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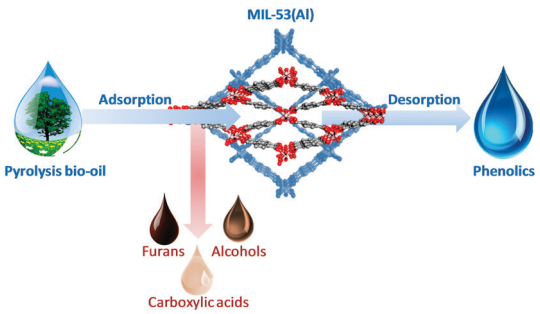

Phenolics isolation from bio-oil using the metal–organic framework MIL-53(Al) as a highly selective adsorbent

Chunmei Jia, Bart Bueken, Francisco G. Cirujano, Kevin M. Van Geem and Dirk De Vos*

The selective uptake of phenolic compounds, a key step of bio-refining, was achieved on MIL-53(Al) and Basolite A100 both from a simulated bio-oil and a real pyrolysis bio-oil.

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Phenolics isolation from bio-oil using the metal–organic framework MIL-53(Al) as a highly selective adsorbent†

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By using flexible metal organic frameworks such as MIL-53(Al), the selective uptake of 4-methylguaiacol was achieved from a simulated bio-oil (40 wt%). Similar high uptake capacity of phenolics (27 wt%) was observed from a real pyrolysis bio-oil, with good selectivity towards a variety of phenolics, *e.g.* guaiacol, 4-methylguaiacol and catechol.

Phenolics are an important class of compounds for the chemical industry, with applications in the food, wine, plastic, tanning, agrochemical and pharmaceutical industry.[1] As of today phenolic compounds are primarily synthesized from fossil feedstocks[2] and only to a lesser extent extracted from biomass.[3] In light of the current drive towards a sustainable chemical industry, the latter route is highly appealing, since the compounds in this feedstock are already extensively functionalized.[4] Following pyrolysis of the lignocellulose fraction, a crude, highly complex bio-oil mixture is obtained. Therefore, the development of efficient methods to harvest and purify the vast amount of phenolics present in this bio-oil is an important target. Adsorption from the liquid phase as a separation method is facile, convenient, and can achieve high uptake capacity, and good selectivity. For selective uptake of C_8 alkylaromatics, such as xylenes, zeolites like faujasite are broadly applied as industrial adsorbents, and confinement effects operating on aromatic isomers inside zeolite pores have been studied in detail.[5] Also for larger alkylaromatics, such as ethyltoluene and cymene isomers, shape-selective uptake has been achieved on zeolite absorbents.[6] However, few cases have been reported where microporous materials succeed in the separation of polar, functionalized aromatics. The emergence of Metal–Organic Frameworks (MOFs) provides alternative materials with new features for selective uptake, including open coordination sites on metal centers, functional organic sites, and a variety of well-defined hydroxyl groups.

MOFs are organic–inorganic hybrid porous solids which have attracted a great deal of research interest for their potential applications, such as gas sorption, catalysis, drug delivery and sensing.[7] MOFs have also seen exploration as adsorbent for liquid phase separations, for instance in the separation of xylenes and ethylbenzene,[8] for fuel upgrading through desulphurisation and denitrogenation,[9] and for purification purposes by the targeted removal of organic contaminants,[10] as well as inorganic contaminants from water.[11] MOFs have also been employed as catalysts for production of compounds related to bio-oil[12a,b] and even as adsorbents for the recovery of bio-based molecules from aqueous mixtures.[12c–e] The MIL-140 series of materials, based on Zr–O chains and aromatic dicarboxylic linkers,[13] has been proposed for adsorption of phenolics from dilute aqueous solutions, using π–π stacking interactions;[12c] we recently revealed that the open coordination sites on the Zr-MOF MOF-808 can be used to selectively adsorb functionalized phenols like guaiacol. Inspired by these achievements, we here aim at identifying further materials that allow selective uptake of phenolics from more complex mixtures containing competing organic molecules; eventually these materials should be applied to fractionation of a real bio-oil mixture.[12e]

In this work we investigate the well-known MIL-53 family of materials (MIL-53(Al), MIL-53(Cr), MIL-47(V) and Basolite A100, a commercial analogue of MIL-53(Al) marketed by BASF) for their performance in the separation of phenolics. Initially, a simulated bio-oil mixture is used, with 4-methylguaiacol (4-MeG) as a representative model for a phenolic molecule because of its abundance in bio-oils after pyrolysis. The model bio-oil is a pyrolysis wheat oil, thoroughly characterized by 2-dimensional GC and NMR, by which 112 compounds were identified in the mixture.[14] According to the results, the bio-oil contains mostly water (30%); phenolics like guaiacol, catechol, vanillin; furans like furfural, furfuryl alcohol; ketones like 2-cyclopentenone; carboxylic acids like propionic acid, acetic acid; sugars like levoglucosan; and alcohols like butanol.[14a] In the bio-oil mixture, many constituents, like alcohols, carboxylic acids, sugars and phenolics can form hydrogen bonds with –OH groups on the inorganic backbone of the MIL-53 type MOFs, or with the carboxyl oxygen atoms of the terephthalate linker ions.

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MIL-53 [M(OH)(bdc)]$_n$ (bdc = 1,4-benzenedicarboxylate, M = Al^{3+}, Cr^{3+}) is a prototypical example of a flexible or breathing MOF consisting of inorganic chains of corner-sharing MO_6 octahedra interconnected by bdc linkers to form lozenge-shaped channels.[15] Protruding into the channels are the μ_2-OH groups connecting the MO_6 octahedra in the inorganic chains. After synthesis, these materials contain free H_2bdc linkers in their channels, in a form of the material known as the as form. The materials from which guest linkers have been removed typically exhibit reversible structural transitions between large pore (LP, alternatively known as ht for high temperature) and narrow pore (NP, alternatively named here as lt, low temperature) forms, as a function of temperature,[16] pressure,[17] and ad- or desorption of guest molecules, due to interactions with the μ_2-OH groups.[18] For example, in MIL-53(Al), a transition between the ht (8.5 Å × 8.5 Å channel dimensions) and the lt (2.6 Å × 13.6 Å channel dimensions) forms occurs upon guest removal at temperatures above 100 °C. The V^{4+}-based[19] counterpart of MIL-53, MIL-47, features the same topology; however due to the higher charge of V^{4+}, μ_2-O rather than μ_2-OH groups are present in the chains, which precludes the flexible behaviour seen in MIL-53. Considering the high acid stability of MIL-53 in aqueous solution, we chose to study it as an adsorbent to isolate phenolic compounds from the bio-oil mixture. Basic characterization which shows the successful synthesis of MIL-53(Al), MIL-53(Cr) and MIL-47(V) includes powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and N_2 physisorption. The results of these characterizations are shown in Fig. S1–S3 (ESI†) and Fig. 1.

First, single compound adsorption isotherms were measured for 4-MeG in a water–methanol mixed solvent system (v : v 1 : 1, 1.8 mL) using MIL-53(Al)-lt and Basolite A100 as adsorbents (~20 mg), as well as the adsorption isotherm for 4-MeG from a purely methanolic solution (1.8 mL), employing MIL-53(Al)-lt (Fig. 2a). All these materials showed high uptake capacity for 4-MeG from both the water–methanol mixed solvent and from pure methanol. In the mixed solvent, the adsorption capacity was saturated at around 0.03 M, with a 4-MeG uptake of about 30 wt% on Basolite A100, while it was slightly higher on MIL-53(Al)-lt, around 40 wt%. The lower uptake capacity of Basolite A100 in comparison with MIL-53(Al) might be caused by its lower BET surface area (1085[14c] *vs.* 1293 m^2 g^{-1}). Steeper uptake isotherms were obtained from solutions richer in water (*e.g.*, water : methanol 2 : 1). In contrast, flatter uptake isotherms were obtained from solvents richer in methanol (*e.g.*, water : methanol 1 : 2) (Fig. S4, ESI†). This also reflects that 4-methylguaiacol is significantly more soluble in methanol than in water. The mass uptake from the pure methanolic solution showed a double sigmoidal behaviour, with a first plateau for a concentration of 4-MeG of 0.11 M, at about 10 wt% uptake in the MOF. The second plateau was achieved at 0.35 M with an uptake capacity of around 30 wt% on MIL-53(Al)-lt. The double sigmoidal behaviour can be attributed to the breathing of MIL-53(Al), which undergoes a transition in its pore size with increasing adsorbate concentrations (*cf.* infra).

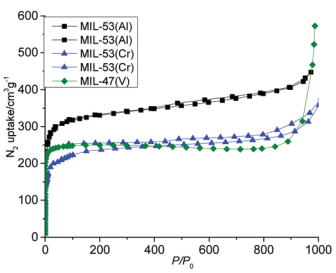


Fig. 1 N_2 physisorption isotherms (and BET surface areas) of MIL-53(Al) (1293 m^2 g^{-1}), MIL-53(Cr) (915 m^2 g^{-1}) and MIL-47(V) (814 m^2 g^{-1}).

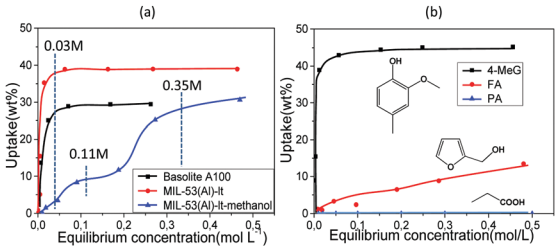
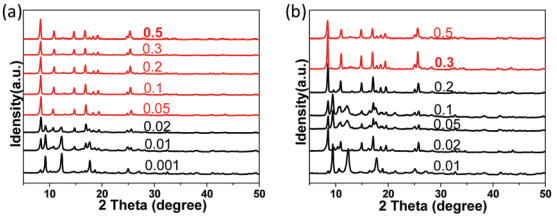


Fig. 2 (a) Single compound adsorption of 4-MeG from methanol : H_2O (v : v 1 : 1) on MIL-53(Al)-lt (red), Basolite A100 (black) and from methanol on MIL-53(Al)-lt (blue). Initially the 4-MeG was supplied in the solution with concentrations of 0.5, 0.3, 0.2, 0.1, 0.05, 0.02, 0.01 and 0.001 M, respectively. (b) Competitive adsorption isotherms of 4-MeG, FA and PA from methanol : H_2O (v : v 1 : 1) on MIL-53(Al)-lt. Initially the three compounds were supplied in concentrations of 0.001, 0.01, 0.02, 0.05, 0.1, 0.2, 0.3 and 0.5 M. Uptake values given as wt% with respect to the MOFs.

Next, competitive adsorption experiments between 4-MeG, propionic acid (PA) and furfuryl alcohol (FA) were conducted in the mixed water–methanol solvent. Using MIL-53(Al)-lt, a high selectivity for 4-MeG over FA and PA, in addition to a high uptake capacity of 4-MeG is observed. The presence of FA and PA did not influence the uptake of 4-MeG at all (Fig. 2b). Only after the 4-MeG uptake saturated, some uptake of FA is seen, while no uptake of PA was observed. This indicates that the adsorption of 4-MeG is not strongly influenced by other hydrogen bond donating guest molecules.

The high selectivity towards 4-MeG over FA was also confirmed by a column breakthrough experiment (Fig. S5, ESI†). Using as a feed a methanol–water mixture containing 4-MeG and FA (both with concentration of 0.05 M), a flow was sent through a column packed with 0.3 g of MIL-53(Al)-lt, at a rate of 0.137 mL min^{-1}. The column outlet was manually sampled and afterwards analysed by HPLC. FA appears in the column outlet immediately; 4-MeG is observed in the column outlet only after 16 minutes.

Upon closer examination of the PXRD patterns of the MOF samples after the adsorption experiments (Fig. 3), the 4-MeG loaded samples show similar diffractograms as previously reported by our group for xylene loaded MIL-53 materials.[10b] Tight packing of the xylene molecules was achieved in MIL-53's channels, with cell parameters close to those of the empty ht phase. Even at very low 4-MeG concentrations (0.001 M), the onset of a structural transition from the lt phase to a pore-filled phase can be identified, mainly from the appearance of a reflection at 8.41° 2θ (Fig. 3a). Up to 0.02 M 4-MeG, both the water-filled lt phase and the 4-MeG filled MIL-53(Al) coexist (Fig. 3a), likely due to the concerted nature of pore opening in single MIL-53(Al) crystals.[20] During this pore opening process, the lt phase is transformed to the ht phase at once, which is accompanied



Q4 Fig. 3 PXRD patterns of (a) MIL-53(Al)-lt after exposure to 4-MeG solutions of different concentrations in methanol–water; (b) MIL-53(Al)-lt after exposure to methanolic solutions of 4-MeG in different concentrations. Note: in each adsorption experiment, around 20 mg of MOF adsorbent was added to 1.8 mL of solutions of different initial concentration (0.001, 0.01, 0.02, 0.05, 0.1, 0.2, 0.3 and 0.5 M).

by a change of cell parameters, instead of gradual opening of the pore. At concentrations equal to or greater than 0.05 M 4-MeG, no further changes in the structure are observed, indicating complete pore filling. This indeed corresponds well with the plateau observed in Fig. 2a at about 0.03 M 4-MeG. Similarly, exposure of Basolite A100 to the 4-MeG solutions in methanol–water results in the immediate adsorption of the 4-MeG substrate, with the uptake and concomitant phase transition completing at concentrations below 0.05 M; in other words, water is not preferred over the more hydrophobic 4-MeG (Fig. S6, ESI†). For adsorption in pure methanol, MIL-53(Al) only achieved a high uptake of 4-MeG at a higher concentration of 0.3 M (Fig. 2a), and according to the PXRD data, there is an obvious gate opening process between 0.2 and 0.3 M (Fig. 3b).

Moreover, FTIR spectra were analysed in order to explore the mechanism of the selective 4-MeG uptake. Interactions that could be decisive for the selectivity of MIL-53(Al)-lt towards phenolics could be π–π stacking and hydrogen bond formation. The stretching and bending vibrations of the μ_2-OH groups in MIL-53(Al)-lt as well as the 4-MeG loaded samples were observed at 3700 (ν) and 984 cm^{-1} (δ; see Fig. S7, ESI†), respectively. The adsorption of 4-MeG also results in a somewhat broadened, yet well-defined new band at 3574 cm^{-1}, corresponding to the ν(OH) of the phenol. In comparison with pure, dilute 4-MeG, with a vibration at 3616 cm^{-1}, the decreased frequency of the phenolic O–H stretching vibration can be taken as evidence for hydrogen bonding between the phenol's OH and a H-bond acceptor on the pore surface, *e.g.* the μ_2-OH groups in the inorganic chains of MIL-53(Al)-lt (Fig. S7, ESI†). The FTIR spectra also evidence the breathing of the MOF material, with a shift of the δ(C–H) frequency of the terephthalate ligands from 1018 cm^{-1}, for the closed form, to 1027 cm^{-1}, for the opened form.[21] In agreement with the PXRD and adsorption data, MIL-53(Al) is in the closed pore form before adsorption, and this conformation is preserved at a 4-MeG concentration of 0.001 M (Fig. S7, ESI†). For initial 4-MeG concentrations between 0.05 and 0.3 M, the signal is cleanly shifted to 1027 cm^{-1} (Fig. S7, ESI†). At the intermediate concentration of 0.02 M, the signal is broadened, which is indicative of a co-existence of both forms, in agreement with the observations from PXRD. This shows that as soon as the adsorption becomes significant, the aromatic rings of the MIL-53(Al) terephthalate linkers become available for π–π interactions with 4-MeG due to pore opening (Fig. S8, ESI†). Other 4-MeG related vibrations in the FTIR spectrum were observed at 1270, 1230, 1208 and 1040 cm^{-1}, corresponding to vibrations of Ar–O (phenolic), Ar–O (ether), OH (phenolic), and O–CH_3 (ether) groups.

For comparison purposes, we also prepared MIL-47(V) and MIL-53(Cr)-lt, and used them for adsorption of 4-MeG from methanol. Both of them showed lower adsorption capacities for 4-MeG of 15 and 11 wt%, respectively (Fig. S9, ESI†). For MIL-53(Cr)-lt, the uptake capacity is also lower in pure water than for MIL-53(Al), with 21 wt% *versus* 51 wt%, respectively (Fig. S10, ESI†). While both MIL-53(Al)-lt and MIL-53(Cr)-lt showed a structural transformation, as expected MIL-47(V) remained in its open pore form given its greater rigidity (Fig. S11, ESI†). We assume that the lower uptake capacity on MIL-47(V) might be due to its lower BET surface area as compared with MIL-53(Al) (Fig. 1) and to the lack of μ_2-OH groups capable of forming hydrogen bonds with 4-MeG. For MIL-53 (Cr), the pore volume calculated according to the N_2 sorption is only 0.26 mL g^{-1}, which is much lower than that of MIL-53(Al) (0.50 mL g^{-1}), which explains the latter's better performance. Interestingly, in a separate adsorption experiment, all three materials showed very small FA uptakes of less than 2 wt% (Fig. S9, ESI†); thus all of these materials maintained their initial pore aperture after the adsorption of FA according to the PXRD (Fig. S11, ESI†).

Considering the small uptake amount of 4-MeG from low initial concentrations in methanol (Fig. 2), it should be easy to desorb 4-MeG from MIL-53(Al)-lt and Basolite A100 by using pure methanol as a de-sorbent. Before the desorption experiment, the material was rinsed with water in order to remove the 4-MeG absorbed on the outer surface of the MOFs. Next, in the desorption stage, by using 7.9 g methanol per 20 mg adsorbent, nearly 99% of the adsorbed 4-MeG could be desorbed from both MIL-53(Al) and Basolite A100 after the first desorption step. MIL-53(Al) undergoes clear reversible breathing between an open, guest-loaded phase and a closed lt structure during each adsorption and desorption cycle, as seen by PXRD (Fig. S12 and S13, ESI†). Similar structural changes were observed for Basolite A100, however, it only partially went back to the small pore model after desorption. Note that Basolite A100 partially retains the ht phase, even upon immersion in pure water (Fig. S14, ESI†); this shows that the material is not flexible[14d] to the same extent as MIL-53(Al).

In order to test the stability and reusability of MIL-53(Al) in this process, recycling studies were performed (Fig. 4). Thereto, the same samples of MIL-53(Al)-lt and Basolite A100 were utilized in consecutive adsorption/desorption runs with 4-MeG from a water–methanol solution (v:v 1:1) with an initial concentration of 0.05 M (6.9 mg in 1 mL). Both materials show only a small variation in uptake amount, ranging between 35 and 40 wt%, after four cycles (Fig. 4; blue bars). Structural degradation of the framework could be ruled out by PXRD, ICP and HPLC measurements, which showed excellent stability of MIL-53(Al) and Basolite A100 during the four cycles (Fig. S12, S13, S15 and S16, ESI†). The PXRD indicated the stability of the crystalline metal–organic framework, also confirmed by ICP and HPLC analysis of the 0.05 M aqueous solution after adsorption on MIL-53(Al)-lt, indicating a very limited leaching of the Al metal ion (less than 0.1 wt%) or of the bdc linker (<1 wt%). Furthermore, the quantity of 4-MeG that is recovered in each cycle also shows only small variations, ranging from 5.6 to 6.1 mg/16 mg MOF for MIL-

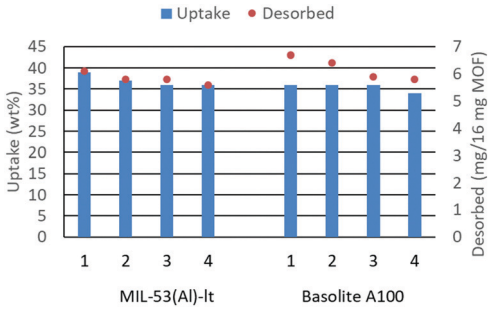


Fig. 4 Uptake amount (expressed as wt% 4-MeG) and the desorbed amount (given as mg 4-MeG/16 mg MOF) using the same sample of MIL-53(Al) and Basolite A100 for four cycles of adsorption from a 0.05 M 4-MeG solution in methanol : water, and desorption by using pure methanol.

53(Al)-lt, and 5.8 to 6.7 mg/16 mg MOF for Basolite A100 (Fig. 4; orange dots).

Considering the high adsorption capacity, the high phenol selectivity and the reusability of MIL-53(Al)-lt, we performed adsorption experiments using a real pyrolysis bio-oil as a feed; next, the adsorbed bio-oil compounds were desorbed by using methanol, and the desorbate was analyzed by GCMS and GC-FID. The results of this experiment are shown in Fig. 5. The data show that also with real bio-oil, MIL-53(Al)-lt has a high uptake capacity, and the preference is clearly towards phenolic compounds, with an uptake amount of 27 wt% (Fig. 5), comprising guaiacols (~5 wt%), catechols (6 wt%) and other phenolics (16 wt%). The uptake of all other compound classes on MIL-53(Al)-lt was less than 10 wt% (Fig. 5). A slightly worse result was recorded for Basolite A100 (Fig. S17, ESI†). Like in the experiments with simulated bio-oil mixtures (Fig. 2b), again carboxylic acids, alcohols, sugars, ketones and furans are much less favoured as adsorbates (Fig. 2b).

Again, on the structurally related materials MIL-53(Cr)-lt and MIL-47(V), only small uptakes were registered (Fig. S18, ESI†). These results are not surprising because, as we have mentioned before, the uptake amount of 4-MeG on both MOFs from both methanol and aqueous solutions is lower than for MIL-53(Al)-lt. The PXRD results of these materials before and after adsorption experiments show that MIL-53(Al)-lt opened its pores during

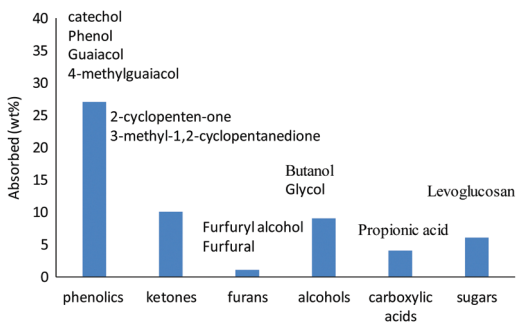


Fig. 5 Uptake of various compounds from real bio-oil on MIL-53(Al)-lt. The amount was calculated based on the GC analysis of desorbed bio-oil, according to the formula $\mathrm{wt\%} = \frac{\mathrm{MG}}{\mathrm{MA}} \times 100$, where MG and MA are the mass of absorbed guest molecule and adsorbent.

the adsorption process, and returned back to the lt form after the desorption. However MIL-53(Cr)-lt failed to open its pore during the adsorption from the bio-oil mixture (Fig. S18). This surely explains the much smaller uptake capacity on MIL-53(Cr)-lt for compounds from the bio-oil mixture, however the underlying reasons are not currently known.

In summary, flexible materials of the MIL-53 type have been used as adsorbents for uptake of phenolics, both from simulated and from real bio-oil. MIL-53(Al)-lt showed the highest uptake capacity and the best selectivity. The commercial counterpart of MIL-53(Al), Basolite A100 showed slightly lower uptake capacity both from simulated bio-oil and pyrolysis bio-oil. MIL-53(Cr)-lt and MIL-47(V) showed much lower uptake amounts due to the more rigid pore structure. According to the PXRD data for the single compound adsorption of 4-MeG on MIL-53(Al)-lt from a methanol–water solution, the adsorption process is associated with the pore opening of this MOF. The better selectivity towards 4-MeG, as compared to other bio-oil constituents like furans and carboxylic acids is ascribed to a combination of hydrogen bonding and π–π interactions. Recycling experiments show that the absorbed 4-MeG is easily desorbed by using methanol, and that the materials have a sufficient stability to be reused in at least four cycles.

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Conflicts of interest

There are no conflicts to declare.

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