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Complete furanics-sugar separations with metal-organic framework NU-1000†

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Metal-organic framework NU-1000 selectively adsorbs furanics, while completely excluding the adsorption of monomeric sugars from the same aqueous mixture. The highly refined degree of molecular recognition exhibited by NU-1000 is exemplified with it selectively adsorbing 5-hydroxymethylfurfural, even in the presence of up to a 300-fold excess of glucose in solution.

Second-generation bioethanol is derived from cellulose-based feedstocks – the most abundant form of biomass on earth, and its production is expected to grow significantly worldwide beyond its 2014 volume, which was at 340 million L per annum.^{1,2} During cellulosic ethanol production, in order to overcome the recalcitrance of crystalline cellulose, some form of chemical pretreatment is required.^{3,4} This pretreatment aims to increase the amount of fermentable sugar that can be extracted from cellulosic biomass, but also comes with undesirable side reactions, which form furanic compounds via sugar dehydration,^{5–8} such as 5-hydroxymethylfurfural (HMF) and furfural. These furanics are known potent fermentation inhibitors (*e.g.*, 8 mM of HMF is toxic to *Saccharomyces cerevisiae* and *Zymomonas mobilis*).^{7,9} As a result, the extent of chemical pretreatment is currently limited by the severity of its toxicity to the fermentation broth. If it were possible to selectively remove furanic compounds from the fermentation broth without also removing precious energy-containing sugar molecules, this would enable a paradigm-shift increase in the optimum amount of chemical pretreatment, because the toxic compounds could be easily removed prior to fermentation. However, the formidable molecular-recognition challenge

presented by this separation is the required degree of selectivity, since typical sugar concentrations are at least 100-fold higher than that of the furanic compounds in a typical fermentation broth.¹⁰ To date, while there are several adsorbents that favor removal of furanic compounds relative to sugars in aqueous solution,^{11–13} none have been identified that possess the required enzyme-like refined degree of molecular recognition to function at the high sugar:furanics ratios representative of fermentation broths, without also causing significant undesired sugar uptake and loss. Here, in this manuscript, we demonstrate such a unique material, consisting of metal-organic framework (MOF) NU-1000,^{14,15} which is composed of hydrophobic pyrene linkers. The generally weak nature of physisorptive interactions with NU-1000 has recently led us to demonstrate high selectivities in the separation of closely related sugars with this material.¹⁶ We postulated that high selectivities might also be feasible in furanics-sugar separations, albeit for a completely different reason: the aromatic pyrene linkers of the MOF might exhibit favorable π – π interactions with furanics such as HMF and furfural, since these compounds also possess aromaticity—in contrast to the simple sugars that they are derived from. Our data demonstrate unprecedented selective molecular recognition by NU-1000, which enables it to adsorb 80% of the HMF from solution, without causing any detectable adsorption of glucose, which is present in the same aqueous mixture in up to 300-fold excess relative to HMF.

Fig. 1 shows the single-component adsorption isotherms at 297 K for HMF and furfural in addition to glucose and fructose (from which HMF is typically derived) as well as xylose (from which furfural is typically derived). For HMF and furfural, adsorption isotherms exhibit typical Type I (*i.e.*, Langmuirian) behavior, where uptakes increase steeply in the lower concentration range and plateau at concentrations above 0.1 M. These isotherms are characteristic of high enthalpies of adsorption, that are commensurate with those found in other microporous adsorbents.^{17,18} This is in contrast to the lower enthalpies of adsorption (being similar to enthalpy of

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† Electronic Supplementary Information (ESI) available: Experimental, Langmuir parameters and plots, single- and multi-component adsorption isotherms for MSC-30, N₂ physisorption and PXRD data for NU-1000, and adsorption ratios of furanics to sugars for reported adsorbents. See DOI: 10.1039/x0xx00000x

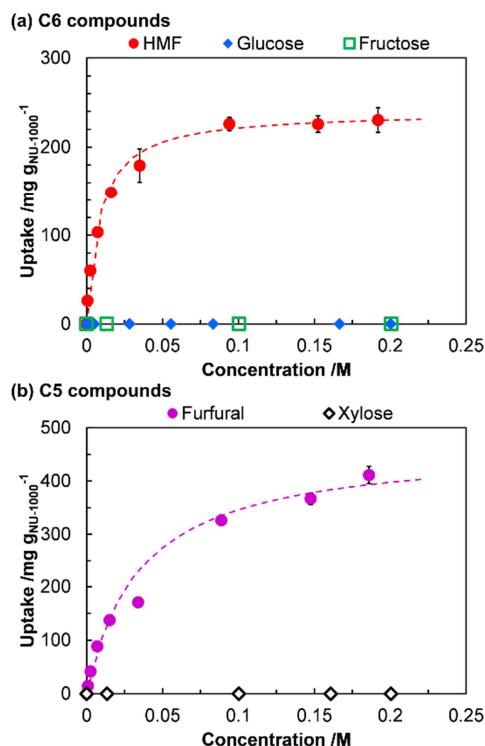


Fig. 1 Single-component adsorption isotherms of furanics and sugars on NU-1000 at 297 K: (a) C6 compounds; (b) C5 compounds. The dashed lines represent the isotherms replicated by the Langmuir parameters (Table S1, ESI†). The Langmuir plots for HMF and furfural are shown in Fig. S1 (ESI†).

crystallization) that we reported previously for sugar dimers with the same MOF—resulting in Type II isotherm behavior.¹⁶ This comparison supports the hypothesized importance of π – π interactions with the pyrene linkers of the MOF. Table S1 (ESI†) summarizes the adsorption equilibrium constant (K_{ads}) and capacity (Q_{max}), which are obtained from a Langmuir fit of the isotherm data (Fig. S1, ESI†). The K_{ads} values for HMF and furfural are calculated to be $120 \pm 16 \text{ M}^{-1}$ and $28 \pm 6 \text{ M}^{-1}$, respectively (Table S1, ESI†). The displayed affinity of NU-1000 to these furanics is similar to previously reported aromatic polymers (e.g., K_{ads} values of 8.5 M^{-1} for HMF and 48 – 67 M^{-1} for furfural),^{12,19,20} while being lower than that reported for amorphous carbon materials (e.g., 1300 M^{-1} for HMF and 5300 M^{-1} for furfural).^{21,22} For instance, in comparison, under similar conditions based on isotherms with amorphous carbon material MSC-30 as adsorbent, K_{ads} values of $714 \pm 450 \text{ M}^{-1}$ and $194 \pm 71 \text{ M}^{-1}$ were calculated for HMF and furfural, respectively (Figs. S2–S3 and Table S2, ESI†). We infer from these data that while each pyrene unit of crystalline NU-1000 is sufficient in its aromatic-domain size for causing a high-affinity Type I uptake of HMF and furfural, it is not large enough to be as effective of an adsorbent compared with the larger graphitic domains (typically greater than 2 nm) present in carbon materials. This can be rationalized on the basis of the known role of furanic compounds as π -electron acceptors when interacting with an aromatic surface,²³ and the greater π -basicity of the carbon surface as a result of its more extended conjugation. An important secondary consideration favoring greater furanic

uptake in amorphous carbon versus crystalline NU-1000 is the site-isolation of aromatic units in the framework of the latter, whereas the ability of aromatic domains to stack adjacent to each other and thereby form microporous cavities in the former allows for a greater extent of multiple-point contact and adsorption affinity. The observed lower affinity of NU-1000 to furanics allows for their rapid and easy extraction via simple elution with water.

The furanics adsorption capacity of NU-1000 is relatively high on a mass-fraction basis (Q_{max} values of $240 \pm 3 \text{ mg g}_{\text{NU-1000}}^{-1}$ for HMF and $467 \pm 28 \text{ mg g}_{\text{NU-1000}}^{-1}$ for furfural, Table S1, ESI†), and comparable to other adsorbents consisting of carbon materials, polymers, and zeolites (100 – $1200 \text{ mg g}_{\text{adsorbent}}^{-1}$ for HMF and 23 – $830 \text{ mg g}_{\text{adsorbent}}^{-1}$ for furfural, see also Table S2, ESI†).^{11–13,19–22,24,25} We rationalize this adsorption capacity of NU-1000 to be the result of NU-1000's high specific surface area, which has a BET value of $2320 \text{ m}^2 \text{ g}^{-1}$.¹⁴

Powder X-ray diffraction measurement (PXRD, Fig. S4, ESI†) shows no structural change in NU-1000 following furanics adsorption. This is the same as what was observed after adsorption of cellobiose of up to $2050 \text{ mg g}_{\text{NU-1000}}^{-1}$ on NU-1000, and can be elucidated on the basis of the crystalline framework topology.¹⁶ N_2 physisorption data demonstrate a decrease in the pore volume with increasing furanics concentration (Figs. S5–S6 and Table S3, ESI†), which indicates that adsorbed furanics consume internal pore volume upon adsorption. A comparison of the pore-size distributions before and after furanics adsorption further demonstrates that both micropores and mesopores are consumed. The quantitative amount of pore-volume decrease is 2.1- to 2.8-fold larger than the molecular volume of the adsorbing furanic compounds. This adsorbed furanic density is consistent with observations in other host-guest systems, where the total volume for example for adsorbed cellobiose in the cleft of cellobiohydrolase II is twice the cellobiose molecular volume, and where the extra volume in the host (*i.e.*, that which is not occupied by cellobiose) is empty space according to the structure derived from single-crystal X-ray diffraction.²⁶ Lacking what would be definitive crystallographic data for the HMF-NU-1000 cocrystal at this time, we cannot assign occupancy to the extra volume for our case; in principle, it could be either empty, or filled with water (as well as the possibility of other non-furanic components for mixtures as dealt with below).

In contrast to HMF and furfural, NU-1000 exhibits no affinity for either fructose or xylose, consistent with prior demonstrated lack of glucose adsorption¹⁶ (Fig. 1 and Table S1, ESI†). These results can be partially rationalized on the basis of the same number of expected axial CH – π interactions between a fructose and xylose molecule and a pyrene unit on the surface of NU-1000, as for glucose, where the limited three CH – π interactions per sugar with the pyrene ring were previously deemed enthalpically insufficient to cause adsorption, based on electronic-structure calculations.¹⁶ These results showing the lack of affinity of NU-1000 to monomeric sugars highlight the difference between the MOF and all previously reported materials, which show varying but crucially

nonzero degrees of affinity to the same simple sugars,^{11–13,24,25,27,28} including amorphous carbon material MSC-30 ($Q_{\max}$ values of 134–208

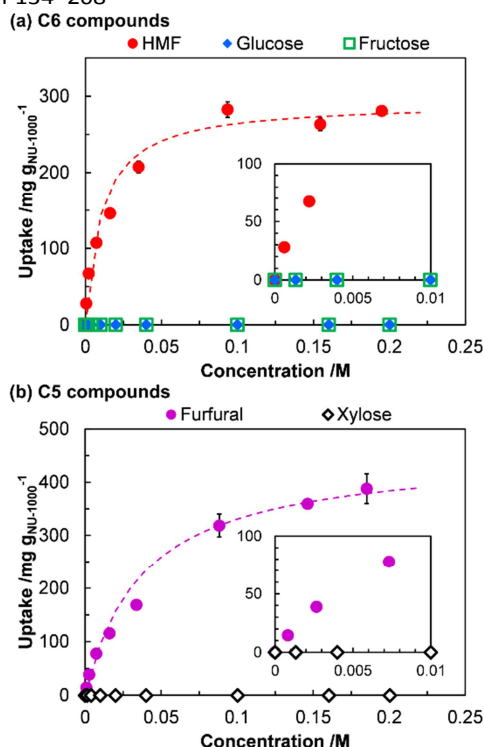


Fig. 2 Competitive adsorption of furanics and sugars on NU-1000 at 297 K: (a) C6 compounds; (b) C5 compounds. The insets represent the enlarged figures in the range of 0 M to 0.01 M. The dashed lines represent the isotherms replicated by the Langmuir parameters (Table S4, ESI[†]). The Langmuir plots for HMF and furfural are shown in Fig. S7 (ESI[†]).

$\text{mg g}_{\text{MSC-30}}^{-1}$ are demonstrated for monomeric sugars in Fig. S2 and Table S2, ESI[†]).

A practical application of NU-1000 requires furanics-sugar separations from a multicomponent aqueous mixture, in which sugar is present in large excess, as encountered in the purification of fermentation broths during bioethanol synthesis. Given the observed on-off adsorption behaviour when comparing single-component affinities of furanics and simple sugars with NU-1000, as summarized in Table 1, we conducted competitive adsorption experiments in order to further investigate separation of furanics and sugars—where both are present at the same time in an aqueous mixture.

Fig. 2 shows competitive-mode adsorption isotherms of furanics and sugars on NU-1000, recorded under equimolar initial-concentration conditions. For C6 compounds, NU-1000 adsorbs only HMF from the aqueous solution mixture, with no detectable uptakes of glucose or fructose, in Fig. 2a. Similarly, NU-1000 adsorbs furfural, with a lack of xylose uptake in Fig. 2b. This selective separation of furanics from the simple sugars that they are derived from in aqueous solution occurs even at the lowest concentrations in Fig. 2, under conditions where vacant adsorption sites on the solid are available. In comparison, when using carbon material MSC-30 at such excess adsorbent conditions, some sugar in addition to

furanics adsorption is also observed (Figs. S8–S9 and Table S5, ESI[†]). Indeed, the ability of NU-1000 to adsorb furanics in reasonably high affinity while completely rejecting sugars differentiates NU-1000 from all

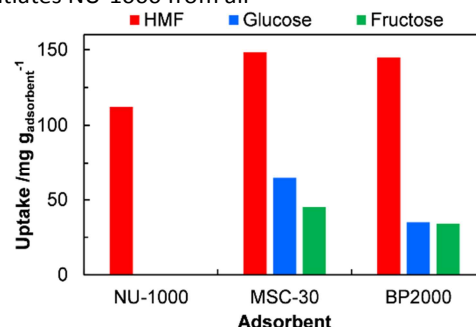


Fig. 3 Competitive adsorption of HMF (initial concentration of 40 mM) and sugars (40 mM) on 50 mg of adsorbents at 297 K.

previously described adsorbents, for which the ratio of adsorbed furanics to sugars by mass is reported to be below 25 (Table S6, ESI[†]) under excess-adsorbent conditions.^{11–13,22}

We also investigated adsorption of furanics and sugars in competitive adsorption mode, by comparing NU-1000 and amorphous carbons MSC-30 and BP2000, the latter of which has been previously employed in similar experiments.²² In these experiments, the initial aqueous concentration chosen was 40 mM for each of the three components (*i.e.*, HMF, glucose, and fructose). Fig. 3 shows the results of treating 1.5 mL of this aqueous solution mixture with 50 mg of each adsorbent at 297 K. Under these conditions, NU-1000 selectively removes 74% of the HMF originally present in solution (corresponding to an adsorbed HMF amount of 112 $\text{mg g}_{\text{NU-1000}}^{-1}$), with no glucose or fructose adsorption. In comparison, MSC-30 and BP2000 remove more than 96% of the HMF originally present in solution (corresponding to an adsorbed HMF amount of greater than 145 $\text{mg g}_{\text{adsorbent}}^{-1}$), but they also adsorb more than 16% of the glucose and fructose present in the original aqueous solution mixture.

A separate competitive adsorption experiment with the same three adsorbents above is demonstrated with a model sugar-feed aqueous mixture that is meant to represent an actual fermentation-broth application. This mixture consists of 8 mM HMF, which corresponds to the toxic threshold for inhibiting ethanol fermentation,^{7,9} and either 111 mM or 500 mM of glucose, which is representative of sugar concentrations in fermentation broths.^{7,9} Data shown in Fig. 4 demonstrate that NU-1000 removes 80% of HMF originally present in both mixtures, while completely rejecting adsorption of glucose. In comparison, the amorphous carbon materials consisting of MSC-30 and BP2000 adsorb at least 2.5-fold and 3.6-fold in mass more glucose than they do HMF for the 111 mM and 500 mM glucose mixtures, respectively, while the amount of HMF adsorbed is greater than 97% of that originally present in both mixtures. This results in the amorphous carbon materials adsorbing more than 12% and 2.5% of glucose originally present in the 111 mM glucose and 500 mM glucose mixtures, respectively.

The data above demonstrate selective removal of aromatic poison HMF from an aqueous mixture also containing glucose with NU-1000, with no glucose adsorption. Such selective removal is impossible to accomplish with amorphous carbons MSC-30 and BP2000, since these result in adsorption of sugars

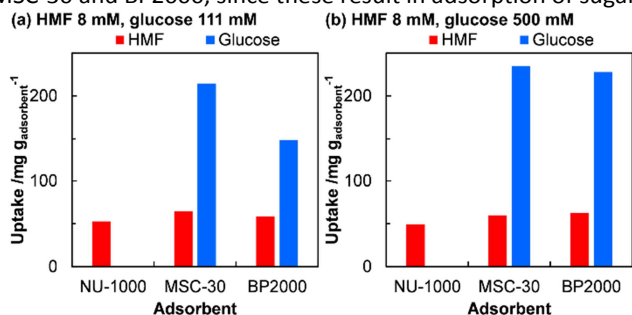


Fig. 4 Competitive adsorption of HMF (initial concentration of 8 mM) and glucose [(a) 111 mM and (b) 500 mM] on 25 mg of adsorbent at 297 K.

in addition to HMF. These data motivate the practical application of NU-1000 for sequestration of furanics from sugar feeds for ethanol fermentation, most likely in either a multiple adsorption-desorption column format (*i.e.*, as in pressure-swing adsorption) or a MOF-containing membrane.

In summary, we have demonstrated unprecedented selective adsorption of furanics such as HMF and furfural, with exclusion of adsorption of the simple sugars that these furanics are derived from, in aqueous solution mixtures, with NU-1000 as adsorbent. We infer that the pyrene units of the MOF exhibit favorable π - π interactions for aromatic moieties on the furanic compounds, whereas the sugars lack these moieties. These results highlight extraordinary specificity by synthetic adsorption sites in a material, which rivals enzymes in its selective molecular recognition.

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