



Tuning the hydrophobicity of mesoporous silica materials for the adsorption of organic pollutant in aqueous solution

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ABSTRACT

The ability of various as-prepared and organically modified MCM-41 and HMS mesoporous silica materials to behave as efficient adsorbents for organic pollutants in aqueous solution was investigated by using different surface functionalization procedures, so as to adjust their hydrophilic/hydrophobic balance. The hydrophilic and organophilic properties of the parent silica materials and their corresponding surface functionalized counterparts were studied by using water and toluene adsorption isotherms. Their quantification was determined by the hydrophobic static index value (HI_{static}), as well as by the silanol and organic group densities after the functionalization step. A clear correlation could be found between the HI_{static} values and either the superficial silanol density, or the amount of organic moieties grafted or incorporated to the silica materials. For the highly organically functionalized samples, the residual superficial silanol groups (<50%) are sufficiently isolated from each other so as to prevent the water capillary condensation within the pores, thereby leading to an increased hydrophobic character of the resulting mesoporous silica. Those hydrophobic samples, for which the water liquid meniscus formation within the mesopores was minimized or avoided, exhibited a storage capacity for an organic pollutant (N,N-diethyl-m-toluamide, DEET) in aqueous solution more than 20 times higher than that of the corresponding unmodified sample, independently of the silica nature (MCM-41 or HMS). For all calcined and silylated samples, the DEET maximum adsorption capacities determined by the Langmuir model could be correlated with the silica surface coverage by trimethylsilyl groups and thus with the remaining silanol amount.

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1. Introduction

Although pesticides play an important role in agriculture, these organic pollutants are characterized by a high toxicity coupled to a poor bio-degradability. Their intensive use provokes their partial release in the environment, thereby leading to contamination of surface waters by leaching. In accordance with the increasingly stringent environmental legislation, economic viable adsorption processes including adsorbent material design have been developed to satisfy the requested objectives in water depollution [1–3]. Activated carbons and hydrophobic zeolites with high Si/Al ratio are usually used for the removal of organic pollutants in wastewater or in gas streams [1,4,5]. However, such microporous adsorbents exhibit a limited pore aperture, thereby leading to a low diffusion and thus to a restricted adsorption of heavy organic molecules (i.e. pesticides) due to steric hindrances. The fact that their narrow pores could also be blocked rapidly makes them not always well suited for an environmentally friendly adsorption process, because of difficult

desorption steps. To circumvent these drawbacks, the replacement of microporous solids by mesoporous adsorbents could be of relevant interest. Mesoporous silica materials involve a high BET surface area coupled to an important pore volume which confers them high sorption capacities. Moreover, these solids exhibit a type V water adsorption isotherm (low water-adsorbent interaction at low P/P_0) [6,7], which classifies them in the family of hydrophobic compounds. They are also considered as organophilic solids due to their ability to adsorb significant quantities of organic molecules in gas phase, such as n-hexane, benzene, toluene as well as various alcohols [8–10]. However, the high superficial silanol density exhibited by mesoporous silica materials greatly affects the organic pollutant adsorption in aqueous solution because of the preferential water molecules adsorption. Among the various strategies available to limit such phenomenon, the direct adsorption of the organic pollutant within the surfactant-containing MCM-41 silica sample was shown to considerably increase the pollutant sorption capacity in the case of phenol and o-chlorophenol compounds by comparison with the corresponding calcined MCM-41 sample [11–13]. Nevertheless, the volume occupied by the adsorbed pollutant molecules inside the micelle hydrophobic core was rather limited, thereby leading to an adsorbent regeneration difficult to

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perform while keeping the micelles intact. To take advantage of the high sorption capacity exhibited by calcined mesoporous silica materials, it is necessary to control their pore size as well as their hydrophobic degree, in order to improve their affinity with the organic pollutant in aqueous solution. In this respect, different synthesis methods including the co-condensation of siloxane and organosiloxane precursors [14–16] or post-synthesis treatments such as silylation of the superficial silanol groups [17,18] can be exploited to design efficient organically functionalized mesoporous adsorbents. The hydrophobic derivatization routes used in this work namely consisted in the grafting of trimethylsilyl moieties (TMS) on the inner surface of the mesopores through reaction of silanols and hexamethyldisilazane (HMDS), as well as in the one step covalent anchoring of phenyl groups within the silica channels by using phenyltrimethylsilane (PTMS) as organic agent.

The main purpose of the present study was to determine the hydrophilic, hydrophobic and organophilic properties of MCM-41 and HMS silica materials involving variable pore diameters and of their corresponding hybrid inorganic–organic counterparts by using water and toluene adsorption isotherms and, in a further step, to evaluate their efficiency in the removal of diethyl-*m*-toluamide as organic pollutant from aqueous solution. DEET was selected as organic compound, because of its environmental risk and ecophysiological properties. It is one of the most prevalent forms of chemical pollutants (insecticide) in water resources in the United States and is characterized by a high biologic toxicity towards the freshwater zooplankton and in a lesser extent to coldwater fishes. The surface functionalization of mesoporous silica materials with appropriate organic moieties is expected to minimize the water adsorption within the pores, while increasing the pollutant sorption capacities thanks to stronger interactions between the adsorbent and the organic pollutant. The quantification of the hydrophilic/hydrophobic balance of the organically functionalized mesoporous silica materials was determined by the hydrophobic static index value (HI_{static}), as well as by the superficial silanol density and by the amount of grafted (TMS) or incorporated (phenyl) organic groups. Such method based on the non competitive water toluene adsorption was indeed rarely reported in the literature.

2. Experimental

2.1. Materials preparation

The MCM-41 mesoporous silica was prepared via an alkali metal-free synthesis method by introducing in the reaction mixture a pH-controlling mineralizing agent from the short-chain alkylamine family. Such amines behave both as efficient mobilizing (toward silica) and buffering agents through stabilizing the synthesis pH range to basic values (10–12) [19]. In this work, methylamine (MA) was used as short-chain alkylamine along with tetramethoxysilane (TMOS) and cetyltrimethylammonium bromide (CTMABr) as starting materials. The gel molar composition was 1 SiO₂/0.215 CTMABr/2 MA/120 H₂O. The heavy precipitate was heated at 373 K in a Teflon coated stainless steel autoclave for 24 h. The product was recovered by filtration, washed with cold water, and dried at 353 K before being calcined under air flow at 823 K (rate of 1 K min⁻¹) and kept for 4 h at that temperature. The as-prepared and calcined MCM-41 samples were referred to as as-MCM-41 and MCM-41, respectively.

The preparation of the HMS mesoporous silica partially followed the synthesis method reported by Macquarrie et al. [20]. Typically, 7.20 g of *n*-dodecylamine (DDA) was added under stirring to an aqueous ethanol solution (66 mL of absolute ethanol and 76 mL of deionized water) and the resulting solution was homogenized for 1 h. 26.83 g of tetraethoxysilane (TEOS) was then slowly added at

ambient temperature to the previous solution. The molar composition of the synthesis mixture was 1 TEOS/0.3 DDA/8.7 EtOH/32.5 H₂O. After 18 h of ageing under stirring, the resulting thick solution was filtered and the solid washed with deionized water before being dried at 348 K overnight. Finally, the product was calcined under flowing air at 873 K for 3 h (heating rate of 1 K min⁻¹) and labeled as HMS, whereas the as-prepared HMS sample was named as-HMS.

The surface functionalization of the MCM-41 and HMS mesoporous silica samples, namely the silylation of the superficial silanol groups, was carried out with hexamethyldisilazane (HMDS, Aldrich). The silylation procedure was described in detail in a previous paper [21]. In brief, the calcined solids (0.5 g) were first heated at 573 K for 1 h under air and then under primary vacuum for 2 h at the same temperature, before being treated with a solution of HMDS in anhydrous toluene (20 mL, Aldrich) under reflux for 2 h. Various volumes of HMDS were used depending on the desired silylation degree. The silylated solids were recovered by filtration, washed with anhydrous toluene (40 mL) and finally dried at 313 K overnight. The final partially or highly silylated MCM-41 and HMS mesoporous silica samples were referred to as MCM-41-S_x (with $x = 1, 2$ or 3) and HMS-S_x (with $x = 1$ or 2).

A second route for hydrophobic derivatization was also carried out with the MCM-41 mesoporous silica. The surface modification was based on the co-condensation of phenyl and silica precursors and the resulting functionalized sample was referred to as MCM-41-Ph. The preparation of the phenyl-incorporated MCM-41 sample was performed according to known procedures using phenyltrimethylsilane (PTMS) as hydrophobic agent [14–16]. Ammonia (28%) and CTMABr were first dissolved in deionized water under stirring until complete homogeneity of the solution. TEOS and PTMS were then added dropwise into the solution containing the templating agent and the stirring was maintained for 2 h. The gel (molar composition: 0.9 SiO₂/0.1 PTMS/0.12 CTMABr/8 NH₄OH/114 H₂O) was transferred into a Teflon-lined stainless steel autoclave and heated at 383 K for 72 h. The as-synthesized product was recovered by filtration, washed with deionized water and dried at 373 K for 12 h. Removal of CTMABr was carried out by extraction over a refluxing mixed solution of methanol and hydrogen chloride acid (1 mol L⁻¹) for 24 h, before filtration and washing with deionized H₂O. Finally, the solid was dried at 313 K overnight affording the hybrid organic–inorganic MCM-41-Ph.

2.2. Materials characterization

The carbon content within the solids was analyzed with a Thermoquest NA2100 analyser by total combustion at 1293 K under helium and oxygen. Nitrogen adsorption measurements were performed at 77 K with a gas adsorption system ASAP 2000 (Micromeritics). Before measurement, samples were outgassed under secondary vacuum at 573 K for 12 h.

Powder small-angle XRD patterns of the samples were obtained on a Bruker AXS D5005 X-ray diffractometer, equipped with a monochromatized CuK α radiation ($\lambda = 1.54184 \text{ \AA}$) and operating at 40 kV, 30 mA. XRD patterns were scanned at a rate of 0.025° s⁻¹ and with a step size of 10 s from 0.8° to 10° 2 θ .

Thermal analysis measurements (TGA-DTA) were carried out in alumina crucibles using a SDT Q600 microbalance (TA Instruments) from 303 to 1073 K at a heating rate of 5 K min⁻¹ in flowing air (100 mL min⁻¹). The samples were placed in a desiccator at 294 K under an air humidity of 50% prior to the analyses.

Water and toluene adsorption isotherms were performed at 298 K by thermogravimetry using a SETARAM microbalance [22]. The samples (10–15 mg) were out-gassed under secondary vacuum at 573 K for 6 h and cooled down to 298 K prior to the sorption measurements. The sorbate pressure was then increased step by step

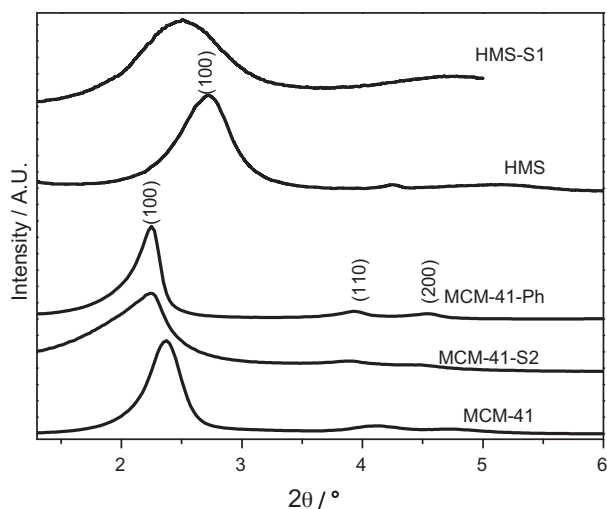


Fig. 1. XRD patterns of the calcined parent MCM-41 and HMS silica samples and their corresponding surface functionalized counterparts.

in order to obtain the entire adsorption isotherm. For each uptake, the equilibrium was reached and the mass recorded versus time.

The *N,N*-diethyl-*m*-toluamide (DEET, 97% Aldrich) solutions were prepared in the concentration range of 40–1000 mg L⁻¹ in deionized water. Adsorption experiments were carried out using a batch equilibration technique. For each equilibrate isotherm [4,23], 40 mg of the adsorbent was added to 20 mL of solution and stirred for 24 h at 298 K in a batch equipment until equilibration. Samples were periodically collected (20 μ L) and analyzed using a HPLC instrument (Varian Prostar) equipped with a reverse-phase column (ChromSpher Pesticides) and a UV detector ($\lambda = 213$ nm, model 340) with a mobile phase of methanol/water (70/30, v/v) with 0.1% acetic acid (flow rate of 1 mL min⁻¹).

3. Results and discussion

3.1. Physico-chemical and textural properties

The trimethylsilyl (TMS) and phenyl (Ph) group density of the functionalized MCM-41-S_x and HMS-S_x silica samples was determined by their carbon content. The corresponding values are listed in Table 1. It appears that the highest carbon amount that is possible to introduce by TMS silylation is around 7% for HMS silica materials, while it reaches 8.5% in the case of the MCM-41 silica, thereby indicating that the surface functionalized samples are highly silylated with a TMS coverage of 90 and 89%, respectively. These values have been calculated assuming that one TMS group covers 47.6 Å^2 [24].

Small-angle X-ray diffraction patterns obtained for the calcined parent MCM-41 and HMS mesoporous silica samples and their corresponding surface functionalized counterparts are presented in Fig. 1. X-ray diffractograms confirmed that the hexagonal ordering in the calcined MCM-41 silica was retained after the post-synthesis surface functionalization treatments. As for the calcined parent MCM-41 sample, the phenyl-incorporated silica (MCM-41-Ph) as well as the silylated MCM-41-S2 displayed well-resolved XRD lines. Note that in the latter case, the interplanar spacing of the first diffraction peak, namely the (1 0 0) reflection, was rather broad due to the high silylation degree of the mesoporous silica. As expected, less well resolved XRD lines were observed for HMS type materials compared with MCM-41 samples, indicating a lower long range order of the pore structure. The X-ray diffraction pattern of the calcined parent HMS silica exhibited a single intense diffraction peak characteristic of the (1 0 0) crystallographic plane of the hexagonal pore structure. As observed for the silylated MCM-41-S2 sample,

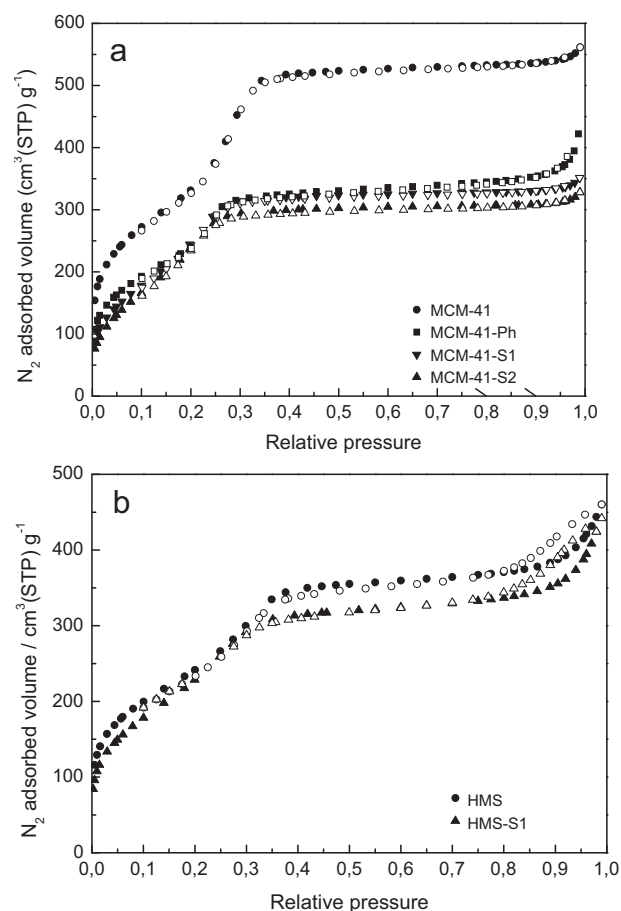


Fig. 2. N₂ adsorption-desorption isotherms at 77 K of the various MCM-41 (a) and HMS (b) silica samples.

the silylation post-synthesis treatment also resulted in a lower regularity of the pore array of the HMS sample, with respect to the unfunctionalized silica. The values of the XRD interplanar spacing ($d_{(100)}$ distances) and a_0 unit cell assuming a hexagonal structure, as well as the wall thickness of each sample (ϵ), are summarized in Table 2. The lattice parameter $a_0 = 2 (d_{100} 3^{1/2})$ is a measure of the average distance between the two neighboring pore centers in the mesoporous silica structure. Whatever the type of the calcined mesoporous silicas (MCM-41 or HMS), a shift of the (1 0 0) reflection to lower 2θ values was observed for the corresponding functionalized samples, leading to higher $d_{(100)}$ distances and cell parameters. The silylated and phenyl-incorporated silica samples exhibited far higher wall thickness values compared with that of the parent support. Such behavior may account for a better stability of the functionalized silica samples in aqueous solution.

Nitrogen adsorption-desorption isotherms at 77 K are shown in Fig. 2a and b for the calcined parent and the surface functionalized MCM-41 and HMS silica, respectively. Their textural properties and pore characteristics are listed in Table 2. Classical type IV isotherms according to the IUPAC classification were observed for all samples. The condensation of nitrogen in the (primary) mesopores of the calcined parent MCM-41 silica took place at a relative pressure of about 0.06, whereas it occurred slightly later ($P/P_0 = 0.16$) for the corresponding silylated and phenyl-incorporated MCM-41 samples. The jump was reversible for all the MCM-41 silica and became less marked when the surface functionalization degree increases. No hysteresis loop was noticed for nitrogen desorption from primary mesopores. This indicates that the cylindrical mesopore diameter is lower than 4 nm and that the mesopore

Table 1
Chemical properties of the calcined parent MCM-41 and HMS silica samples and of their corresponding surface functionalized counterparts.

Samples	C content (%)	TMS or phenyl density ^a (group nm ⁻²)	Silanol density ^b (OH nm ⁻²)
MCM-41	0.26	0	2.31
MCM-41-S1	5.49	1.26	2.05
MCM-41-S2	7.56	1.80	1.58
MCM-41-S3	8.55	1.77	0.87
MCM-41-Ph	9.23	1.03	ND
HMS	0.71	0	2.26
HMS-S1	5.81	1.52	1.44
HMS-S2	6.96	1.70	1.01

ND, not determined.

^a Determined from C content and BET area values.

^b Determined from C content, TGA-DTA analysis and BET surface values.

Table 2
Physical properties of the calcined parent MCM-41 and HMS silica samples and of their corresponding surface functionalized counterparts.

Samples	BET area ^a (m ² g ⁻¹)	External area ^b (m ² g ⁻¹)	V _{meso} ^b (cm ³ g ⁻¹)	d _{pore} ^c (nm)	d ₁₀₀ (nm)	d ₀ (nm)	ε _{wall} (nm)
MCM-41	992	36	0.793	3.32	3.63	4.19	0.68
MCM-41-S1	693	23	0.488	2.91	ND	ND	ND
MCM-41-S2	678	16	0.461	2.79	3.95	4.56	1.16
MCM-41-S3	783	84	0.503	2.88	ND	ND	ND
MCM-41-Ph	749	81	0.464	2.78	3.93	4.53	1.15
HMS	735	90	0.497	3.08	3.43	3.96	0.95
HMS-S1	562	82	0.330	2.75	3.51	4.05	1.30
HMS-S2	613	77	0.386	2.88	ND	ND	ND

ND, not determined.

^a A value of 0.136 nm² is used for N₂ area adsorbed on hydroxylated surface (see text).

^b Estimated from α_s plot.

^c Estimated from the Gurvitch method, $d = 4 V_{\text{meso}} / (A_{\text{BET}} - A_{\text{ext}})$.

size distribution is uniform [25]. The surface area was calculated by the Brunauer–Emmet–Teller (BET) method by using a value of 0.136 nm² for N₂ area. This value is generally used for nitrogen adsorption on hydroxylated surfaces [26,27]. A decrease in both specific surface area, mesopore volume (determined from α_s plot) and pore diameter was logically observed after the surface functionalization procedure (silylation and anchoring of phenyl groups) of the MCM-41 samples. Moreover, the external surface area values are low, thereby indicating a very low secondary mesoporosity inside all of the MCM-41 type silica materials. In contrast to those samples, the shape of the N₂ isotherms as well as the external surface area data of the HMS type samples, clearly confirmed that they exhibited a secondary mesoporosity, namely mesopores with a diameter ≥ 15 nm. A hysteresis phenomenon was systematically observed during N₂ desorption from these mesopores. The presence of such larger non ordered mesopores stemmed from the less well organized pore arrangement of the HMS structure than that of the MCM-41 type silica. As expected, silylation induced a clear decrease of the primary mesopore size of the modified HMS samples and of the corresponding mesoporous volume. All MCM-41 and HMS samples exhibited comparable mesopore accessibility after the surface functionalization procedure.

3.2. Organophilicity/hydrophilicity characterization

Sample organophilic properties were evidenced by toluene adsorption isotherms. Fig. 3a shows the toluene adsorption isotherms for the calcined and modified MCM-41 silica samples at 298 K. The shape of toluene adsorption isotherm for the silylated sample did not perfectly fit that of the corresponding nitrogen isotherms. Toluene capillary condensation was shown to occur at higher relative pressure than the nitrogen one. Thus, for these modified samples, toluene adsorption isotherms were closer to type IV isotherms than did the nitrogen ones. The fact that the toluene capacity decreased when the silylation degree increased can be easily explained by the reduction of the mesoporous volume due to

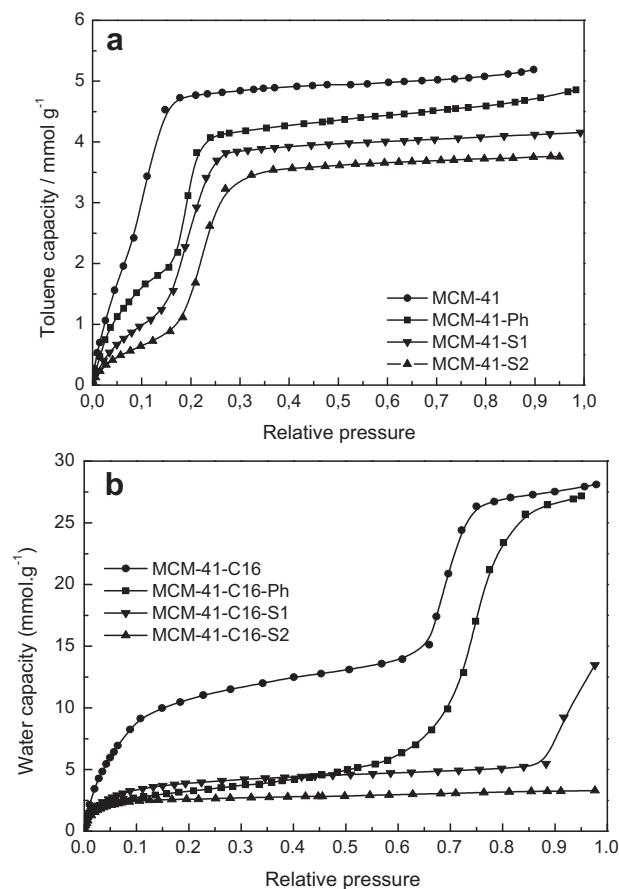


Fig. 3. Toluene (a) and water (b) adsorption isotherms at 298 K of the various MCM-41 silica samples.

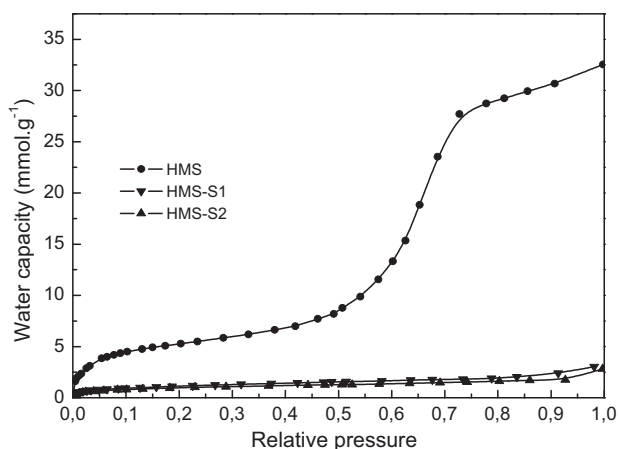


Fig. 4. Water adsorption isotherms at 298 K of the various HMS silica samples.

the TMS group steric hindrance. Nevertheless, a quite high toluene mesopore filling was observed since around 80% of the available mesoporous volume was occupied by toluene molecules, thereby indicating the organophilic characteristics of all the samples. In the case of the MCM-41-Ph sample, the presence of phenyl groups anchored on the mesopore walls clearly enhanced the organophilic properties of the grafted silica material. The toluene occupation rate is close to 100% for this sample, whereas it exhibited mesoporous volume and mesopore apertures very close to the silylated MCM-41-S2 silica. The organophilicity enhancement could be explained by π - π interactions between the toluene aromatic rings and the phenyl organic moieties of the functionalized MCM-41-Ph sample [28].

As demonstrated in a previous paper, superficial silanols are responsible for the hydrophilicity of mesoporous materials [21]. The silylation of the surface silanol groups is considered as an efficient way to increase the hydrophobicity of silica materials. For the calcined mesoporous silica, the silanol density was estimated from the weight loss observed between 473 and 1073 K by TGA-DTA and from the specific surface area of the materials [29–31]. By contrast, the silanol density for the organically modified MCM-41 and HMS silica samples was deduced by subtracting the number of grafted TMS groups per mass unit to the number of superficial silanol groups per mass unit of the calcined parent sample. Table 1 summarizes the silanol density values for the parent and modified silica samples. The silanol density depends on the silica synthesis conditions and on the nature of the post-synthesis treatment [29,31,32]. While being prepared according to different experimental conditions, calcined MCM-41 and HMS materials exhibited comparable silanol densities close to those reported in the literature for amorphous silica [33–35]. Silylation was shown to induce a significant decrease of the silanol densities for all modified MCM-41 and HMS silica samples.

The water adsorption isotherms are reported in Fig. 3b and 4 for the calcined parent and modified MCM-41 and HMS samples, respectively. The non-silylated MCM-41 and HMS water isotherm exhibited a significant water molecule condensation at relative pressure values higher than 0.65. Conversely, the silylation of the samples induced a drastic decrease of the water capacity within the silica mesopores. For high silylation degree (case of MCM-41-S2, HMS-S1 and HMS-S2 samples), no capillary water condensation occurred within the mesoporous channels, demonstrating an increase of the hydrophobic properties of the highly silylated MCM-41 sample. The presence of phenyl groups inside the mesopores also induces a hydrophobic character, as demonstrated by a significant decrease of the water capacity at low pressure

compared to calcined MCM-41. As shown in Fig. 3b, the water isotherm adsorption resembles to a type V.

From the water isotherms, the water monolayer density (water molecule per square nanometer) is calculated from Eq. (1).

$$\text{Water monolayer density} = \frac{N_{\text{mono}} \cdot N_A}{A_{\text{BET}} \cdot 10^{18}} \quad (1)$$

where N_{mono} is the water monolayer capacity (mol g^{-1}) estimated from the water isotherm BET equation [6,29,30], A_{BET} is the surface area evaluated from the nitrogen isotherm ($\text{m}^2 \text{g}^{-1}$), N_A is the Avogadro's number.

The obtained values are reported in Table 3. A significant decrease of the water monolayer density was observed for all organically modified MCM-41 and HMS silica samples, which is related to the decrease of the silanol density after the functionalization step. The silanol as well as the organic group densities can be correlated to the Hydrophobic static Index ($\text{HI}_{\text{static}}$). The Hydrophobic Index has been extensively used by several authors to describe the hydrophobicity in zeolites [36] and more recently in silica mesoporous materials. The HI index can be directly related to the surface chemistry of mesoporous silica samples. Because water adsorption occurs on silanols, a correlation between the $\text{HI}_{\text{static}}$ value and the remaining silanol number is indeed expected. The $\text{HI}_{\text{static}}$ index was calculated from single component water and toluene adsorption isotherms by Eq. (2):

$$\text{HI}_{\text{static}} = \frac{X_{\text{toluene}}}{X_{\text{water}}} \quad (2)$$

where X_{toluene} and X_{water} refer to the toluene or water weight capacities determined at a relative pressure equal to 0.8.

Table 3 lists the $\text{HI}_{\text{static}}$ values as well as the toluene and water capacities for the calcined and modified MCM-41 and HMS silica samples. The variations of the $\text{HI}_{\text{static}}$ values as a function of either the silanol density or the TMS or Ph group surface coverage for all modified MCM-41 and HMS samples are reported in Fig. 5a and b, respectively. It is clearly observed that the $\text{HI}_{\text{static}}$ values increased when the remaining silanol amount decreased (Fig. 5a) or when the organic group density increased (Fig. 5b). However, the increase of the hydrophobic static index value is not linear all over the silanol or organic moieties densities range. For both figures, two different behaviors with very different rates were indeed observed. As shown in Fig. 5a, for a high silanol density (low silylation degree), the resulting $\text{HI}_{\text{static}}$ values raised slowly whereas a large increase was observed for highly silylated samples (low remaining silanol amount values). A strong $\text{HI}_{\text{static}}$ increase was observed for a remaining silanol density around 1.3 silanol per square nanometer, which corresponds to a $\text{HI}_{\text{static}}$ index value equals to 6. A similar behavior was also evidenced on the figure showing the variation of the $\text{HI}_{\text{static}}$ index versus the organic moiety density (Fig. 5b). A significant increase of the hydrophobic static index (value ≥ 6) was again observed for the organically functionalized samples (case of MCM-41-S2, MCM-41-S3, HMS-S1 and HMS-S2 samples), for which no capillary water condensation occurred on the corresponding water adsorption isotherms (Fig. 3). This phenomenon was independent on the silica nature, which demonstrates that as soon as 50% of the superficial silanols are removed by silylation, the remaining silanol groups are sufficiently far from each other so as to avoid the water liquid meniscus formation within the mesopores. The resulting hydrophobic character displayed by the highly silylated samples was then significantly enhanced. Such highly functionalized silica samples are therefore expected to exhibit an increased stability in aqueous solution compared with their corresponding calcined and low silylated counterparts, for which the mesopore inner walls still reveal a pronounced hydrophilic character.

Table 3
Monolayer water density, hydrophobic static index value (HI_{static}), as well as water, toluene and DEET adsorption properties of the calcined and modified MCM-41 and HMS samples.

Samples	Monolayer water density ^a ($H_2O\text{ nm}^{-2}$)	HI_{static} ^b	Water capacity ^c ($mg\text{ g}^{-1}$)	Toluene capacity ^c ($mg\text{ g}^{-1}$)	DEET capacity ($mg\text{ g}^{-1}$)
MCM-41	5.3	1	484	467	8.2
MCM-41-S1	3.0	4.1	92.0	375	97.1
MCM-41-S2	1.7	5.9	57.6	342	156.0
MCM-41-S3	0.7	17.2	24	412	175.4
MCM-41-Ph	3.6	1.0	421	422	76.3
HMS	3.6	0.9	518	492	7.7
HMS-S1	1.0	7.7	35.1	271	156.2
HMS-S2	0.8	10.4	29	302	178.6

^a Estimated from water isotherm using BET equation.

^b $HI_{static} = X_{toluene}/X_{water}$ where $X_{toluene}$ and X_{water} refer to the toluene or water weight capacities determined at $P/P_0 = 0.8$.

^c Evaluated at $P/P_0 = 0.8$.

3.3. *N,N*-diethyl-*m*-toluamide (DEET) adsorption in aqueous solution

The ability of the surface functionalized (silylated and phenyl-incorporated) MCM-41 and HMS samples to adsorb an organic pollutant, namely DEET, was then evaluated in aqueous solution. The performances of the modified samples were compared with those of the as-synthesized and calcined analogs and with those of a conventional adsorbent, namely a hydrophobic HY zeolite ($Si/Al = 40$). DEET adsorption isotherms at 298 K in aqueous solution for the HY zeolite and the various mesoporous samples are reported in Fig. 6a and b for MCM-41 and HMS silica, respectively. Whatever

the type of the silica, it appears that the shape of the isotherm and the maximum adsorption capacity did not depend on the available mesoporous volume. Calcined silica materials (MCM-41 and HMS) were shown to exhibit a low DEET adsorption. Even if these samples are considered as organophilic, they are also reported in the literature as materials having very low organic pollutant adsorption capacity in aqueous solution [11–13]. This *a priori* surprising result can be easily explained if we consider that such samples exhibit a high silanol density within the mesopores, which induces a preferential water adsorption, thereby avoiding the adsorption of the organic pollutant into the channels. In contrast, the adsorption capacity obtained for both MCM-41 and HMS as-synthesized samples (as-MCM-41 and as-HMS) was higher than those of the calcined ones. Such a behavior has also been reported in the literature [11–13] and is due to the ability of organic pollutant molecules

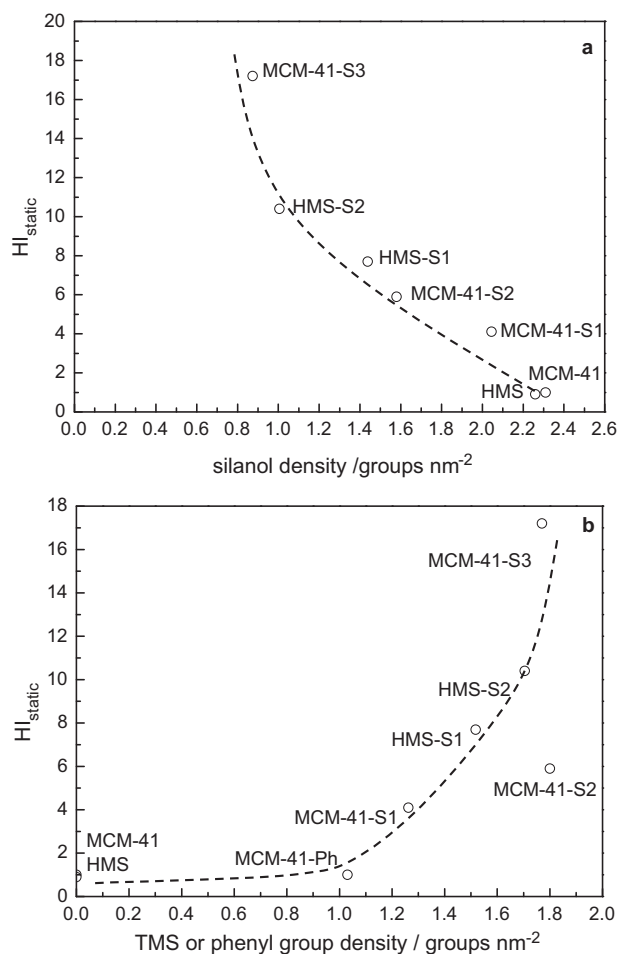


Fig. 5. Variation of the hydrophobic static index (HI) value as a function of the silanol density (a) and as a function of TMS or phenyl group density (b) for the calcined and surface functionalized MCM-41 and HMS silica samples.

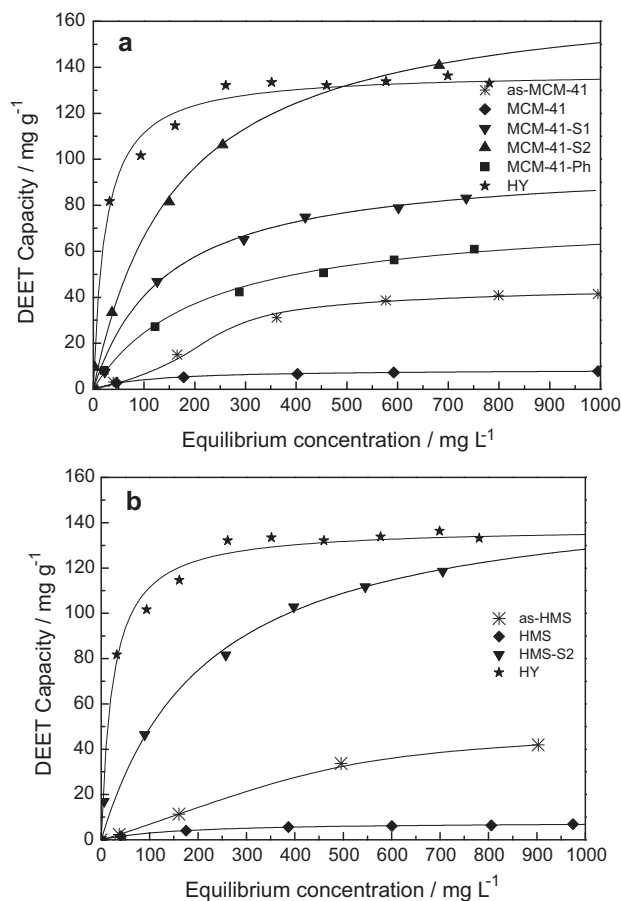


Fig. 6. DEET adsorption isotherms at 298 K of MCM-41 (a) and HMS (b) silica samples.

to be adsorbed by solubilization inside the hydrophobic templating micelles [11]. The DEET adsorption isotherm of the as-synthesized MCM-41 silica gave rise to a S-shape curve which can be modeled by the Fowler–Guggenheim equation (Eq. (3)):

$$C_e = \frac{K_{FG}\theta}{(1-\theta)} \exp(-C\theta) \quad (3)$$

where C_e is the equilibrium pollutant concentration in aqueous solution, $\theta = Q/Q_{max}$ the fractional coverage, Q the adsorbed quantity at C_e concentration, C a constant independent of the temperature, K_{FG} the Fowler–Guggenheim constant.

In this case, the adsorption capacity at low equilibrium concentration is very low indicating very weak interaction between the pollutant and the adsorbent. By contrast, the DEET adsorption on silylated mesoporous silica resulted in type I isotherms which can be fitted by the Langmuir model (Eq. (4)):

$$\theta = \frac{C_e K_L}{1 + C_e K_L} \quad (4)$$

where C_e is the equilibrium pollutant concentration in aqueous solution, $\theta = Q/Q_{max}$ the fractional coverage, K_L the Langmuir constant.

Even at very low pollutant concentrations, the adsorption capacity values were far higher than those obtained with the as-synthesized materials.

Moreover, DEET maximal adsorption capacities were calculated according to the Langmuir model (Eq. (4)) for calcined and silylated silica samples and to the Fowler–Guggenheim model (Eq. (3)) for the as-synthesized MCM-41 and HMS solids. The results presented in Table 3 indicated that all silylated silica samples were able to adsorb high DEET amounts, especially those exhibiting no capillary water condensation. The presence of phenyl groups on the surface of the MCM-41 mesopores also resulted in a significant increase of the DEET capacity by comparison with the corresponding calcined silica. However, the DEET maximal quantity of the MCM-41-Ph sample was lower than that of the silylated samples because of its important silanol density. The variation of the DEET maximal amount was then plotted as a function of the TMS (or Ph) group density (Fig. 7a) or of the hydrophobicity static index for the modified silica samples, with the aim of highlighting the major role played by the adsorbent silanol amount on the organic pollutant adsorption. In fact, a clear correlation could be found between the pollutant maximal sorption capacities and the organic group density (Fig. 7a) or the HI_{static} (Fig. 7b) values for the calcined and silylated MCM-41 and HMS samples. The DEET sorption capacities were shown to increase significantly with the amount of organic groups within the mesopores. However, a maximum of the DEET sorption capacity was reached (Fig. 7a) in the case of the highly silylated materials (MCM-41-S2, -S3, HMS-S1, -S2 samples). When more than 50% of the superficial silanol groups have been removed by functionalization (which corresponds to HI_{static} values higher than 6), DEET sorption capacities could not raise any longer even if a clear increase of the HI_{static} value was observed when increasing the silylation degree (Fig. 7b). According to these data, the maximal DEET quantity that can be adsorbed by the silylated MCM-41 and HMS silica samples seems to be fixed to 180 mg g^{-1} , which corresponds to an occupation of around 50% of the mesoporous volume by DEET molecules. This amount can be reached when the silica adsorbents exhibit a significant hydrophobic character, so as to avoid water capillary condensation within the mesopores.

In the case of the hydrophobic HY zeolite, the maximal adsorbed DEET quantity was lower (138 mg g^{-1}) than that of the organically modified mesoporous silica ($\sim 180 \text{ mg g}^{-1}$). This zeolite exhibits a higher DEET sorption capacity at low concentration than the one of the functionalized silica samples, indicating stronger adsorbent–pollutant interactions. As a consequence, the recovery

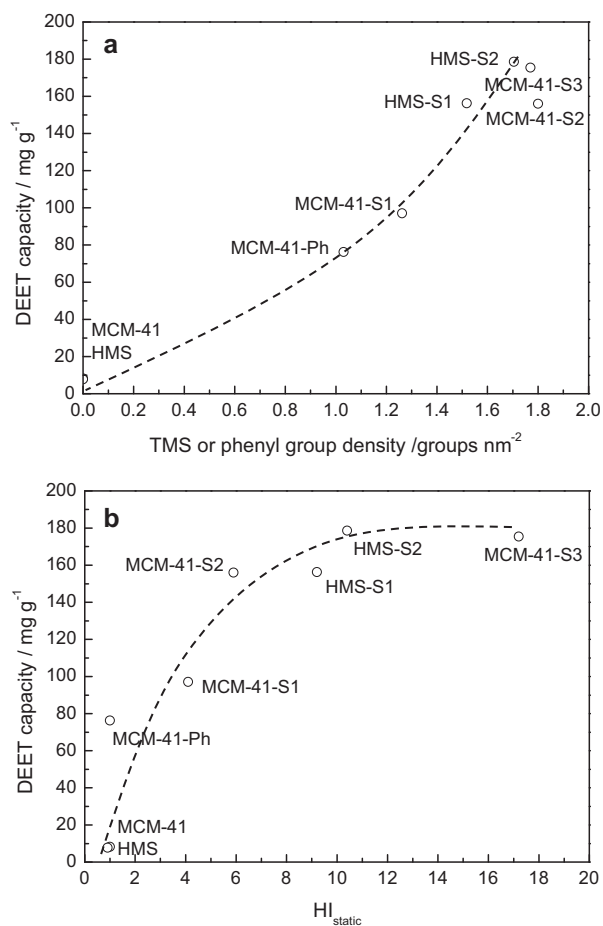


Fig. 7. Variation of the DEET maximal capacity as a function of TMS or phenyl group density (a) and of HI_{static} values (b) for the calcined and surface functionalized MCM-41 and HMS silica samples.

of the zeolitic adsorbent during DEET pollutant desorption steps (by thermal treatment) is thereby more difficult than in the case of the silylated mesoporous silica adsorbents, for which the interactions are weaker. The corresponding values of the K_L Langmuir constants calculated from Eq. (4) are 0.042 and 0.0061 for the HY zeolite and the MCM-41-S3 samples, respectively.

4. Conclusion

The fine tuning of the hydrophilic/hydrophobic balance of mesostructured silica materials through proper hydrophobic derivatization is a key factor to design competitive mesoporous adsorbents in gas phase or in aqueous solution. With respect to the phenyl groups surface functionalization route, silylation of the superficial silanol groups of mesoporous MCM-41 and HMS materials was shown to be an appropriate post-synthesis treatment to both reduce their mesopore size and to enhance their hydrophobic character. The grafting of trimethylsilyl moieties on the inner surface of the mesopores allowed us to decrease considerably the amount of initial silanols and thereby to increase the hydrophobic properties of the silica samples as a function of the silylation degree. Silanol density appeared to be the only factor responsible for hydrophobicity. A clear correlation was found between the hydrophobic index (HI) and either the silanol group density, or the amount of organic groups for all functionalized silica samples. Below 50% of the superficial initial silanols, the hydrophobic character of the highly silylated silica samples was significantly enhanced, because the silanol groups are sufficiently dispersed and

isolated, thereby avoiding the water capillary condensation. The use of the hydrophobic static index thereby appears as an efficient tool to forecast the hydrophobic character of porous materials for the adsorption of organic pollutants.

In the case of toluene adsorption in gas phase, the silylation procedure did not result in a clear enhancement of the organophilic properties of the silica material. Despite all the modified materials exhibited important organophilic properties since the mesoporous filling by toluene in gas phase is close to 80%, silylation did not favor the adsorption of high toluene quantity at low relative pressures. No type I toluene isotherms were indeed observed, due to the TMS group steric hindrance that induced a delay of the capillary toluene condensation.

By contrast, all silylated MCM-41 and HMS mesoporous silica materials exhibited high DEET sorption capacities in aqueous solution, by reducing or even avoiding the adsorption of water molecules for increasing silylation degrees. The elimination of the water capillary condensation within the mesopores appeared as a prerequisite in order to enhance the hydrophobicity of the silica samples. The DEET adsorption capacities for the highly silylated silica samples were more than 20 times higher than that of the corresponding unmodified calcined silica, demonstrating that such surface functionalized mesoporous materials could behave as efficient adsorbents in aqueous solution.

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