

Selective Liquid Phase Adsorption of 5-Hydroxymethylfurfural on Nanoporous Hyper-Cross-Linked Polymers

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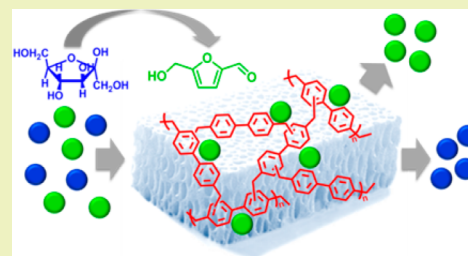
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S Supporting Information

ABSTRACT: Hydroxymethylfurfural (HMF) is considered a high potential biogenic platform chemical that can be produced from carbohydrates by hydrothermal or acid-catalyzed dehydration processes. Its separation from polar liquid phase reaction mixtures still remains a challenge on the way to commercialization. Recently, liquid phase adsorption of HMF has been considered a viable and energy efficient method. While conventional adsorbents show competitive adsorption in the reaction mixture, we herein report for the first time the highly selective adsorption of HMF from aqueous solutions on nanoporous hyper-cross-linked polymers (HCP). Excess adsorption isotherms of fructose (F), HMF, and its follow-up products levulinic acid and formic acid were measured under equilibrium conditions, and the data were modeled accordingly. Additionally, the desorption behavior was investigated. Overall, the evaluated HCP as well as similar nonpolar adsorbents exhibit great potential for future process development regarding efficient adsorptive separation technologies for the utilization of renewable feedstock.

KEYWORDS: Hydroxymethylfurfural (HMF), Liquid phase adsorption, Solid phase extraction, Porous hyper-cross-linked polymer, Adsorbent, Excess adsorption isotherm



INTRODUCTION

The depletion of fossil resources and growing concern for pollution and greenhouse gas emissions has caused an increase in bioenergy and biochemical research in recent years. In this context, the transformation of renewable biomass into chemicals offers the potential to substitute, at least partially, fuels and chemicals from petroleum. Among numerous feasible platform chemicals, hydroxymethylfurfural (HMF), which can be produced from a variety of biomass-derived carbohydrates,^{1,2} is considered one of the most promising ones. It is a versatile chemical building block considered for the production of a wide variety of chemicals and final products such as polymers and fuels.

HMF can be produced by the dehydration of carbohydrates such as fructose in aqueous solutions using acid catalysts.³ However, under acidic conditions HMF subsequently rehydrates to form levulinic and formic acid. To prevent these sequential reactions and thus improve the yield and selectivity of HMF alternative approaches were suggested such as extraction of the HMF in biphasic systems. HMF extraction from a reaction mixture using, e.g., methyl isobutyl ketone (MIBK) was proposed by several groups.^{4,5} However, the challenge of this approach is determined by the quite small partition coefficients that are usually obtained.⁶ Thus, large amounts of MIBK or other respective solvents are required in order to extract HMF from the aqueous phase.⁷ Another option to avoid HMF and consequently fructose loss due to formation of side products is the use of organic solvents as reaction media.

It is known that especially polar organic solvents such as dimethyl sulfoxide (DMSO) enable high selectivity and high yields of HMF.^{8,9} However, they usually possess low vapor pressures and high boiling points and thus require HMF separation processes, which demand even more energy than by using water. This renders them less feasible for an economic or ecologic HMF production process.¹⁰

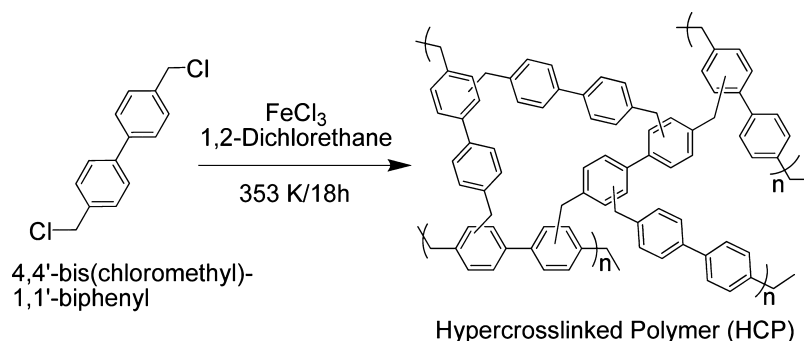
Another separation method for HMF from reaction solutions based on various solvents including water is liquid phase adsorption. It was first proposed by Vinke and Bekkum to use activated carbons as adsorbents.¹¹ In recent years, this method attracted attention again because it became more obvious that the separation of HMF is the main challenge in the production process development. So far only few studies have been reported applying activated carbons as well as hydrophobic zeolites as adsorbents. In 2009, Ranjan et al. presented the adsorption of HMF and other compounds using moderately hydrophobic zeolites to remove fermentation inhibitors for the production of bioethanol from lignocellulose hydrolyzates.¹² In two further studies, they presented selective adsorption of HMF from fructose/HMF-containing water/DMSO solutions using three different activated carbons¹³ as well as surface-modified carbon adsorbents.¹⁴ The authors linked adsorption capacity and HMF adsorption selectivity to two properties of

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Scheme 1. Preparation Route for the Hyper-Cross-Linked Polymer (HCP)



the activated carbon: microporosity and oxygenate functionality, i.e., carbon polarity. León et al. presented the adsorption of fructose, HMF, and levulinic and formic acid from aqueous solutions using H-BEA ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 18$) zeolite as adsorbent.¹⁵ Therein, the authors reinforced the idea of the importance of nonpolar surfaces for selective adsorption of HMF. Recently, Dornath and Fan presented the formation of HMF from the dehydration of fructose over zeolite Beta in the aqueous phase using a reactive adsorption system and carbon black as adsorbent.¹⁶ The results proved that the selectivity for the production of furans (HMF and furfural) could be enhanced from 27% to 44% with a furan yield of 41%.

Despite the proof of concept for the preferred adsorption of HMF over fructose using nonpolar adsorbents, the adsorption selectivity remains rather low. This raises the question of whether new materials concepts could improve the adsorption performance, especially because in the last two decades the pool of porous materials was significantly extended beyond the well-known activated carbons and zeolites. Especially in recent years, organic framework compounds were established as an own field of nanoporous polymeric materials. They provide great structural variability in combination with high specific surface areas and a tunable surface chemistry.^{17–19} One of various synthetic pathways featuring a convenient procedure and commercially available monomers is the cross-linking of building blocks by Friedel–Crafts alkylation resulting in hypercross-linked polymers (HCP).²⁰ They have attracted attention for potential applications in separation,^{21,22} heterogeneous catalysis,²³ and gas storage.^{24–26} Porous polymers of that kind are alternative adsorbents due to their controllable pore structure and physical and chemical stability, as well as high specific surface area compared to activated carbons.^{21,22,27} Xu et al. presented a critical review using data from industrial processes that polymers can maintain their structural integrity for more than five years in water treatment plants in China, lasting for more than 2000 regeneration cycles.²⁸ Activated carbon, on the other hand, needs to be replaced after approximately 15–20 regeneration cycles. Additionally, polymers also present organic fouling resistance, which often incapacitates activated carbons.

On the basis of the properties of porous polymers and the requirement for an adsorptive HMF separation process, in this work, we investigated in detail the selective adsorption of HMF from aqueous solutions using a nanoporous HCP as adsorbent. Its capacity and selectivity for HMF is compared to fructose as a substrate as well as its follow-up products levulinic acid and formic acid as pure substances as well as mixtures in coadsorption studies. Additionally, desorption behavior is

investigated, and isotherm data obtained under equilibrium conditions are modeled accordingly.

EXPERIMENTAL SECTION

Materials. Supra EUR activated carbon (AC) was supplied by Cabot, Norit activated carbon. Y zeolite (HY, CBV 712: $\text{SiO}_2/\text{Al}_2\text{O}_3 = 12$) was supplied by Zeolyst International. Fructose ($\geq 99.0\%$) and FeCl_3 ($\geq 98\%$) were purchased from Merck. Levulinic acid (98%), formic acid ($\geq 95\%$), acetone (99.8%), HMF ($\geq 99.9\%$), formic acid (95%), 4,4'-bis(chloromethyl)-1,1'-biphenyl (BCMBP, 95%), 1,2-dichloroethane (DCE, 99.8%), and methyl isobutyl ketone (MIBK, $\geq 99\%$) were purchased from Sigma-Aldrich. Methanol (99.8%) and ethanol (99.9%) were purchased from ChemSolute (Th. Geyer), and 2-methyltetrahydrofuran (2-MeTHF, 99%) was purchased from ABCR. All the chemicals were used without further purification. Y zeolite was calcinated at 823 K for 6 h (10 K min^{-1}) to obtain the acid form (HY). Purified water from a Werner Reinstwasser system ($>18.2 \text{ M}\Omega \text{ cm}$) was used to prepare the solutions.

Methods. *Synthesis of Hyper-Cross-Linked Polymer (HCP).* The synthesis of HCP was performed as described by Wood et al.²⁹ In a typical synthesis procedure, 2 g (7.96 mmol) of BCMBP was dissolved in 20 mL of DCE, and a suspension of 1.29 g (7.96 mmol) of FeCl_3 in 10 mL DCE was prepared. When the FeCl_3 suspension was added to the monomer, an instantaneous gelation of the solution is observed that turned dark blue/black. The obtained gel was heated at 353 K for 18 h under reflux conditions and a N_2 atmosphere (Scheme 1). After cooling to ambient temperature, the HCP was separated from the reaction mixture and extracted in a Soxhlet setup with methanol for 24 h. After extraction, it was dried at 333 K in an oven and ground and sieved to a particle size of maximal 0.2 mm.

Liquid Phase Adsorption Measurements. The adsorption experiments were performed in batch mode using water shaking bath equipment with temperature control and with reciprocating agitation. Before the adsorption tests, adsorbents were dried/degassed in an oven for approximately 15 h at 373 K. The evaluation of the excess adsorption behavior of three different materials (HY zeolite, Supra EUR activated carbon, and synthesized HCP) was done using HMF and fructose in the same solution at mass equivalent concentrations ($0.05 \text{ g g}_{\text{sol}}^{-1}$) and at 293 K. Excess adsorption isotherms were performed using equimolar concentrations of the respective adsorbents with the aim of a better scientific understanding of the adsorption behavior. The adsorption experiments were performed at different temperatures (293, 323, and 353 K) and with different initial concentrations of fructose, HMF, and levulinic and formic acids ($0.005\text{--}1.1 \text{ mmol g}^{-1}_{\text{solution}}$) as pure component solutions and as mixtures. In a typical adsorption experiment, 0.04 g of adsorbent was added to 2 g of solution, and it was kept at isothermal conditions. The adsorption experiments were all performed for 1 h because experiments on the kinetics proved that equilibrium is reached in less than 10 min. The amount adsorbed at the equilibrium, q_e (mmol g^{-1}), was calculated by eq 1

$$q_e = \frac{(C_0 - C_e) \times m}{W} \quad (1)$$

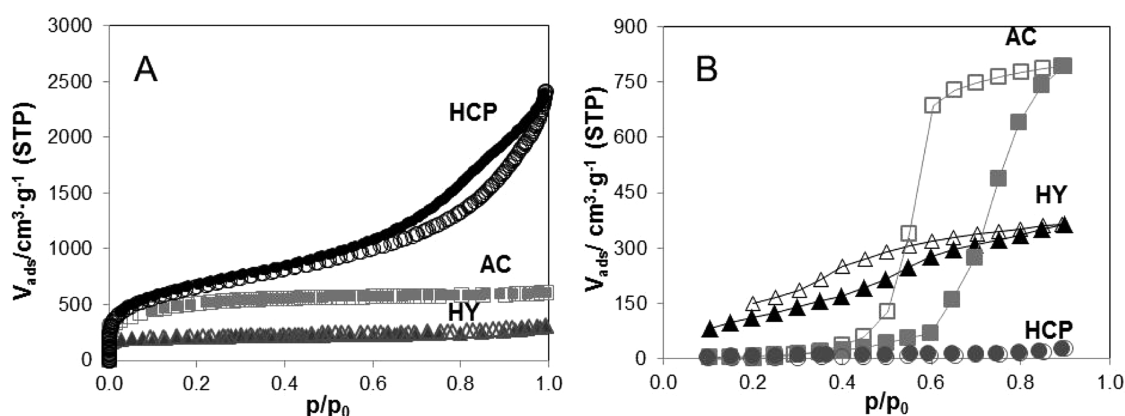


Figure 1. Physisorption isotherms of N₂ at 77 K (A) and water vapor at 301 K (B).

where C_0 and C_e are the initial and equilibrium liquid phase concentrations of the substances ($\text{mmol g}^{-1}_{\text{solution}}$), respectively. m is the total mass of solution, and W is the mass of the dry polymer used. The equation parameters for the isotherm models were estimated using Statistica 7.0 software using a nonlinear estimation. The separation factor, α , was determined as the molar ratio of (HMF/fructose) adsorbed divided by the ratio of (HMF/fructose) in the initial solution.¹³

HPLC Analysis. After the adsorption experiments, samples of the solutions were analyzed using HPLC (LC-20AD, Shimadzu) equipped with refractive index (RID-10A) and UV-vis (SPD-20A) detectors. An organic acid resin column was used in the measurement with an oven temperature of 313 K. A total of 0.002 M trifluoroacetic acid was used as a mobile phase with a flow rate of 1.0 mL min⁻¹. Fructose, was detected by the refractive index detector. HMF and organic acids were detected by the UV-vis detector with a wavelength of 210 and 254 nm, respectively.

HMF Desorption. Prior to desorption experiments, adsorption of HMF and fructose in molar equivalent concentrations were performed as described previously, using 0.1 g of polymer in 5 g of solution (0.25 mmol g⁻¹). Desorption experiments were performed in a Soxhlet apparatus for 16 h and filtration/washing as extraction methodologies, testing different solvents. The filtration experiments were performed at room temperature (296 ± 2 K). Desorption experiments by filtering were performed by washing the adsorbent with 5 g of solvent five times; each filtrate was analyzed by HPLC. The percent desorption was calculated using eq 2, with $n_{ad} = n_0 - n_e$ as the adsorbed amount of substance (n_0 is the initial amount of substance in solution before adsorption, and n_e is the equilibrium amount of substance in solution after adsorption) and n_{de} as the desorbed amount of substance in solution.

$$\text{Desorption (\%)} = \frac{n_{de}}{n_{ad}} \times 100 \quad (2)$$

Adsorbent Characterization. Textural properties and pore characteristics of the adsorbents were investigated by nitrogen physisorption measurements. They were performed at 77.4 K using Micromeritics ASAP 2000 equipment (AC and HY) and a Quantachrome Autosorb IQ (HCP). Samples were evacuated and heated prior to analysis for 12 h (HCP, 393 K; HY, 573 K; AC, 423 K). The relative pressures used to calculate micropore and total pore volume and BET specific surface area are specified in Table S1 of the Supporting Information. Water physisorption to evaluate the surface hydrophobicity was performed at 301 K on a Quantachrome Autosorb IQ. Samples were evacuated prior to the analyses at the same conditions used for N₂ physisorption.

RESULTS AND DISCUSSION

Adsorbent Characterization. Because the liquid phase adsorption behavior of porous solids is strongly related to the

specific surface area and pore properties, the HCP as well as the activated carbon and zeolite as reference materials were investigated by nitrogen and water vapor physisorption measurements. While AC and HY are exclusively microporous materials displaying a type I isotherm, the HCP shows a combined type I, II, and IV isotherm (Figure 1A), indicating a broad pore size distribution from micropores up to small macropores. Thus, HCP is rather designated a nanoporous material. While HCP exhibits the highest specific surface area (Table 1), t-plot analysis shows that the micropore surface area

Table 1. Textural and Pore Properties of Adsorbents Determined by N₂ Physisorption Measurements at 77 K

adsorbent	S_{BET}^a ($\text{m}^2 \text{g}^{-1}$)	S_{micro}^b ($\text{m}^2 \text{g}^{-1}$)	S_{external}^b ($\text{m}^2 \text{g}^{-1}$)	V_{total}^c ($\text{cm}^3 \text{g}^{-1}$)	V_{micro}^b ($\text{cm}^3 \text{g}^{-1}$)
AC	1838	1750	88	0.92	0.81
HY	813	626	188	0.44	0.24
HCP	2398	682	1716	3.73	0.29

^aSpecific area (S_{BET}) was calculated by the BET isotherm method using the Rouquerol plot to determine the accurate relative pressure region. ^bMicropore area (S_{micro}), external + mesopores area (S_{external}), and the micropore volume (V_{micro}) were calculated according to the t-plot method. ^cTotal pore volume (V_{total}) was calculated according to Gurvich. Relative pressures for data evaluation are given in Table S1 of the Supporting Information.

is comparable to the zeolite, while in case of AC, nearly all surface area is assigned to the micropores. The surface area of HCP is ascribed to approximately 70% of the non-micropore surface, termed as “external”. This includes the surface of mesopores and small macropores as well as the external surface due to small particle sizes. The high specific surface area and total pore volume of the HCP are essential properties for the HMF adsorption as shown later.

The polarity of the available surface, which is said to have a significant influence on the liquid phase adsorption behavior especially in polar solvents, was characterized by water vapor physisorption experiments (Figure 1B). The isotherms’ shape qualitatively describes the surface polarity. The HY zeolite with a comparable polar surface shows water vapor adsorption at low relative pressure, slightly increasing until the pores are filled up to 67% at $p/p_0 = 0.9$. In comparison, the activated carbon provides a much more hydrophobic inner surface, which is indicated by the main water vapor uptake that occurs at $p/p_0 = 0.6$ – 0.8 and finally achieves a pore filling degree of 69% at $p/p_0 = 0.9$. These data are in accordance with the literature.³⁰ In

contrast, the HCP shows only negligible water vapor adsorption with a minor pore filling of <1% at $p/p_0 = 0.9$. This is related to the low polarity of its surface that consists exclusively of nonpolar organic building blocks. Concluding, such a nonpolar surface area should show weak interactions with polar molecules such as water. Thus, the adsorption of less polar substances such as HMF compared to fructose from aqueous solution should be favored. This effect is proven in the following by the respective liquid phase adsorption experiments.

Liquid Phase Adsorption with Different Adsorbents.

As proposed by Ranjan et al. HMF adsorption is favored by hydrophobic adsorbents.¹² The authors evaluated the behavior of some zeolites with different Si/Al ratios, and they observed the HMF adsorption capacity being directly proportional to the hydrophobicity of the material. In this study, we compared three adsorbents with significantly varying surface polarity in the competitive adsorption of HMF and fructose from aqueous solution at 293 K at mass equivalent concentrations (Figure 2).

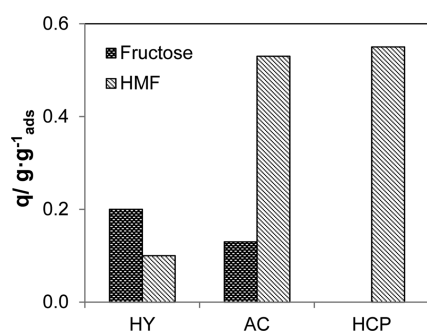


Figure 2. Competitive adsorption of HMF and fructose using adsorbents with different pore properties and varying polarity of the surface.

The low specific surface area and pore volume, associated with the comparable high surface polarity of the HY, are reflected in the results of fructose and HMF adsorption. The amount of adsorbed HMF is significantly lower than for the other adsorbents due to the lower specific surface area and pore volume. The higher polarity gives rise to the significantly lower selectivity of HMF adsorption. HMF and fructose adsorbed amounts on AC and HCP are similar, while HCP presents >99% of selectivity for the adsorption of HMF. Figure S1 of the Supporting Information presents competitive adsorption of HMF and fructose in equimolar concentrations using HY, AC, and HCP as adsorbents. As mentioned before, HCP shows a higher specific surface area combined with a higher total pore volume. These features associated with high hydrophobicity are important to achieve high and selective HMF adsorption from aqueous solutions. On the other hand, the activated carbon is essentially a microporous material with a high specific surface area and higher micropore volume but with a less hydrophobic surface. Thus, it is possible to infer that not just the surface polarity of the material but also the textural/pore properties such as the presence of micropores and mesopores, specific surface area, and pore volume are important for selective HMF adsorption. In a detailed study relating to pore structure and polarity of the adsorbent surface, it was observed that when tuning the oxygen content independently of microporosity a decreasing oxygenate functionality (i.e., increasing hydrophobicity) leads to an increase in HMF adsorption selectivity

(from approximately 0.03 $g \cdot g^{-1}$ for HMF and 0.06 $g \cdot g^{-1}$ for fructose to 0.1 $g \cdot g^{-1}$ for HMF and 0.03 $g \cdot g^{-1}$ for fructose).¹⁴ The authors also observed that in the presence of unchanging oxygen content and increasing ultramicropore volume HMF capacity increases while fructose capacity decreases.

Liquid Phase Adsorption Isotherms of HCP. Equilibrium adsorption isotherms are essential for the optimization of the adsorption mechanism pathways, expression of the surface properties, and capacity of the adsorbents, as well as for an effective design of adsorption systems.³¹ In this study, three adsorption isotherms models (Langmuir, Freundlich, and Redlich–Peterson, Table 2 and Supporting Information) were applied in their nonlinear forms to model the equilibrium data of the adsorption of fructose, HMF, levulinic acid, and formic acid.

Table 2. Adsorption Isotherm Models Used To Fit the Adsorption Data

adsorption isotherm model	eq
Langmuir ^{a,d}	$q = \frac{Q_L K_L C_e}{1 + K_L C_e}$
Freundlich ^{b,d}	$q = K_F \times C_e^{1/n}$
Redlich–Peterson (RP) ^{c,d}	$q = \frac{K_{RP} C_e}{1 + \alpha C_e^\beta}$

^aLangmuir constants: K_L is the constant describing the affinity of binding sites ($K_L = g_{\text{sol}} \text{ mmol}^{-1}$), and Q_L is the max adsorption capacity of the adsorbent ($Q_L = \text{mmol } g^{-1}$). ^bFreundlich constants: K_F is the adsorption or distribution coefficient that represents the quantity of adsorbate on the adsorbent for a unit equilibrium concentration³² ($K_F = \text{mmol } g_{\text{ads}} (g_{\text{sol}} \text{ mmol})^{1/n}$), and n is the adsorption intensity or surface heterogeneity. ^cRedlich–Peterson constants: K_{RP} ($K_{RP} = g_{\text{sol}} \times g_{\text{ads}}^{-1}$), α ($\alpha = (g_{\text{sol}} \text{ mmol}^{-1})^\beta$) and β . ^d C_e is the equilibrium concentration.

Single Solute Adsorption Isotherms. The excess adsorption isotherms of fructose, HMF, levulinic acid, and formic acid were measured for aqueous single compound solutions (Figure 3). Regarding typical HMF synthesis conditions, especially slightly elevated temperatures below the boiling point of the solvent under atmospheric pressure are relevant for an adsorptive separation process. Thus, temperatures of 293, 323, and 353 K have been chosen for the experiments. Langmuir, Freundlich, and Redlich–Peterson models were used to fit the data of the isotherms. The estimated parameters for each model and temperature are presented in Table S2 of the Supporting Information. Fructose and formic acid (Figure 3A,D) adsorption in the HCP present a linear isotherm. This behavior is typical of low surface coverage and poor affinity between the adsorbate and adsorbent, especially when the isotherm is represented by Henry's law.³³ Liquid phase adsorption depends not only on the affinity of the solute for the solid surface but also on the affinity of the solvent for the solid and the solute for the solvent. Thus, the small amounts of fructose and formic acid adsorbed on HCP can be explained by the higher densities of polar groups in these substances, which might increase their preference for remaining in the aqueous phase instead of being adsorbed. HMF and levulinic acid present a higher affinity for adsorption on the HCP. Hence, even at low concentrations, high amounts are adsorbed (Figure 3B,C). HMF adsorption isotherms (Figure 3B) are better described by the Freundlich model, except for

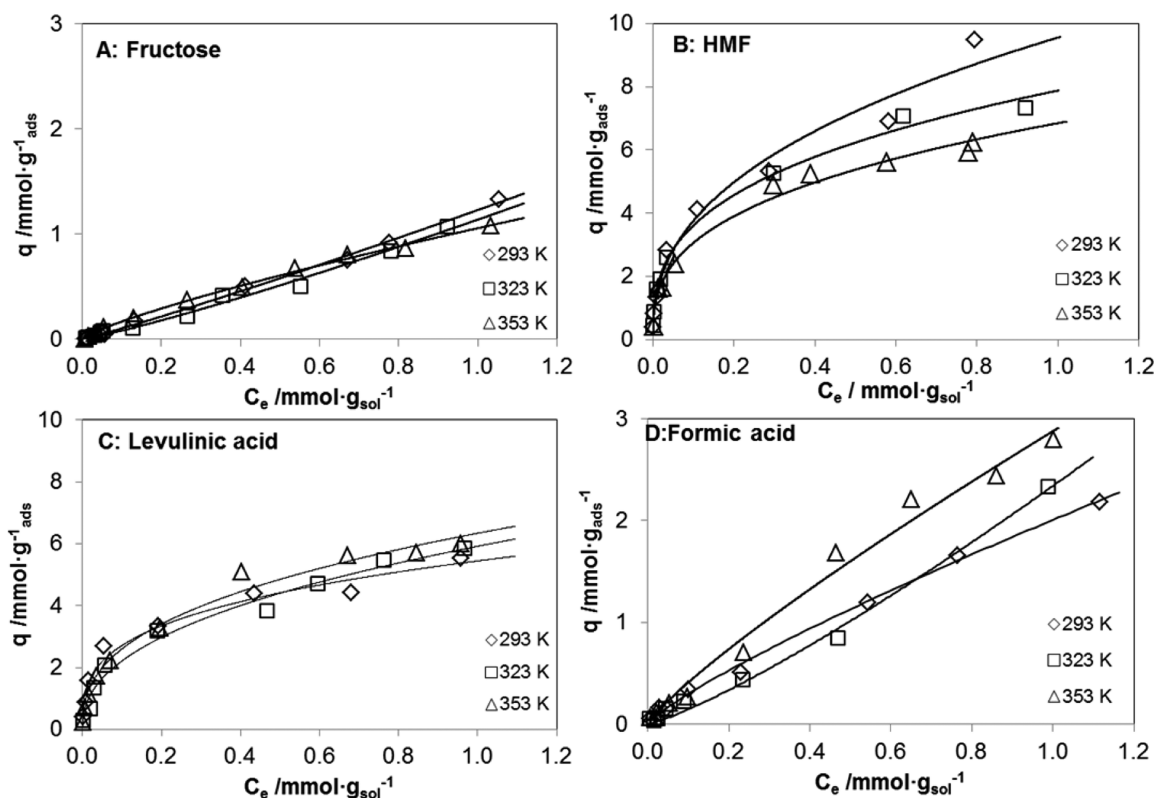


Figure 3. Adsorption isotherms of single compound solutions of (A) fructose, (B) HMF, (C) levulinic acid, and (D) formic acid at different temperatures fitted by the Freundlich model.

the isotherm measured at 353 K that also fits the Redlich–Peterson model. Because the Redlich–Peterson model reduces to the Freundlich model at high solute concentrations and high coverage and the Freundlich model presents a good adjustment to the experimental data (Table S2, Supporting Information), it was considered that adsorption of HMF on HCP at different temperatures is better described by the Freundlich model. In all the studied temperatures $1/n$ values are below unity (0.40 at 293 K, 0.34 at 323 K, and 0.35 at 353 K), meaning the adsorption is favorable. Levulinic acid adsorption isotherms (Figure 3C) are also better described by the Freundlich model for all the studied temperatures, and $1/n$ values are also below unity (0.30 at 293 K, 0.43 at 323 K and 0.39 at 353 K). Increasing the adsorption temperature results in slightly smaller amounts of adsorbed HMF and fructose, respectively. The estimated Freundlich parameter K_F (Table S2, Supporting Information) relates to the decreased adsorption capacity of the material with increasing temperature. This is consistent to the exothermic nature of the adsorption process.¹⁵ On the other hand, the effect of temperature for the adsorption of formic acid and levulinic acid is contrary to the expected; the adsorption capacity of the material is increased with increasing temperature. It may be related to the fact that for weak acids an increasing temperature causes a slight decrease in the acid dissociation constant (K_a) and thus affects the way acids are adsorbed. It was observed experimentally that the pK_a of formic acid increases with temperature.^{34,35} Furthermore, fructose and formic acid solutions presented a poor affinity with the adsorbent probably due to the differences in surface polarity and thus a nonideal wettability of the HCP's inner surface by aqueous solutions.

Multiple Solute Adsorption Isotherms. For the development of an adsorptive HMF separation process based on real reaction mixtures, the investigation of the coadsorption behavior is essential. Thus, HCP was tested as an adsorbent in the competitive adsorption of HMF and fructose at different temperatures and at equimolar concentrations (Figure 4). In all of the evaluated temperatures, HMF was preferentially adsorbed on HCP compared to fructose being consistent with the adsorption data from single compound solutions. It was also observed that even at low HMF concentrations a high HMF adsorption was obtained, proving the high affinity of HMF to HCP in aqueous solution. The adsorption of HMF on HCP at 293 K was performed in triplicate, and error bars in Figure 4A represent the standard deviation. It is shown that this HMF/fructose/water adsorption system shows the best reproducibility mainly at low concentrations. Estimated parameters considering the Freundlich model as the most appropriate one to describe this system (Table S3, Supporting Information) show that increasing the temperature also increases the total amount of HMF adsorbed on HCP. This effect of temperature is more pronounced at 353 K, when K_F for HMF adsorption is $10.42 \text{ mmol g}^{-1}$, while the influence of temperature on K_F at 293 and 323 K is negligible ($K_{F,293}$: 8.23 mmol g^{-1} and $K_{F,323}$: 8.23 mmol g^{-1}). These results differ significantly from the results obtained for HMF adsorption on HCP from single compound solutions. Also, at 293 and 323 K, the amounts of adsorbed fructose are almost negligible. When the temperature was increased to 353 K, the fructose and HMF amount adsorbed increased significantly. It is known that changing the temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate. However, in this case, the unexpected increase in both adsorbed compounds,

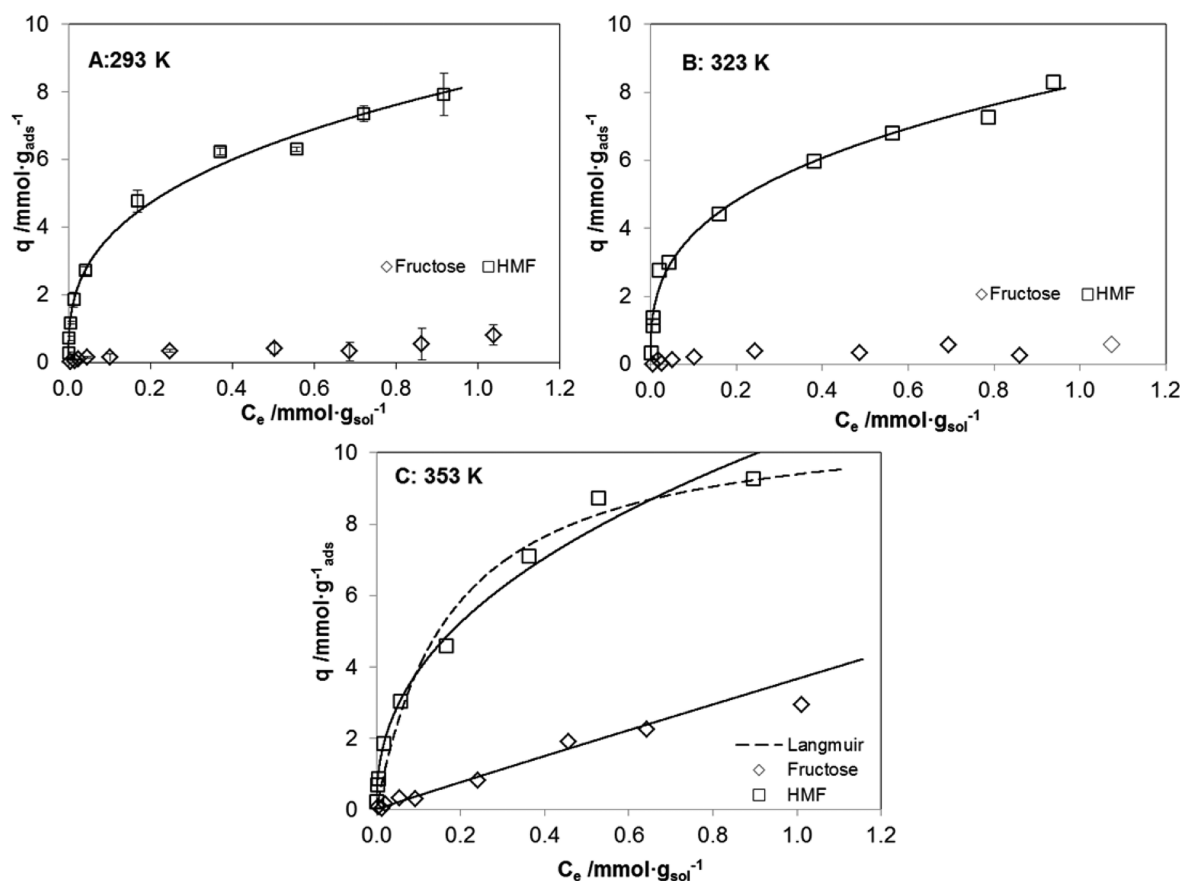


Figure 4. Competitive adsorption of HMF and fructose at different temperatures: (A) 293 K (error bars correspond to the standard deviation at each point), (B) 323 K, and (C) 353 K.

which is even more pronounced at higher equilibrium concentrations compared to the experiments at lower temperatures, must be initiated by a different effect. At higher concentrations, the viscosity of the solutions is higher, and the effect of the temperature on the viscosity is more pronounced. With an increasing temperature, it is known that the viscosity of solutions decreases. Overall, this effect might influence the wettability of the nonpolar pore walls by the quite polar solution. Due to the significant difference in polarity of the fluid and the solid phase, nonideal binary surface interactions might play an important role. Also, typical effects known from conventional polymers are conceivable, e.g., swelling or shrinking in the presence of different solvents and their respective interactions. Thus, by a thermally induced swelling of the flexible network of the HCP, a higher surface area might be accessible for the adsorption process. Nevertheless, this effect is well reproducible. Although, it has to be investigated in greater detail in the future.

The high affinity of HMF for adsorption on a nonpolar adsorbent could be of critical significance for reactive adsorption because a low equilibrium concentration of HMF should minimize its apparent amount in the aqueous phase and thus reduce the further conversion and possible side reactions of HMF.¹⁶ This increasing selectivity of the HMF adsorption at higher HMF concentration can be better evaluated from Figure S2 of the Supporting Information that presents the adsorption of HMF and fructose in competitive adsorption at different temperatures but with equal mass concentrations (initial molar ratio of 1.4:1.0 of HMF/fructose). Even at slightly higher HMF molar concentration, its adsorption is favored significantly, and

temperature does not play an important role for HMF adsorption and selectivity.

For equimolar concentrated solutions, the Freundlich model provided the best fit for the adsorption of HMF in the presence of fructose (Figure 4). The only exception is the isotherm measured at 353 K that fit well in the Freundlich model at lower concentrations, but at higher concentrations, it was well described by the Langmuir model. This may indicate that the material is close to reaching its saturation. The values of $1/n$ for 293, 323, and 353 K were 0.35, 0.33 and 0.43, respectively, confirming a favored adsorption of HMF on HCP in the presence of fructose at the evaluated temperatures.

In order to evaluate how the follow-up products (levulinic acid and formic acid) of HMF production from fructose dehydration behave in competitive adsorption, isotherms combining the components were measured at 293 K (Figure 5). Estimated parameters for Langmuir, Freundlich, and Redlich–Peterson models are presented in Table S4 of the Supporting Information. The adsorption isotherm of levulinic acid and fructose (Figure 5A) show that levulinic acid is preferentially adsorbed compared to fructose. This behavior is similar to the adsorption of HMF in the presence of fructose. It is probably related to the higher affinity of levulinic acid to HCP than of fructose to HCP. Additionally, in the presence of fructose, levulinic acid adsorbed amounts are higher compared to the single compound solution. Comparing K_F for the adsorption of levulinic acid at 293 K in pure component solutions (Table S2, Supporting Information) with the values for competitive adsorption with fructose (Table S4, Supporting Information), the adsorption capacity is higher in the presence

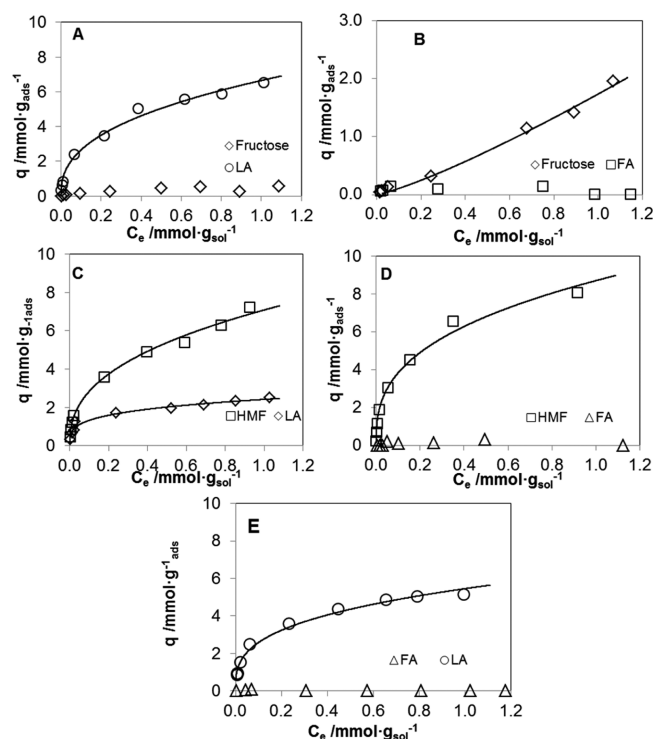


Figure 5. Competitive adsorption of (A) fructose and levulinic acid, (B) fructose and formic acid, (C) HMF and levulinic acid, (D) HMF and formic acid, and (E) levulinic acid and formic acid at 293 K.

of fructose. This effect can probably be explained by nonideal repulsive intermolecular interactions of the compounds in the mixed solution due to the significant differences in polarity of the solutes themselves as well as the solvent. It is the opposite than for HMF and fructose in the same solution and for equimolar concentrations when the presence of fructose in solution results in decreased amounts of HMF adsorbed on the polymer. Adsorption of levulinic acid in the presence of fructose fits well in the Freundlich and Redlich–Peterson models. Because the fitting of both models overlap and, as mentioned before the Redlich–Peterson model reduces to Freundlich at high surface coverage and high concentrations, using the Freundlich model was preferred. With $1/n = 0.40$, the adsorption of levulinic acid on HCP in the presence of fructose is considered to be favorable.

Competitive adsorption of fructose and formic acid on HCP (Figure 5 C) shows that fructose adsorption is linear in accordance with the performed single compound solution adsorption isotherm. On the other hand, formic acid adsorption in the presence of fructose is negligible. This is probably due to its higher affinity for the polar aqueous phase and higher water solubility if compared to fructose. The adsorption of fructose in the presence of formic acid seems to be favorable because $1/n = 0.40$, while $1/n = 1.09$ at 293 K in single compound solution adsorption of fructose that indicates a less favorable adsorption of fructose on HCP.

The presence of levulinic acid in the same solution with HMF decreases the amount of HMF adsorbed on HCP (Figure 5C). It is obvious that K_F of levulinic acid dropped by half in the presence of HMF. There is a competition for the adsorption sites between HMF and levulinic acid. This is consistent with the respective adsorption results of single compound solutions that show both components to be favorably adsorbed on HCP at significantly higher amounts than fructose or formic acid. The decrease in the adsorbed HMF amount is proportional to the amount of levulinic acid, which is additionally adsorbed. Both isotherms are fitted well by the Freundlich model. $1/n$ values were 0.40 for HMF and 0.26 for levulinic acid, suggesting the adsorption of both compounds on HCP and in the same solution is favorable. Regarding the use in a technical reactive adsorptive process for HMF separation, these results imply that the HMF should be adsorbed from the solution as soon as it is formed. Thus, adsorption at low HMF concentration and low conversion of the substrate should be preferred to avoid the subsequent hydration and decomposition of HMF to levulinic acid and formic acid. Dornath and Fan studied the adsorption of fructose, HMF, and levulinic acid in the same solution using an activated carbon as adsorbent.¹⁶ They observed a similar behavior concerning the competition of HMF and levulinic acid adsorption with the amounts of levulinic acid adsorbed in the presence of HMF decreasing by half.

The adsorption of HMF in the presence of formic acid follows a similar behavior presented by the adsorption of HMF in the presence of fructose. Formic acid adsorption is negligible, while the adsorbed amounts of HMF are even slightly increased compared to the ones obtained when HMF is adsorbed in the presence of fructose (Tables S3 and S4, Supporting Information). Parameter estimation for this adsorption system indicates the best model to describe the adsorption of HMF on

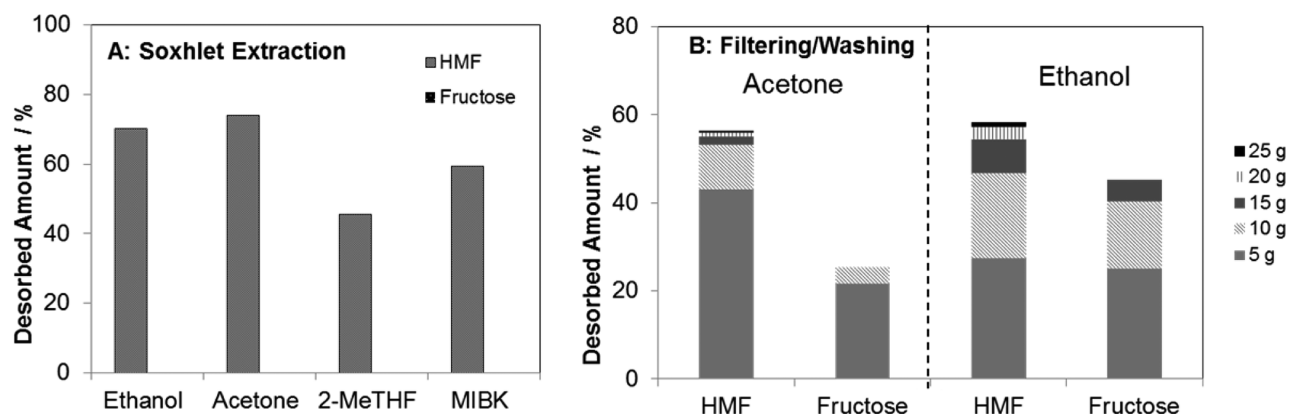


Figure 6. HMF and fructose desorption (A) by Soxhlet extraction and (B) by filtering/washing at ambient temperature with cumulative amounts (5 g each time) of the respective solvents.

HCP in the presence of formic acid is Redlich–Peterson, while the Freundlich model also fits the isotherm. Also, a favored adsorption is indicated by $1/n = 0.36$.

For the adsorption of levulinic acid and formic acid from the same solution, the adsorption capacity of HCP for levulinic acid was identical to the values observed when the adsorption was performed in the single compound solution. This indicates that the presence of formic acid does not affect the adsorption of levulinic acid. On the other hand, in the presence of levulinic acid, the adsorption of formic acid is negligible. The levulinic acid adsorption is fitted well by the Freundlich and Redlich–Peterson models. The $1/n$ values suggest favorable adsorption of levulinic acid on HCP in the presence of formic acid.

Desorption Experiments. Desorption experiments were performed to evaluate the recovery of HMF and the regeneration of the adsorbent. First of all, preliminary experiments were performed by Soxhlet extraction testing four different organic solvents for HMF/fructose desorption (Figure 6A). Acetone and ethanol showed the most promising results. No fructose desorption was observed, which is probably related to the detection limit of the equipment. As presented in Figure 6A, it is possible to recover 74% of the adsorbed HMF by Soxhlet extraction using acetone, although a certain error must be taken into account due to the possible solvent evaporation during the extraction time. After preliminary evaluation and intending to reduce the amount of solvent used in the extraction and the energy expended in the desorption process, a second experiment was performed testing the two best solvents in a filtration/washing system at ambient temperature. Therefore, the adsorbent was washed by filtering five times using 5 g of solvent. Each different aliquot was analyzed separately. Thus, it was observed that ethanol performs slightly better in HMF desorption and superior for fructose desorption (Figure 6B). Higher amounts of fructose desorbed by ethanol are related to its higher polarity. Using acetone as solvent, 56% of adsorbed HMF and 25% of adsorbed fructose were desorbed by filtering/washing. Thus, it was observed that the majority of the recovered HMF (42% desorption in total) and fructose (21% desorption in total) were desorbed after the first washing step when acetone was used as solvent. In contrast, after the third washing step, only small amounts of HMF (<3%) were recovered. On the other hand, double the amount of ethanol was necessary to desorb the same amount of HMF. For more reliable data, future experiments will aim at continuous adsorption/desorption experiments.

A certain amount of HMF could not be desorbed under the tested conditions. We assign this observation to HMF being chemically bound to the polymer structure by a condensation reaction with residual terminal chlorine groups present in the monomer. This hypothesis is confirmed by a decrease in the pH value of the solution after the adsorption process from pH_0 5 to pH_f 3. This pH change is probably related to the release of HCl, which was qualitatively proven by precipitating AgCl by addition of a 0.1 M AgNO_3 solution. Hence, the polymer from desorption with acetone was submitted to another HMF/fructose adsorption experiment under the same conditions. Therein, the adsorbed amount corresponds to the HMF desorbed beforehand ($\text{HMF}_{\text{desorbed}} = 0.033 \text{ mmol g}^{-1}$ and $\text{HMF}_{\text{adsorbed}} = 0.032 \text{ mmol g}^{-1}$) and thus indicates the total working capacity of the polymeric adsorbent. Consequently, these polymeric adsorbents require preconditioning by trans-

forming the residual functional groups into inert groups before liquid phase adsorption processes.

CONCLUSION

Adsorption from aqueous solutions of fructose and HMF as well as its follow-up products, levulinic acid and formic acid, as pure substances as well as mixtures using a nanoporous hyper-cross-linked polymer (HCP) as adsorbent was investigated in detail. The selectivity for HMF adsorption from the aqueous phase depends strongly not only on the specific surface area and pore volume but rather on the hydrophobicity (low polarity) of the adsorbents' surface. Additionally, the presence of coadsorbates such as levulinic acid affects the HMF adsorption. A high adsorption capacity in combination with an improved selectivity for the adsorption of HMF vs fructose was identified for HCP compared to conventional adsorbents such as zeolites and activated carbons. It was found that levulinic acid and HMF compete in adsorption because both show a rather high affinity to the polymeric adsorbent. For a practical implementation, this suggests that HMF should be separated by adsorption directly upon formation at low concentrations to initially avoid the formation of the follow-up hydration products levulinic acid and formic acid.

Overall, the evaluated HCP presents great potential for application in liquid phase adsorption for product separation not only in HMF production but also generally in future biorefinery schemes. This is mainly due to the fact that often polar solvents such as water are used, and the reactants are typically more polar than the formed products. Considering a technical implementation in an integrated process, detailed analysis of the performance and especially the energy requirements compared to other feasible separation processes is essential and currently under investigation. Additionally, the economic viability has to be validated not only concerning alternative processes but also compared to conventional adsorbents.

ASSOCIATED CONTENT

Supporting Information

Detailed description of adsorption isotherm models, additional information on nitrogen adsorption measurements, and additional liquid phase adsorption data including detailed information on the parameters of the adsorption isotherm modeling. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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