^{-9} - 1.88 \times 10^{-8}$ mol/L), the sharp reflection implies guest-guest repulsion, and the association constant decreases to $K_{II} = 9.3 \times 10^7$ L/mol. Klotz analysis seems to be no longer applicable with further increase of SDBS in the liquid.

Analysis of the adsorption kinetics implies that it complies with a Lagergren adsorption model (Fig. 5), *i.e.*, pseudo-first order rate of adsorption, with a rate constant of $k_1 = 0.166 \text{ h}^{-1}$. The adsorbent is recyclable, when subjected to alkaline water (pH 12), 40%–92% of the adsorbed SDBS can be released, depending on the water amount, and at least in the tested 6 cycles, the adsorbing ability remains almost intact.

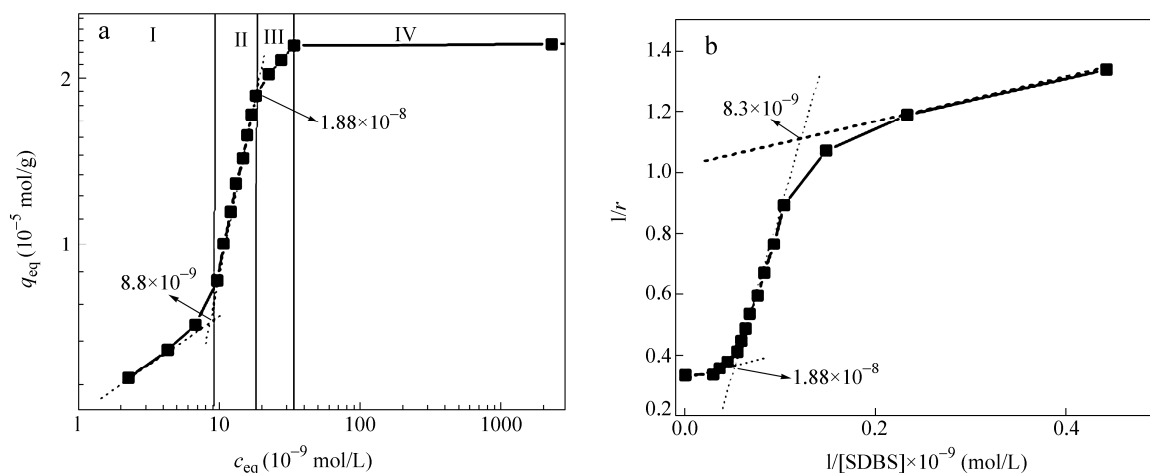


Fig. 4 (a) Adsorption isotherm for SDBS by Sil@PEI@C16-0.15 and (b) Klotz plot of the adsorption Condition: pH 7.4 (PB buffer 0.01 mol/L); The errors are within 2%.

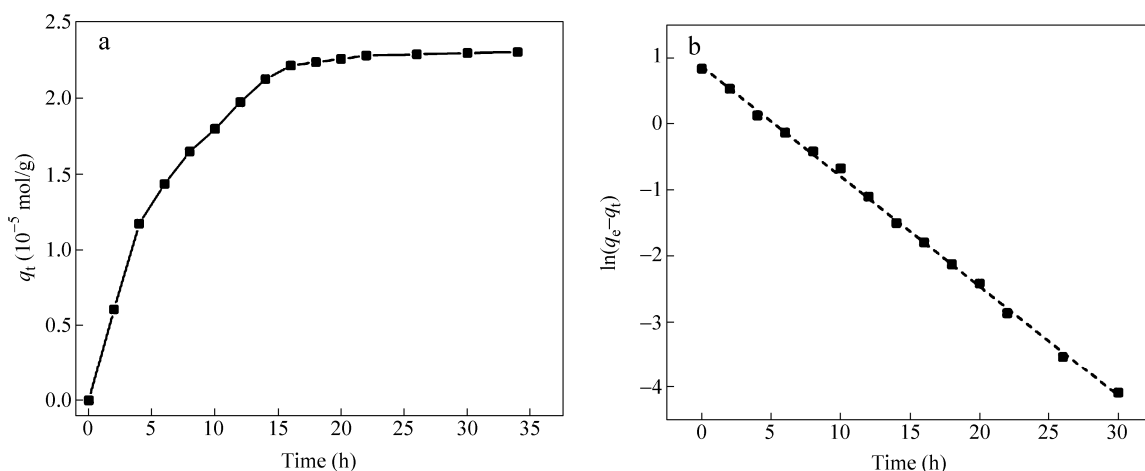


Fig. 5 Dependence of adsorption on time (a) and pseudo-first order adsorption rate analysis (Eq. 4) (b) of the adsorption (Conditions: liquid-solid adsorption at pH 7.4 (PB buffer 0.01 mol/L))

Capture of Anionic Dyes

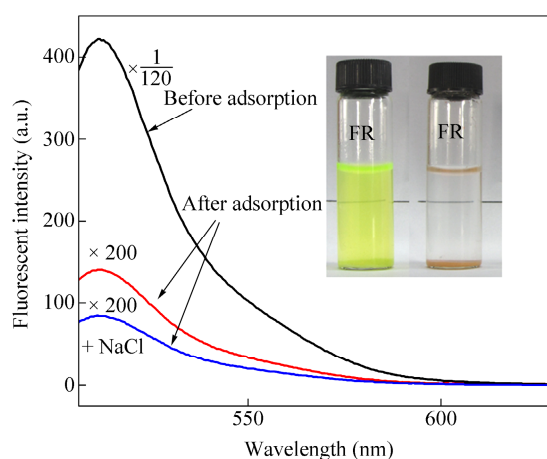
Dyes are representative pollutants in water and many adsorbents, such as mesoporous organosilica, have been reported to deal with aqueous dyes^[6]. However, few adsorbents have been reported to deal with microscale and nanoscale dyes in water^[27]. Generally speaking, a small dye usually defies to be removed for its limited statistical interaction sites that can afford complement with an adsorbent^[28]. Figure 2 shows structures of several small dyes of MO, FR and EY. Sil@PEI, like most reported adsorbents, shows rather limited affinity to such dyes (Table 3), meaning that there will be a considerable dye residue in water after treatment with Sil@PEI. Again if cetyl groups are introduced onto Sil@PEI, the resulting adsorbents show significantly improved ability to capture the anionic FR (Table 3). Optimization shows that if 60% of the PEI units are alkylated with cetyl groups, the residual concentration of FR in water can be reduced from 4.04×10^{-6} mol/L to 5.42×10^{-11} mol/L, an unprecedentedly high value, as determined by fluorescent detection (Fig. 6). The corresponding association constant is improved by nearly 10^5 -fold, as compared with that of Sil@PEI.

Table 3. Ability to capture FR by different adsorbents ^a

Adsorbents	q_e (mg/g)	Residue (10^{-11} mol/L)	K^b (L/mol)
Sil@PEI	1.39	268000	3.73×10^5
Sil@PEI-OH	1.43	127000	7.87×10^5
Sil@PEI@C16-0.15	1.28	47300	2.10×10^6
Sil@PEI@C16-0.30	1.09	1850	5.40×10^7
Sil@PEI@C16-0.60	0.83	5.42	1.85×10^{10}
		3.29 ^c	3.04×10^{10}

^a Samples are concentrated when necessary and detected by fluorescence spectra, conditions: $\lambda_{\text{ex}} = 490$ nm; $[\text{FR}]_0 = 4.04 \times 10^{-6}$ mol/L; pH 7.4 (PB buffer 0.01 mol/L); The errors are within 2%; ^b Derived from Eq. (1);

^c With a content of 0.5% NaCl

**Fig. 6** Fluorescent detection of FR before and after adsorption by Sil@PEI@C16-0.6

Conditions: adsorption under buffer of pH 7.4 (PB buffer, 0.01 mol/L); $[\text{FR}]_0 = 4.04 \times 10^{-6}$ mol/L, but dilution by a factor of 120 before measurement; while after adsorption, the sample is concentrated by a factor of 200 before measurement; and in one case, NaCl (0.5%) is present.

Regarding the mechanism, it is supposed that a dense hydrophobic shell can isolate the bulky water from the PEI domain and constitute a less polar microenvironment. It is known that electrostatic complement in an apolar environment will be much stronger than that in a polar environment, which is favorable for the cationic-anionic interaction between PEI and FR. A control experiment shows that if a small amount of NaCl is added to the aqueous solution (0.5%), the association constant is almost doubled (Table 3). Since inorganic electrolytes can further dehydrate the PEI core and lead to a still less polar interior environment^[29], the favored binding of FR is reasonable. This fact is consistent with the above mentioned mechanism. On the other hand, it was previously pointed out that the hydrophobic shell of a UIM could result in collapse of the polar core, and the latter could significantly favor the capture of dyes as well^[19]. This mechanism cannot be excluded from our system, and we also cannot exclude the case that both mechanisms exist in the system. There is still one issue need to be clarified. Upon introduction of cetyl groups onto PEI, hydroxyl groups are simultaneously introduced into the PEI core. One may argue that the hydroxyl groups result in the improved affinity to FR. To clarify this issue, equivalent hydroxyl groups are introduced onto Sil@PEI, and the resulting Sil@PEI-OH can very slightly improve the affinity to FR. Therefore, a safe conclusion can be drawn that the cetyl groups are responsible for the significantly improved affinity to FR. In the case of FR, it seems that the phosphate exerts very limited impact on capture of FR by the adsorbent, perhaps due to the limited statistical interacting sites of the phosphate. Similarly, when the FR-containing adsorbent was dropped into alkaline water (pH > 11), up to 86% FR can be released, and the adsorbing capacity and fraction of FR released are almost the same in the tested 6 cycles. Generally speaking, the introduction of the aliphatic chains onto the adsorbent somewhat decreases the adsorbing capacity but significantly improves the guest binding strength.

When MO and EY are used in place of FR, the association constants are found to be improved also by a factor of 10^4 to 10^5 as well, as compared with that of Sil@PEI (Table 4), suggesting this is a rather general case. Although the introduction of aliphatic chains kinetically retards the adsorption, the equilibration can be reached within 30 h for the tested surfactants and 39 h for the tested dyes. Considering the significantly enhanced thermodynamic binding strength, the lower adsorption rate is acceptable.

Table 4. Cleanup of several dyes with Sil@PEI@C16-0.60 ^a

Dyes	q_e (mg/g)		Residue ^b (mol/L)		K^c (L/mol)	
	Sil@PEI	Sil@PEI@C16-0.60	Sil@PEI	Sil@PEI@C16-0.60	Sil@PEI	Sil@PEI@C16-0.60
MO	3.54	2.36	1.06×10^{-6}	$< 9 \times 10^{-10}$	9.43×10^5	$> 1.11 \times 10^9$
EY	12.38	6.64	5.36×10^{-7}	6.28×10^{-12}	1.86×10^6	1.59×10^{11}

^a Adsorption at pH 7.4 (PB buffer at 0.01 mol/L) within 39 h; The errors are within 2%; ^b Detected by UV/Vis after 200 times concentration of the water sample for MO and by fluorescence ($\lambda_{ex} = 465$ nm) for EY after 200 times concentration; ^c Derived from Eq. (1)

CONCLUSIONS

When certain amount of hydrophobic cetyl groups (C16) are introduced onto the surface of a conventional adsorbent of polyamine-modified silica (Sil@PEI), the ability of the resulting adsorbents of Sil@PEI@C16-*x* to capture anionic surfactant and anionic dyes are significantly improved. Optimization shows that the strength of Sil@PEI@C16-0.15 to bind aqueous anionic surfactant is at least 10-fold improved, while that of Sil@PEI@C16-0.6 to bind aqueous dyes is 10^4 to 10^5 -fold improved, as compared with those of Sil@PEI. In the case of dyes, the dense hydrophobic shell can shielding the competitive binding of bulk water to the adsorbent and to the dye, thus enhancing the adsorbent-dye complement; while in the case of surfactant, Sil@PEI@C16-0.15 is the best adsorbent for simultaneously meeting electrostatic complement and hydrophobic complement with the surfactant. Such adsorbents can reduce surfactant and dyes in water to extremely low residues and are well recyclable. These properties render them potential water treating agent for quality water. The adsorbents may be applicable to remove other anionic pollutants in water.

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