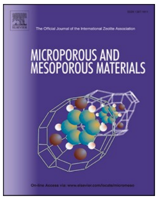
Microporous and Mesoporous Materials 313 (2021) 110809

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: http://www.elsevier.com/locate/micromeso



# Effect of surface chemistry on the uptake of lignin-derived aromatic molecules on ordered mesoporous silica

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ARTICLE INFO

*Keywords:*
Ordered mesoporous silica
Guaiacol
Surface functionalization
Adsorption

ABSTRACT

A series of functionalized ordered mesoporous silica (OMS) materials were synthesized, characterized, and tested for their ability to uptake lignin-derived molecules such as guaiacol from dilute aqueous solution. A key observation was that OMS materials functionalized with hydrophobic groups have modest guaiacol uptake (<0.5 mmol/g), similar to what was observed with poly(styrene-*co*-divinylbenzene). Contact angle measurements show that samples with intermediate hydrophobicity in terms of wetting (between 60 and 100°) display superior uptake properties. Oasis HLB, an example of such a material displays higher guaiacol uptake (0.8 mmol/g) as does as-made MCM-41, wherein the CTAB is left in the pores (AM-MCM-41, 0.7 mmol/g). Pore-expanded FDU-12 with a range of surface chemistries was synthesized and tested in an effort to generate a covalently grafted analogue of AM-MCM-41, however none of the materials showed uptakes above 0.35 mmol/g. Finally, other aromatic molecules such as vanillin, catechol, pyrogallol also showed high uptake (0.4 mmol/g or high) over Oasis HLB and AM-MCM-41. The findings suggest new routes for designing hybrid materials that can selectively remove lignin derivatives from dilute aqueous solutions.

## 1. Introduction

Lignocellulosic biomass has garnered much attention as an alternative feedstock for fuels [1–5] and specialty chemicals [6,7]. It is thought of as a renewable and environmentally friendly energy source compared to fossil fuels because it is a major component in the cell walls of plants and consequently inexpensive and replenishable [8]. However, the major components of biomass (cellulose, hemicellulose and lignin) must be depolymerized as part of upgrading to chemicals [9], which requires high-temperature pyrolysis or hydrolysis [10–12]. This produces a wide range of molecules with the major component being sugars, but also many aromatic lignin-derived compounds such as guaiacol, catechol, vanillin, and many similar molecules [13,14]. These aromatic side products have been shown to be detrimental to enzymatic sugar conversion [15] and also could potentially be upgraded to more valuable chemicals, giving rationale for separation from the depolymerization broth.

Solid-phase adsorption has been shown to be an efficient and low energy input method to separate dilute aqueous aromatic molecules [16], but traditional high-surface area separation materials such as zeolites [17] and activated carbon [18,19] are inherently non-selective towards specific molecules. As an alternative, hybrid inorganic-organic materials have been synthesized and tailored with organic moieties in an attempt to extract the desired molecules. This has been demonstrated for the adsorption of biomass relevant compounds with a variety of different materials including metal-organic frameworks [20,21], organically functionalized silica gel [22], and organically functionalized ordered mesoporous silica (OMS) [23–28]. The organic groups were reported to mostly rely on hydrophobicity [23,24], electrostatics [23,26,27], and π-π interactions [20–22] to perform the selective separation of the aromatic groups, but since the depolymerization broth likely contains a large amount of water, functionalizing with a large amount of hydrophobic groups could lead to significant issues with the wettability of the adsorbent [29].

Hydrophobic polymer sorbents cross-linked with hydrophilic monomers have been shown to more efficiently capture polar aromatic compounds from water [29] when compared to purely hydrophobic compounds and have been used in removal of a variety of polar contaminates [30–34]. There are a range of proprietary adsorbents available with one of the most reported on in literature being Oasis HLB, a poly(*N*-vinylpyrrolidone-divinylbenzene) copolymer [29], as well as many academic laboratory synthesized adsorbents with of a variety of

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https://doi.org/10.1016/j.micromeso.2020.110809
Received 3 July 2020; Received in revised form 29 November 2020; Accepted 1 December 2020

chemical functionalities reported [32,35–37]. However, due to synthesis difficulties it is not straightforward to compare monomers while keeping porosity consistent between samples. An alternative would be to utilize an easily synthesizable high surface area silica-based adsorbent that allows for surface functionalization of chemically tailored hydrophilic/hydrophobic groups.

OMS has been extensively used as a support in separations [38–41], catalysis [42–44], and drug delivery [45,46] due to the wide-variety of chemical moieties that have been successfully grafted on the silica surface as well as its chemical inertness, high surface-area, and mechanical robustness. For these reasons OMS is used in this study as a support for incorporation of functional groups that are selective towards the extraction of model aromatic compounds relevant to lignocellulose depolymerization solutions. Guaiacol was chosen as the model aromatic molecule because of its relatively high concentration (around 0.5% by volume) in standard lignocellulose depolymerization broths [47–49]. Additionally, because guaiacol contains a hydroxyl and methoxy chemical moiety it makes for an interesting molecule to tune ligand affinity.

Herein, guaiacol uptake is investigated using OMS covalently grafted with hydrophobic groups as well as molecules that contain a long chain aliphatic carbon chain and a quaternary ammonium group to obtain a hydrophobic adsorbent that is also wettable in aqueous solution. These quaternary ammonium functional groups have been recently shown to have advantageous properties for a variety of applications [26,27,50,51], but have yet to be applied to biomass relevant separations nor has their surface chemistry been fully explored. Additionally, the in-house synthesized materials were compared to two commercial polymeric adsorbents. The results presented here show that samples that partially wet, likely due to a combination of hydrophobic and hydrophilic groups, display the best uptake.

## 2. Experimental

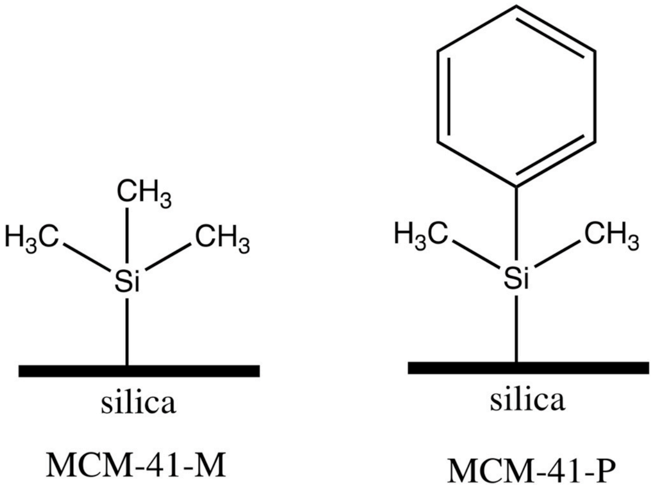
*Materials.* Tetraethoxysilane (TEOS, 99.9%), cetyltrimethylammonium bromide (CTAB, 98%), and 1,3,5-trimethylbenzene (98%) were purchased from Alfa Aesar. 2 M hydrochloric acid (HCl), 0.5 M sulfuric acid ($H_2SO_4$), sodium hydroxide (NaOH), sodium chloride (NaCl), and toluene were purchased from BDH (ACS reagent grade). Pluronic F127 ($EO_{101}PO_{56}EO_{101}$, MW = 12,600), poly(styrene-*co*-divinylbenzene) microspheres, and hexamethyldisilazane (99%) were purchased from Sigma-Aldrich. 11-bromoundecyltrimethoxysilane (95%), *N*-trimethoxysilylpropyl-*N,N,N*-trimethylammonium chloride (50% in methanol), 1,3-diphenyl-1,1,3,3-tetramethyldisilazane, and dodecyltrichlorosilane were purchased from Gelest. ACS grade methanol was purchased from EMD Millipore. N® sodium silicate (28.7 wt% $SiO_2$, $SiO_2/Na_2O = 3.22$ (weight)) was provided by the PQ corporation. Pyrogallol (99%), guaiacol (99%), trimethyloctadecyl[3-trimethoxysilyl)propyl]ammonium chloride (TOTSA, 60% in methanol), and trimethylamine (TMA, 4.2 M in ethanol) were purchased from Acros Organics. Vanillin (98%) and catechol (99%) were purchased from BeanTown Chemical. Oasis HLB (removed from 30 mg sorbent/cartridge) was purchased from Waters Corporation. Toluene was purified using an MBRAUN MB-SPS solvent purification system. All other chemicals were used as received.

*OMS Synthesis.* MCM-41 was synthesized using the synthesis procedure of Edler and White [52]. As an example, 15.8 g of sodium silicate solution were added to a Teflon vessel, and mixed with 75.2 mL deionized water. Then, 0.54 g of solid NaOH was added to the solution followed by the addition of 14.58 g CTAB. The sample was stirred for 1 h at room temperature. Subsequently, 31.2 mL of 0.5 M $H_2SO_4$ was added to this and stirred for 15 min at room temperature. The mixture was then placed in an oven at 100 °C for 24 h under static conditions. After 24 h the sample was taken from the oven, cooled down to room temperature, and 1.0 N $H_2SO_4$ was added to the solution dropwise to adjust the pH to approximately 10. The sample was then put back in the oven at 100 °C. The titration step was performed two additional times in regular 24-h intervals. The total heating period was 96 h. The mixture was then cooled, the solid products filtered, washed with deionized water, and dried at 80 °C overnight. If it was desired to remove the CTAB from the pores, the solid products were then calcined to remove the organic molecule used in synthesis. The calcination procedure was as follows: the air-dried samples were heated from room temperature to 100 °C at a rate of 1 °C/min; held at 100 °C for 2 h; subsequently increased from 100 to 550 °C at a rate of 1 °C/min; and then held at 550 °C for 8 h.

*Synthesis of FDU-12.* Pore-expanded FDU-12 was synthesized with a modified procedure first reported by Fan et al. [53] 0.666 g of Pluronic F-127, 1.66 g KCl, and 0.8 g of 1,3,5-trimethylbenzene were added to 40 mL of 2 M HCl in a 100 mL Teflon vessel. This was then vigorously stirred for 1 h to dissolve the solids. Then, 2.76 g of TEOS was added and vigorously stirred for 24 h at room temperature. The mixture was then pipetted from the Teflon vessel to a 60 mL Teflon lined steel autoclave and place in a 140 °C oven and kept under static conditions for 24 h. The autoclave was then allowed to cool for 2 h and the solid products were filtered with excess DI water and dried at 80 °C overnight. For samples where it was desired to fully remove the surfactant from the pores, the powders were then calcined to remove the organic molecules used in synthesis. The calcination procedure was as follows: the air-dried samples were heated from room temperature to 100 °C at a rate of 1 °C/min; held at 100 °C for 2 h; subsequently increased from 100 to 550 °C at a rate of 1 °C/min; and then held at 550 °C for 8 h. If it was desired to keep surfactant in the pores, the process was the same except there was no calcination step.

*Synthesis of Functionalized MCM-41.* Hydrophobic functionalized MCM-41 was prepared post-synthetically by placing 1 g of calcined powder in a 250 mL round-bottom flask and dried under vacuum on a Schlenk line. The pressure was then equilibrated with argon and an aliquot of hexamethyldisilazane, MCM-41-M, or 1,3-diphenyl-1,1,3,3-tetramethyldisilazane, MCM-41-P, (419 or 580 μL for 2 mmol/g, respectively) in 100 mL of anhydrous toluene was added. This mixture was stirred overnight in a closed container at room temperature. The product was collected by filtration, washed sequentially with toluene, methanol, deionized water, and then dried under vacuum for 24 h. Scheme 1 shows a cartoon of the idealized functionalized surface.

*Synthesis of Functionalized FDU-12.* Pore-expanded FDU-12 functionalized with hydrophobic dodecyl carbon chains (F–C12), quaternary ammonium bromide (F-Quat1), or trimethyloctadecyl (propyl)ammonium chloride (F-Quat3) was prepared post-synthetically by placing 1 g of calcined powder in a 250 mL round-bottom flask and dried under vacuum using a Schlenk line. The pressure was then equilibrated with argon and an aliquot of dodecyltrichlorosilane (593 μL for 2 mmol/g),



**Scheme 1.** Cartoon of idealized functionalized MCM-41-M and MCM-41-P.

11-bromoundecyltrimethoxysilane (635 μL for 2 mmol/g), or trimethyloctadecyl[3-trimethoxysilyl)propyl]ammonium chloride, 60% in methanol, (4.7 mL for 5 mmol/g) in 100 mL of anhydrous toluene was added. This mixture was stirred overnight in a closed container at room temperature. For F-Quat1, the flask was then transferred to an oil bath and heated to 80 °C while stirring. Then, 5 mL of 4.2 M trimethylamine in ethanol was added and stirred for 48 h to form the quaternary ammonium bromide group. The products were collected by filtration, washed sequentially with toluene, methanol, deionized water, and then dried under vacuum for 24 h.

Pore-expanded FDU-12 functionalized with quaternary ammonium or polyethylene glycol on the outside surface and dodecyl carbon chains in the internal pores, labeled F-Quat2 or F-PEG respectively, was prepared post-synthetically by placing 1 g of uncalcined powder in a 250 mL round-bottom flask and dried under vacuum using a Schlenk line. The pressure was then equilibrated with argon and an aliquot of *N*-trimethoxysilylpropyl-*N,N,N*-trimethylammonium chloride, 50% in methanol, (111 μL for 0.2 mmol/g) or 2-[methoxy(polyethyleneoxy)$_{6-9}$trimethoxysilane, (98 μL for 0.2 mmol/g) in 100 mL of anhydrous toluene was added. This mixture was stirred overnight in a closed container at room temperature. The product was collected by filtration, washed sequentially with toluene, methanol, deionized water, and then dried under vacuum for 24 h. The FDU-12 functionalized with quaternary ammonium on the outer surface was then transferred to a 250 mL round bottom flask. 150 mL of methanol and 100 mL of DI water were then added, and the mixture was heated to 110 °C while connected to a condenser. The mixture was then refluxed for 12 h, then filtered and washed with 100 mL of methanol and water then dried under vacuum. This process was repeated three times to fully remove the F-127 from the pores. The internal pores were then grafted with hydrophobic dodecyl carbon chains by placing 1 g of calcined powder in a 250 mL round-bottom flask and dried under vacuum using a Schlenk line. The pressure was then equilibrated with argon and an aliquot of dodecyltrichlorosilane (593 μL for 2 mmol/g) in 100 mL of anhydrous toluene was added. This mixture was stirred overnight in a closed container at room temperature. The product was collected by filtration, washed sequentially with toluene, methanol, deionized water, and then dried under vacuum for 24 h.

Co-condensation of trimethyloctadecyl[3-(trimethoxysilyl)propyl] ammonium chloride with pore-expanded FDU-12 was synthesized as follows. 0.666 g of Pluronic F-127, 1.66 g KCl, and 0.8 g of 1,3,5-trimethylbenzene were added to 40 mL of 2 M HCl in a 100 mL Teflon vessel. This was then vigorously stirred for 1 h to dissolve the solids. Then, 2.76 g of TEOS and either 750 μL or 75 μL of trimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride, 60% in methanol, (10:1 and 100:1 respectively) was added and vigorously stirred for 24 h at room temperature. The mixture was then placed in a 110 °C oven and kept under static conditions for 24 h. The Teflon vessel was then allowed to cool for 2 h and the solid products were filtered with excess DI water and dried at 80 °C overnight. The dried powder was then transferred to a 250 mL round bottom flask. 150 mL of methanol and 100 mL of DI water were then added, and the mixture was heated to 110 °C while connected to a condenser. The mixture was then refluxed for 12 h, then filtered and washed with 100 mL of methanol and water then dried under vacuum. This process was repeated three times to fully remove the F-127 from the pores. Scheme 2 shows the various functional groups attached to FDU-12.

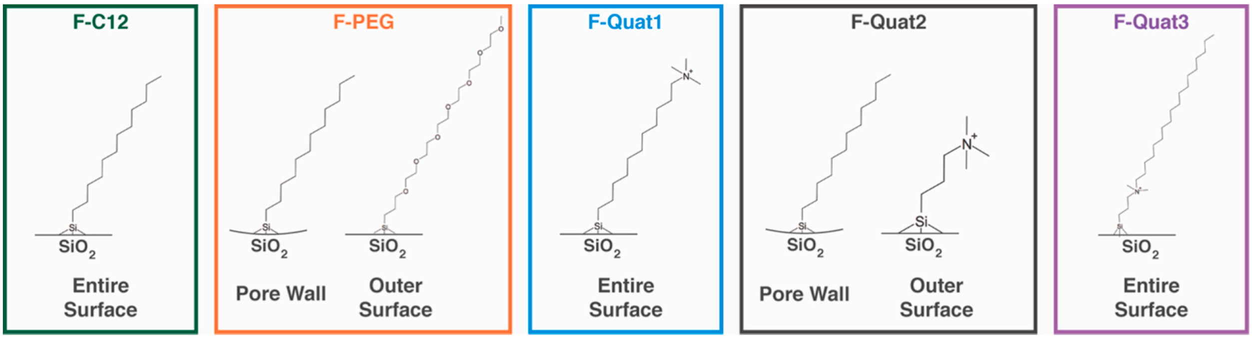
*Uptake of Phenolic Compounds.* The desired sample was added to a 11 mL vial and mixed with 2 mL of aqueous solution. The slurry was mixed for 12 h then centrifuged at 5000 rpm (2795 *g*) for 10 min. The supernatant was then removed and filtered with a 0.45 μm PTFE syringe filter. Equilibrium concentrations were determined using high-performance liquid chromatography (HPLC) on an Agilent 1260 Infinity fitted with an ACE Equivalence C18 HPLC Column. A mobile phase flow rate of 0.6 mL/min and the absorbance at 210 nm on a UV–vis detector was used for all measurements. The mobile phase was a gradient of water/acetonitrile (60/40–45/55 for 10 min). The HPLC injections were done in triplicate for each experimental point. Uptake was calculated with Equation (1) where $C_0$ is initial concentration, $C_{eq}$ is equilibrium concentration, $m$ is mass of powder used, and $V$ is volume of the solution.

$$q_e = \frac{C_0 - C_{eq}}{\frac{m}{V}} \tag{1}$$

Eq. (1). Calculation of the equilibrium uptake.

*Analytical Methods.* X-ray diffraction (XRD) patterns were collected using a Rigaku MiniFlex 600 instrument. Thermogravimetric analysis (TGA) measurements were conducted on a TA Q500 instrument over a temperature range of 25–600 °C and a ramp rate of 1 °C/min. Nitrogen adsorption experiments were measured on a Micromeritics ASAP 2020 instrument using approximately 50 mg of sample. Prior to analysis the samples were degassed at 100 °C for 24 h. The mesopore volume and surface area was determined from the $\alpha_s$-method. The mesopore size distributions were calculated from the desorption branch of the isotherms using the Barrett-Joyner-Halenda (BJH) with a modified equation for statistical film thickness.

*Contact angle measurements.* Static contact angles were captured on a Ramé-Hart Model 250 Standard Goniometer/Tensiometer using DROPimage Advanced. In a typical measurement, a 10 μl drop of deionized water was placed on the pelletized samples. The water drop was allowed to equilibrate for approximately 15 s before a silhouette of the drop was captured by the software and the contact angle on each end of the drop was measured. The average contact angle was recorded. For each sample, at least 3 contact angle measurements were performed on different locations of the pelletized samples. All measurements were performed at room temperature. In cases when the drop either completely wetted the surface or wicked into the sample within ten seconds, the samples were considered completely wetting with a zero-degree contact angle.



**Scheme 2.** Comparison of organic functional groups grafted on FDU-12.

## 3. Results and discussion

### 3.1. OMS characterization

MCM-41 and pore-expanded FDU-12 were characterized using nitrogen adsorption and XRD to confirm pore volume and pore ordering with the calcined materials shown in Fig. 1(a). It can be seen that the MCM-41 has smaller pores approximately 3.7 nm in diameter when compared to 12 nm for FDU-12. The XRD patterns, Fig. 1(b) and (c), are consistent with previous reports and confirm successful synthesis of both materials [52,53].

Organic functional group loading was confirmed by TGA. Loading was quantified based on the mass of functional group combusted with loading values reported as mmol functional groups/g adsorbent.

### 3.2. Ligand screening

The goal of this work is to determine how surface chemistry can be used to maximize guaiacol uptake with OMS hybrids. Previous studies have shown hydrophobicity [23,24] and π-π interactions [20–22] are the primary governing factors in extracting aromatic compounds from aqueous systems giving rationale to test OMS capped with various aromatic and hydrophobic ligands. Experiments on MCM-41-M and MCM-41-P (not shown) where the ligand content in solution was varied showed that using 2 mmol/g of ligand during functionalization led to the highest surface loading of functional groups as determined by TGA, which was approximately 1.5 mmol/g. An initial concentration of 0.5% by volume (0.045 M) guaiacol was chosen for the batch uptake measurements as this is similar to the guaiacol concentration found in common biomass depolymerization products.

Fig. 2 shows the guaiacol uptake at 0.5 vol% (0.045 M) for the parent MCM-41, and methyl- (MCM-41-M) and phenyl- (MCM-41-P) functionalized MCM-41. It can be observed that the functionalized MCM-41 showed higher uptake than pristine MCM-41 (0.18 mmol/g), but there was little observable difference between MCM-41-M and MCM-41-P. The uptake values for MCM-41-M and MCM-41-P correspond to 51% and 54% uptake of the guaiacol present in solution. It is also worth noting that the MCM-41-M and MCM-41-P did not appear to disperse well in solution during the experiments, i.e. there were potential issues with wettability. This could be one possible cause of the uptake being lower than hoped, as the interfacial surface area was likely much lower than the high bulk surface area of the adsorbents. The interplay of wettability and hydrophobicity has previously been observed for the extraction of very dilute polar water-soluble molecules [32,34], and the wettability of these samples is quantified below via contact angle measurement (*vide infra*).

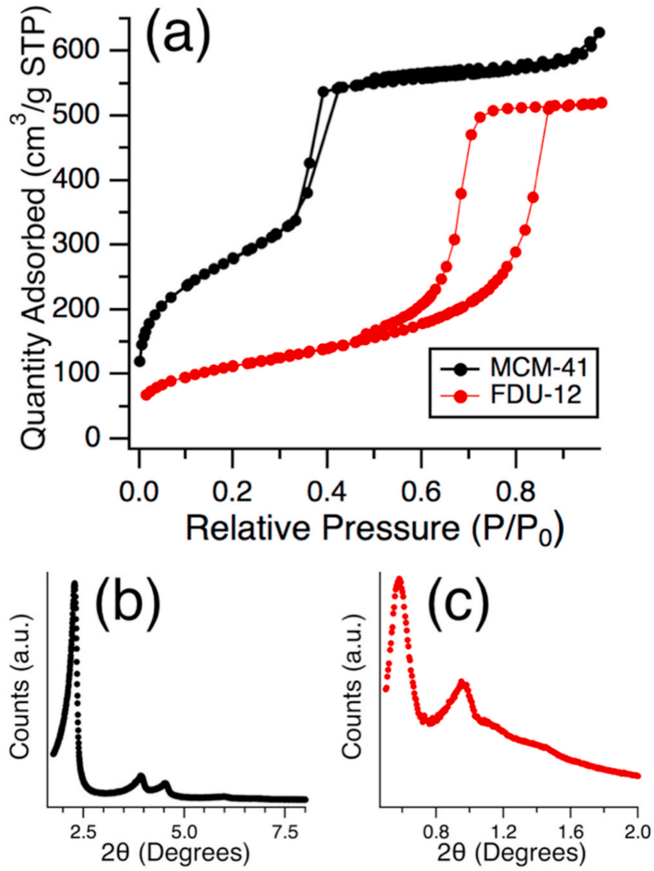


**Fig. 1.** (a) Nitrogen sorption isotherms for calcined MCM-41 and FDU-12. (b) XRD pattern for calcined MCM-41. (c) XRD pattern for calcined FDU-12.

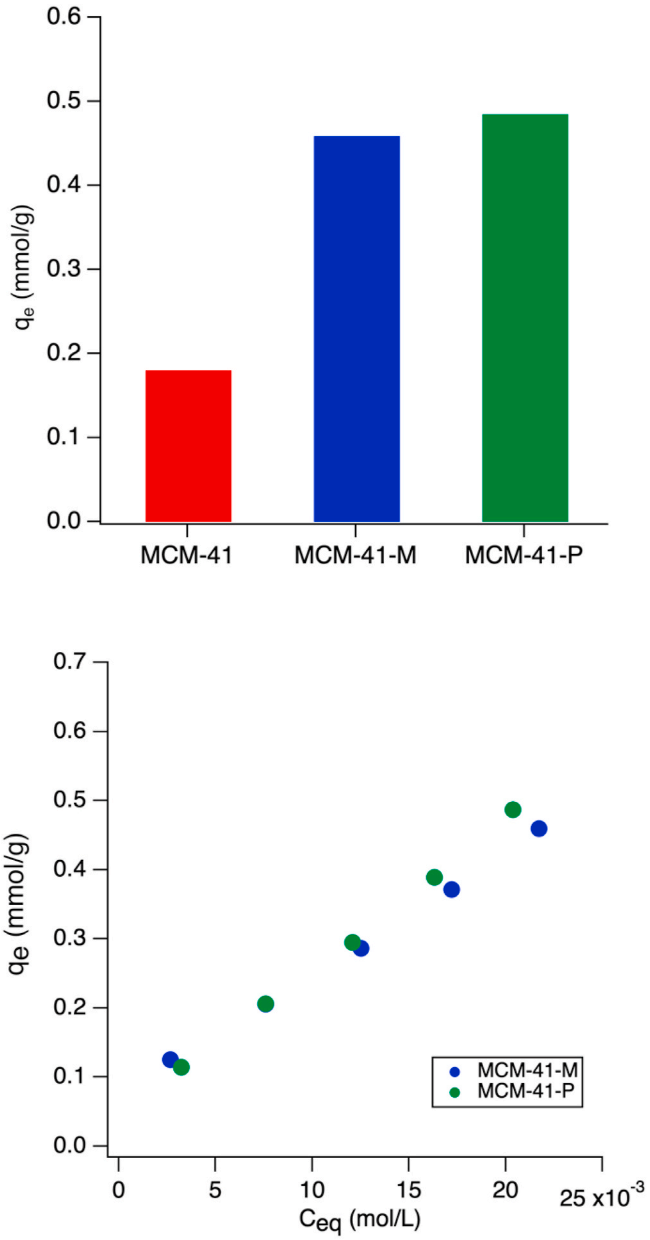


**Fig. 2.** (Top). Uptake from a 0.5% (0.045 M) guaiacol solution for MCM-41, MCM-41-M and MCM-41-P. (Bottom) Full isotherms of MCM-41-M and MCM-41-P.

For comparative purposes, two commercially available adsorbents, poly(styrene-*co*-divinylbenzene) (PSDVB) beads and Oasis HLB were also tested. PSDVB is a common aromatic hydrophobic adsorbent [32], and Oasis HLB is a proprietary polymeric structure manufactured by Waters Corporation, which has proven to be one of the industry standards for these adsorbents [32]. The uptake of these two materials, along with as-made MCM-41 are shown in Fig. 3. Consistent with Fig. 2, the highly hydrophobic PSDVB has modest uptake, whereas the Oasis HLB shows nearly twice the uptake of MCM-41-M and MCM-41-P. This is consistent with prior work whereby using hydrophobic polymers cross-linked with hydrophilic monomers, extraction of nonpolar phenolic compounds was much more successful.

Fig. 3 also shows that in the case of MCM-41 where CTAB was not removed from the pores by calcination, that a similar behavior was observed to that of the Oasis HLB adsorbent. CTAB is used as a structure directing agent during MCM-41 synthesis and the as-synthesized samples have mesopores full of CTAB. Typically, the CTAB is then removed by calcination to expose the high internal pore volume of MCM-41, but if not removed the pores are full of CTAB with the quaternary ammonium group near the surface and the $C_{16}$ group inside the pores. The guaiacol uptake of AM-MCM-41 was comparable to the Oasis HLB adsorbent. In terms of percent guaiacol removed from solution this corresponded to approximately 90% for Oasis HLB and 80% for AM-MCM-41. It was also observed that the AM-MCM-41 visually exhibited similar wettability to the Oasis HLB, suggesting adsorbent wettability may be important.

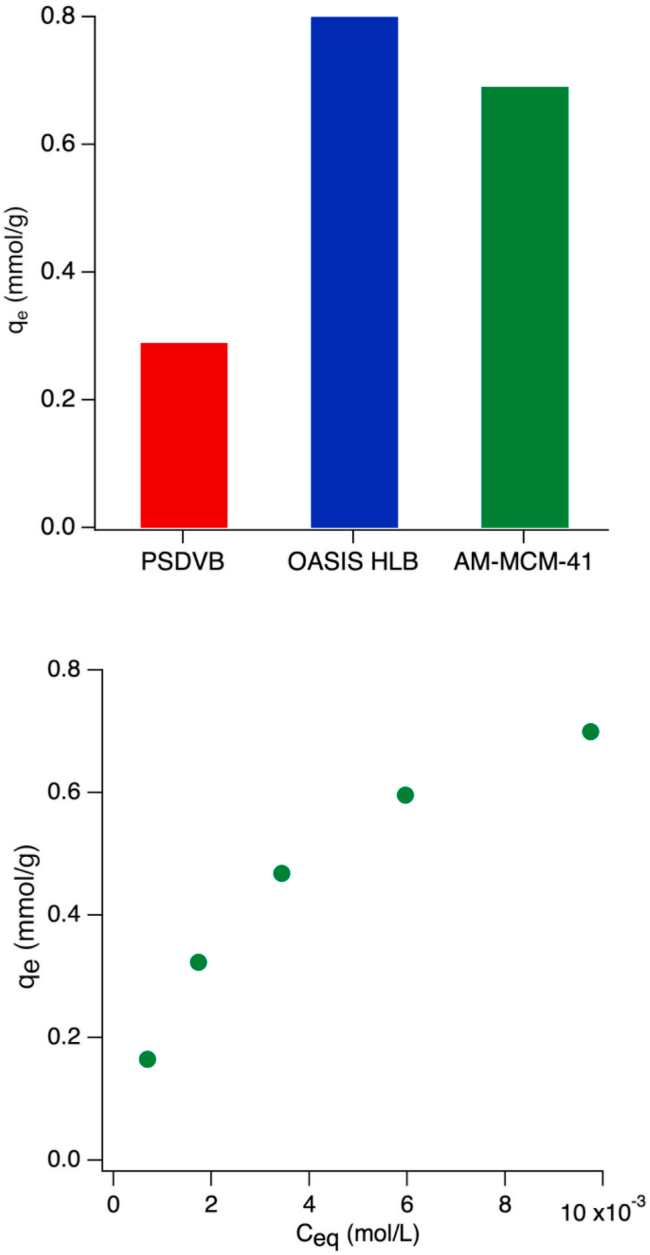


**Fig. 3.** (Top). Uptake of 0.5% (0.045 M) guaiacol on PSDVB, Oasis HLB, and as-made MCM-41 (AM-MCM-41). (Bottom) Full isotherm of AM-MCM-41. Note that in the case of AM-MCM-41 the sample was suspended in methanol for 4 h and then dried prior to uptake measurements to remove excess CTAB.

Contact angle measurements were performed on the samples shown in Figs. 2 and 3. The key finding was that all samples displayed complete wetting except AM-MCM-41, OASIS-HLB, and PSDVB. MCM-41-M and MCM-41-P took slightly longer to wet than the parent calcined MCM-41. The contact angle results for the AM-MCM-41, OASIS-HLB, and PSDVB are $64 \pm 2^\circ$, $92 \pm 1^\circ$, and $107 \pm 4^\circ$ respectively. This result suggests that the MCM-41-M and MCM-41-P uptake was *not* limited due to poor wetting, but rather purely hydrophobic adsorbents have limited guaiacol uptake. The contact angle results also suggest that partial wettability captures the mixed hydrophobic/hydrophilic character of the samples, which is key for a high-performing material.

### 3.3. *Recyclability of as-made MCM-41*

For an adsorbent to have industrial relevance at large scale, it must be shown to retain adsorption capacity over multiple recycles and the extracted molecule must be able to be recovered. For aromatic compounds extracted from aqueous solutions, the common method to remove the adsorbed material is by simply washing with a solvent polar enough, such as methanol, to remove the molecule of interest from the hydrophobic surface. The wash can then be collected, and the molecule utilized.

Recyclability of guaiacol extraction was tested on AM-MCM-41 because the physisorbed nature of CTAB makes it susceptible to loss during recycles, which would likely decrease the guaiacol adsorption capacity. Fig. 4(a) shows the results when washing the adsorbent with 30 mL of methanol then drying in between each recycle. The uptake after in the second cycle was significantly enhanced, likely due to removal of surface bound CTAB that does not participate in the uptake mechanism and only contributed to adsorbent mass. After this the uptake slightly decreased with each recycle and Fig. 4(b) shows the TGA weight loss of the AM-MCM-41 before and after 3 recycles. Clearly there is a significant mass loss (approximately 20%) which is likely responsible for the marginal loss of uptake. If one assumes the difference in the weight loss between the two traces is simply a result of CTAB leaching, then approximately 45–50% of the CTAB in AM-MCM-41 is lost over three cycles. Due to this CTAB removal, it would be advantageous to have covalently bound functional groups as opposed to physically adsorbed functional groups, with the functional group density tuned to maximize uptake.

### 3.4. *More complex covalently functionalized materials*

The most interesting finding above is that as-made MCM-41 displays very high uptake of guaiacol, comparable to a commercial material. This is consistent with prior literature that has shown long chain quaternary ammonium groups have unique properties towards extraction of aromatic compounds [26,27]. However, due to the loss of CTAB over multiple adsorption cycles since it is physisorbed in the mesopores, we desired to synthesize a material with covalently bound functional groups. Replicating the packing of CTAB in as-made MCM-41 with a covalent grafting approach is non-trivial due to the high density of close-packed CTAB chains. It is known that using alkoxy silane chemistry, one of the most common surface functionalization methods, leads to preferential coating of the pore openings leading to a significant decrease in accessibility of the functional groups [54,55]. However, fast

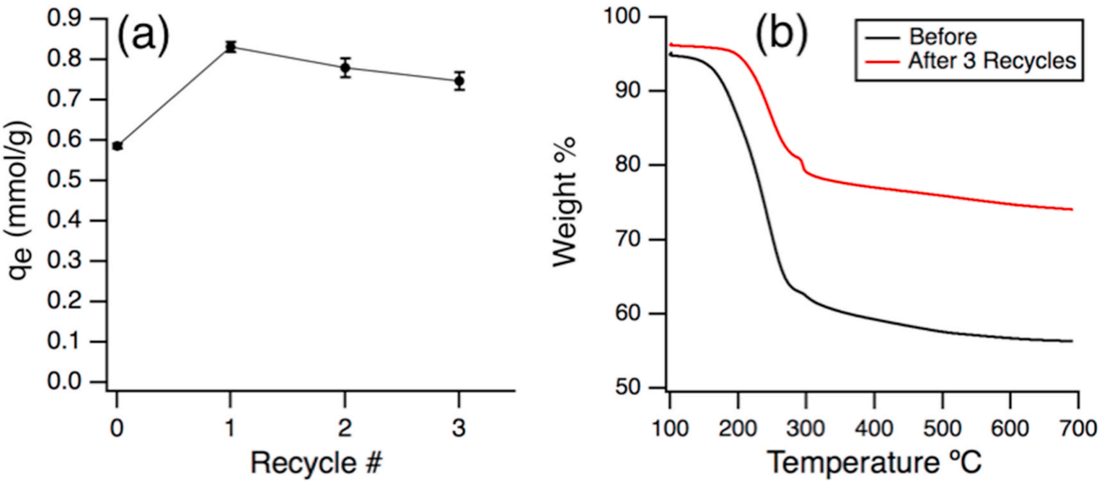


**Fig. 4.** (a) Uptake of AM-MCM-41 after multiple recycles. Error bars calculated from three separate samples. (b). TGA weight loss curves comparing AM-MCM-41 before and after uptake experiments. The lower uptake shown here for Recycle #0 versus Fig. 3 is that this sample was not suspended in methanol for 4 h, to be consistent with how the sample was handled in each recycle.

reacting trichloro silanes slightly alleviate this issue [56]. Three methods were initially attempted to mimic AM-MCM-41 with covalent functional groups containing different quaternary ammonium groups, hydrophobicity, and surface reactivity. However, it was found that MCM-41 was not an ideal support material as uptake values when covalently functionalized were significantly lower than even purely hydrophobic functionalizations (not shown). This was potentially caused by bulky molecules blocking the pore openings, leading to low ligand densities and significantly reducing the available surface area. To alleviate this, pore-expanded FDU-12 was used as a support because of its interconnected three dimensional pore system with large (12 nm) cages and larger (~6 nm) apertures compared to 3.7 nm of MCM-41 [57].

Several chemistries shown in Scheme 2 were investigated. These included samples grafted with hydrophobic alkyl chains (F–C12), samples grafted with quaternary ammonium compounds (F-Quat1) and a mixed chain with a quat group interior to the alkyl chain (F-Quat-3). Two samples were made where the outer surface was functionalized with a quaternary ammonium group (F-Quat-2) or PEG ground (F-PEG), the Pluronic extracted from the pores [58,59], and the remaining silanols, predominantly in the mesopores, were grafted with C12 groups. Lastly, trimethyloctadecyl[3-trimethoxysilyl)propyl]ammonium chloride (TOTSA) was used to graft silica during synthesis by co-condensation of TOTSA and the silica source (tetraethyl orthosilicate in this case). This synthesis method results in an organic-silica hybrid material with more uniform distribution of organic surface functionalities compared to post-synthetic grafting [60,61]. This was completed with molar ratios of tetraethyl orthosilicate to TDTMS of 100:1 and 10:1, labeled as CC-100 and CC-10.

Fig. 5 shows the guaiacol uptake of the various covalent functionalization methods on the FDU-12 supports compared to the bare FDU-12 and hydrophobic FDU-12 (F–C12), which was functionalized with dodecyltrichlorsilane on both the inner and external surface. It can be seen that there is an uptake enhancement when compared to the parent FDU-12 support. Of all the samples in Fig. 5 the F-Quat series show the best results pointing to the value of the quaternary ammonium group on the exterior surface. However, all these samples take up significantly less guaiacol than AM-MCM-41 and Oasis HLB. There could be multiple reasons for this. Contact angle measurements of F-Quat-1 for instance show that it completely wets, i.e. the material does not truly possess both hydrophobic and hydrophilic character. This potentially points to incomplete reaction at the surface silanol groups; TGA data of the FQUAT materials (Supporting Information) support this conclusion. However, the results in Fig. 5 do point to the presence of the quaternary ammonium group enhancing uptake and specifically functional groups that have quaternary ammonium moieties that are in the terminal position on a hydrophobic alkyl group perform slightly better. This can be seen in a comparison of F-Quat1 to F-Quat3, where average uptake is

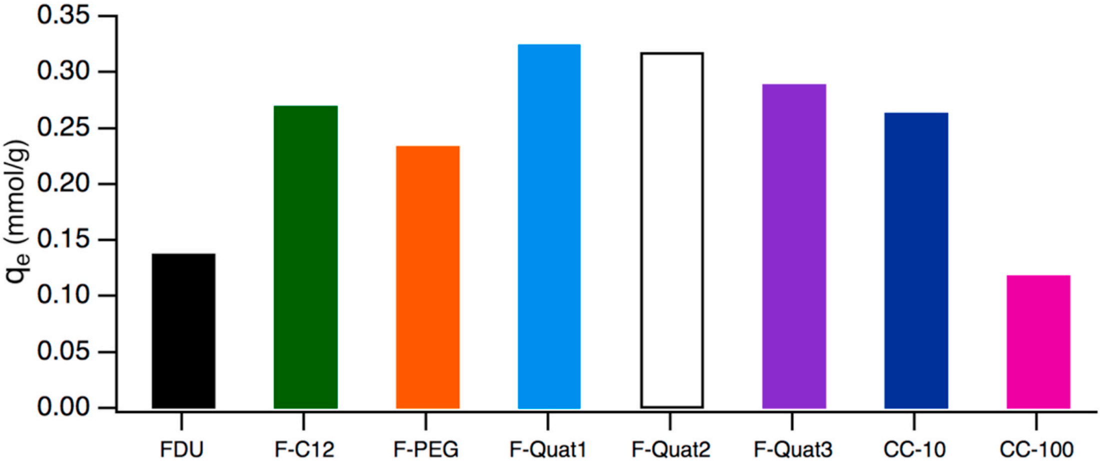


**Fig. 5.** Uptake comparison of various methods to covalently graft FDU-12.

slightly enhanced (0.33 mmol/g compared to 0.28 mmol/g). Finally, using the co-condensation method in an attempt to more uniformly graft functional groups showed no improvement, CC-10 compared to F-Quat3. This suggests that the pristine OMS pore structure and uniformity is beneficial to the adsorption process, and that maintaining that while maximizing functional group loading could be crucial for high-performing adsorbents.

### 3.5. *Structure effects of model aromatic compound*

To probe the chemical interactions at play during uptake, three additional aromatic compounds common in cellulose depolymerization solutions were tested; vanillin, catechol, and pyrogallol.

Uptake of each single molecule from aqueous solutions at 45 mM can be seen in Fig. 6 (top left) for AM-MCM-41, PSDVB, and Oasis HLB. Fig. 6 (bottom) compares the structure of these molecules along with their solubility in water. Uptake on both PSDVB and Oasis HLB decrease when water solubility of the extracted molecule is significantly higher. However, in the case of AM-MCM-41 uptake is high and similar for all model aromatic compounds, which is evidence that the adsorption mechanism is more complex then purely hydrophobicity.

Fig. 6 (top right) compares an equimolar mix of guaiacol and pyrogallol, both at 0.045 M in water. As expected, the PSDVB and Oasis HLB selectively extract the more hydrophobic guaiacol, but in the case of MCM-CTAB both guaiacol and pyrogallol are extracted at similar high quantities. The percent of the total (guaiacol+pyrogallol) molecules removed from solution for the mixed system corresponded to 73% for Oasis HLB and 82% for AM-MCM-41. This shows that long chain quaternary ammonium groups could prove more effective than other hydrophilic-hydrophobic adsorbents for extraction of all biomass relevant aromatic compounds regardless of polarity.

## 4. Conclusions

As-made MCM-41 (AM-MCM-41) performed much better than methyl, dodecyl, or phenyl modified OMS for adsorption of dilute guaiacol from aqueous solution. The reason for this is likely the hydrophilic character of the quaternary ammonium paired with the hydrophobicity of the $C_{18}$ alkyl group allowing for a material that had a mixed hydrophobic/hydrophilic character. The AM-MCM-41 was then compared to the most commonly used hydrophilic-hydrophobic adsorbent, Oasis HLB, and adsorption capacities were slightly lower. However, when these were compared with more water-soluble phenols, catechol and pyrogallol, it was shown that MCM-CTAB had a higher adsorption capacity than Oasis HLB. This finding suggests combining quaternary ammonium groups with hydrophobic groups allows for the capture of biomass relevant phenols from solution.

Since AM-MCM-41 relies on physisorption, it was tested for its adsorption capacity over multiple recycles. Although performance was only slightly decreased after each cycle, mass loss was significant. A system that mass is constantly being lost is not practical for separations,

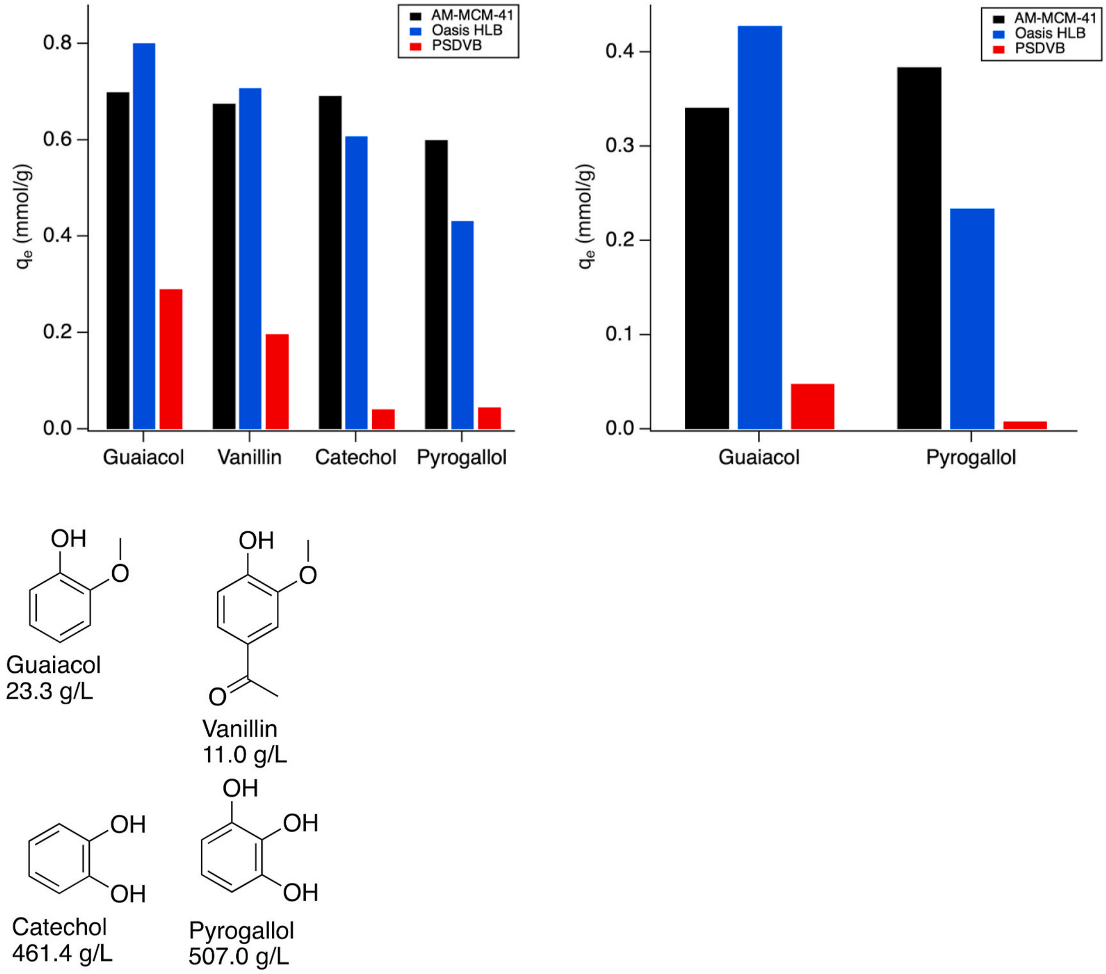


**Fig. 6.** (Top left) Comparison of uptake of guaiacol, vanillin, catechol, and pyrogallol from separate solutions each at an initial concentration of 45 mM. (Top right) Uptake comparison of a mixed solution of guaiacol and pyrogallol each at a concentratoin of 22.5 mM. (Bottom) Structures of the four molecules with their respectively solubility in water.

hence different functionalization techniques were tested to covalently link hydrophobic-hydrophilic groups. Pore expanded FDU-12 was used as the OMS support to allow for maximum internal pore volume for the bulky functional groups and it was found the best functional groups were alkyl quaternary ammonium groups, but when compared to AM-MCM-41 their adsorption capacities were significantly lower. However, these results give insight into material properties that would allow for high-performing adsorbents and a basis for synthetic strategies to increase adsorption capacity of lignin-derived phenolic molecules.

## Credit author statement

DFS and PJM designed the experimental work plan.

PJM made 75% of the samples, and did all uptake tests and characterization except contact angle measurements.

EB made several of the bare parent samples.

AK remade selected samples and performed contact angle measurements.

DFS and PJM analyzed the experimental results and wrote the manuscript.

All authors have seen and approve the manuscript.

## Declaration of competing interest

The authors declare no competing financial interests.

## Acknowledgements

The authors gratefully acknowledge support from NSF award 1703251.

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