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Adsorption kinetics of Dowex™ Optipore™ L493 for the removal of the furan 5-hydroxymethylfurfural from sugar

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Abstract

BACKGROUND: Recently much research has been focused on the production and refinery of biobased fuels. The production of biofuels derived from lignocellulosic biomass is recognized as a promising route to produce biobased fuels responsibly. Often, product streams (e.g. glucose) still contain small amounts of undesired components (e.g. furans such as HMF). This study focuses on the removal of furans produced during the fermentation. In earlier work, styrene based resins have been identified as promising materials for this separation. In this work the kinetic properties of the most promising resin: Dowex™ Optipore™ L493 are studied.

RESULTS: The diffusion coefficient of 5 mg L⁻¹ HMF was $\sim 8 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ in water and $3.0 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ in a glucose solution. The reduced diffusion coefficient in the particle when glucose is present is caused by the higher viscosity of the glucose solution and it indicates that diffusion is controlled by surface and pore diffusion. The breakthrough curves of HMF on Optipore showed that the column is very efficient under conditions of interest.

CONCLUSION: This study shows that Optipore is a much more efficient resin for HMF removal than currently used resins. Its fast kinetics and capacity make it possible to efficiently remove HMF from glucose solutions.

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Keywords: HMF; glucose; breakthrough; zero length column; biorefinery; Optipore L493

INTRODUCTION

Recently much research has been focused on the production and refinery of biobased fuels. The production of biofuels derived from lignocellulosic biomass is recognized as a promising route to produce biobased fuels responsibly.¹ Lignocellulosic biomass consists of cellulose, lignin and hemicellulose. Bioconversion into valuable products is done in two steps: hydrolysis of polysaccharides into monosaccharides and subsequent fermentation into the product of interest. Unfortunately the harsh conditions used during pretreatment of the biomass produce toxins that inhibit fermentation and consequently need to be removed.² The main classes of toxins are identified as acids, phenols and furans.¹ This study focuses on the removal of one of these classes, i.e. furans from glucose product streams. In earlier work, styrene based resins have been identified as promising adsorbents for the separation of furans from sugars.^{3–5} Adsorption of furans is established by $\pi - \pi$ stacking of the furan ring with the styrene group of the resin. In previous work we investigated several styrene based resins, with and without anion exchange groups, for the removal of 5-hydroxymethylfurfural from glucose.³ Dowex™ Optipore™ L493 (Optipore) was identified as the most promising adsorption resin for HMF adsorption over a broad HMF concentration range, based on equilibrium adsorption isotherms.³ Table 1 summarizes the main properties of the Optipore resin. The excellent adsorption qualities are due to the high surface area of the resin ($> 1100 \text{ m}^2$

g^{-1}).³ Furthermore, the apolar resin does not adsorb the polar glucose, and sugar loss due to adsorption is therefore negligible, nor does the presence of glucose influences the adsorption of HMF.

Dowex classifies Optipore as an enhanced resin with well-connected pores.⁶ This does not only affect the adsorption capacity but also the adsorption kinetics. Adsorption in the particle is achieved through pore diffusion or over pore surface or by a combination of both. If the pores are not well connected, the diffusion path is long. In that case, long times are required to reach equilibrium adsorption capacity and adsorption kinetics are slow. However, since the pores of Optipore are well connected, adsorption kinetics are assumed to be fast, as was also observed by Wegmann *et al.*⁷ for the removal of acrylonitrile from water using Optipore. In addition to our previous study where we investigated static equilibrium adsorption behavior, we here investigate the adsorption kinetics of the adsorption of HMF in Optipore, which

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Table 1. Properties of Dowex Optipore L493⁶

Matrix structure	Macroporous styrenic polymer
Crosslinker ^{29,30}	Divinylbenzene
Particle diameter ³	557 µm
BET surface area	>1100 m ² g ⁻¹
Average pore diameter	46 Å
Apparent density	0.62 × 10 ⁶ g m ⁻³
Total porosity	1.16 × 10 ⁻⁶ m ³ g ⁻¹

are essential to design a process for practical application. The effective diffusion coefficient of HMF in Optipore is studied by zero length column (ZLC) experiments and breakthrough experiments. The experimental values of the ZLC experiments are modelled with a homogeneous solid diffusion model to obtain the effective diffusion coefficient of HMF inside the particle and the external mass transfer coefficient (k_f). Although other research has shown that a similar resin, Amberlite XAD4, shows good kinetic results for the removal of furan derivatives from water or a glucose solution,^{4,8} it is expected that Optipore, due to its enhanced and well-connected pores will show even better results.⁶ All experiments are conducted with HMF in water and HMF in aqueous glucose (100 g L⁻¹). Since previous research³ showed that the presence of glucose does not affect HMF adsorption, it is expected that glucose will influence the HMF adsorption kinetics only by increasing the viscosity of the solution.

HOMOGENEOUS SOLID DIFFUSION MODEL (HSDM)

Adsorption of a solute on a macroporous adsorbent consists of several steps. First the solute diffuses from the bulk solution to the boundary layer formed by the stagnant layer surrounding the adsorbent. Then it diffuses through the boundary layer to the surface of the particle, from where it diffuses into and through the particle. The diffusion into a macroporous adsorbent is usually through the pores of the particle (pore diffusion),⁹ over the adsorption sites on the pore walls (surface diffusion)¹⁰ or by a combination of both.¹¹

For the determination of the diffusion coefficient, a zero length column is used.¹² In this experiment the adsorbent material is fixed in a column with a very short bed length and a solution is circulated over the column. Due to the short bed length, the concentration difference between the inflow and outflow of the column is very small and the system approaches an ideally mixed finite bath. When the concentration of the solution is monitored over time, the effective diffusion coefficient can be determined by fitting the experimental data to a kinetic model.

While the exact adsorption mechanism in an adsorbent is a complex interaction between the diffusion in the external film, the pore, the surface and bulk material and sorbate-sorbent interaction, it is usually modelled with simplified models.¹³ Those models regard the adsorbent as a two-component (macroporous) system with diffusion through the pores or over the pore surfaces (heterogeneous) or the adsorbent is considered as a bulk material (homogeneous) with diffusion in the bulk phase. Also a combination of both is possible.¹⁴ The homogeneous solid diffusion model (HSDM) is frequently used to describe adsorption kinetics of solutes on adsorbents. This model assumes that molecules are first adsorbed at the external surface of the resin bead, and then

diffuse further into the particle as a result of surface concentration gradients.¹⁰ In the HSDM, diffusion in a resin is assumed to be diffusion in a homogeneous solid particle. The diffusion coefficient is then calculated based on the particle diameter. The real diffused path length through the pore, determined by the pore tortuosity is not taken into account. In the case of macroporous resins, where adsorption is mainly through the pores or over the pore surfaces, the effective diffusion constant obtained gives the practical bulk diffusion coefficient of the resin, but does not provide further insight in the specific diffusion coefficient of the material. However for gel-type resins the diffusion coefficient obtained does give proper insight to the kinetic properties of the material. There are two reasons why we chose the HSDM to model the bulk diffusion coefficient. First, the specific particle parameters, such as tortuosity, that are required for proper modeling using other models are not well known. Second, although Optipore is classified as a macroporous resin that contains small pores,⁶ literature on hypercrosslinked resins states that the porous structure is different from common heterogeneous macroporous resins and that is rather regarded as a homogeneous single phase polymeric gel.¹⁵ For homogeneous materials, such as gel type materials, the HSDM very well describes the mass transfer mechanism.¹⁴

The kinetic HSDM model that describes adsorption in a column is based on the mass balance of the adsorbate. The following is assumed:¹⁰

- There is no concentration gradient over the bed. This is achieved by using a zero length column in which the bed is very short (~2 mm).
- The adsorbent is spherical with uniformly distributed pores.
- Equilibrium is described by the Freundlich equation as was determined earlier.³
- The diffusion is described by Fick's law. The concentration of adsorbent is very low and therefore Fick's law can be assumed.

For these conditions the following equations can be solved in order to obtain the effective surface diffusion coefficient, the liquid film mass transfer coefficient and subsequently, the Biot number.¹⁰

The differential mass balance of the HSDM of a solute in a spherical particle is given by:

$$\frac{\partial q}{\partial t} = D_{\text{eff}} \left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r} \frac{\partial q}{\partial r} \right) \quad (1)$$

where q is the HMF adsorption capacity of the resin ($g_{\text{solute}} g_{\text{resin}}^{-1}$), t is the time (s) and r is the radial position within the particle (m) with an origin at the center of the particle. D_{eff} is the effective surface diffusion coefficient (m² s⁻¹) and is a measure for how fast the molecules diffuse inside the particle.

The adsorption equilibrium between solute and adsorbent is described by the Freundlich³:

$$q = K \cdot c_{\text{eq}}^{1/n} \quad (2)$$

q ($g_{\text{solute}} g_{\text{resin}}^{-1}$) is the adsorption capacity at equilibrium concentration c_{eq} ($g_{\text{solute}} \text{ L}^{-1}$), K is the Freundlich equilibrium constant ($\text{L} g_{\text{resin}}^{-1}$).

Equation (1) is solved assuming the following boundary condition (Equation 3):

$$\frac{\partial q(r=0, t)}{\partial r} = 0 \quad (3)$$

signifying that there is no flux across the center of the particle.

When a stagnant film (liquid film boundary layer) is present around the particle and the effective diffusion inside the particle is fast compared with the mass transfer through this stagnant layer the following boundary condition is also necessary:

$$\rho_p D_{eff} \frac{\partial q(r=r_{p,t})}{\partial r} = k_f (c_b - c_s) \quad (4)$$

where ρ_p is the apparent particle density (g L^{-1}), c_b , c_s are the bulk and solid–liquid interface concentration respectively ($\text{g}_{\text{solute}} \text{L}^{-1}$). In this equation the kinetic parameter, k_f is introduced. This is the liquid film boundary layer mass transfer coefficient (m s^{-1}) and is a measure for how fast the molecules diffuse across the stagnant liquid film boundary layer around the particles. Equation (4) states that the flux of the solute from the bulk through the liquid film boundary layer around the particle to the particle itself is equal to the flux from the surface of the particle to the center of the particle.

The initial conditions to solve Equation (1) are:

$$c_b(t=0) = c_0 \quad (5)$$

$$q(r, t=0) = 0 \quad (6)$$

where c_0 is the bulk solute concentration ($\text{g}_{\text{solute}} \text{L}^{-1}$). The initial conditions of Equations (5) and (6) state that initially the bulk concentration is equal to the initial concentration and the particle is free of adsorbent.

This set of equations can be solved using Matlab with different combinations of the kinetic parameters k_f and D_{eff} to determine the best fit with the experimental data. k_f and D_{eff} can then be optimized by minimizing the sum of squares between the calculated c_b and the measured c_b .

The Biot number [$Bi(-)$] is an indication of the ratio of the rate of transport through the liquid film boundary layer (k_f) and the transport inside the particle (D_{eff}). For $Bi < 1$ the external mass transport is the rate limiting step while for $Bi > 100$ the diffusion in the particle is the rate limiting step.¹⁰ The Biot number is calculated using the following equation:¹⁰

$$Bi = \frac{k_f \cdot r_p \cdot c_0}{D_{eff} \cdot \rho_p \cdot q_0} \quad (7)$$

with k_f the liquid film mass transfer coefficient (m s^{-1}), r_p (m) the particle radius, c_0 ($\text{g}_{\text{solute}} \text{L}^{-1}$) the initial concentration, D_{eff} ($\text{m}^2 \text{s}^{-1}$) the effective diffusion coefficient of the solute in the particle ρ_p (g L^{-1}) the particle density, including the open volume, and q_0 ($\text{g}_{\text{solute}} \text{g}^{-1}_{\text{resin}}$) the adsorption capacity in equilibrium with c_0 .

MATERIALS AND METHODS

Materials

The resin Dowex Optipore L-493 (Optipore), 5-hydroxymethyl-furfural (HMF), glucose and sulfuric acid (H_2SO_4) were purchased from Sigma Aldrich. Impurities present in the resin were removed by rinsing with MilliQ water prior to use until impurities were no longer detectable in the rinse water by UV–VIS (200–400 nm).

Solute analysis

HMF in water was analysed with a UV–VIS detector at 284 nm. When HMF was mixed with glucose, the HMF and glucose concentrations were determined with a Waters HPLC with a 515 pump, a 2487 dual λ absorbance detector and Millenium³² (version

Figure 1. Schematic representation of experimental zero length column (ZLC) set-up.

3.20) software. Analysis was carried out with a Resex ROA-organic acid 300 x 7.8 mm column (Phenomenex). The mobile phase was $0.005 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$. The column operating temperature was 90°C and the mobile phase flow rate was 0.3 mL min^{-1} . Peak detection was performed using UV at 284 nm (HMF) and 205 nm (glucose). For both analysis methods solute calibration curves were determined.

Zero length column experiments

The effective diffusion coefficient was determined with a zero length column (ZLC) set-up as depicted in Fig. 1. The ZLC set-up used an Äkta Purifier liquid chromatographic system. This system was equipped with two pumps and a UV detector. The resin was packed in a column (Omnifit, 6.6 mm internal diameter) that was connected between the pump and the UV detector. The stream leaving the UV detector was recirculated to the feed container.

To conduct the ZLC experiments, the column was packed with the resin with a bed height of 2 mm. The column was subsequently equilibrated with water by rinsing the entire system, including the packed column, with MilliQ water (10 times the entire system volume). After equilibration, the column was disconnected and the entire system, including the feed container and the tubes, was filled with the adsorption solution (5 mg L^{-1} HMF or 5 mg L^{-1} HMF in 100 g L^{-1} glucose). 5 mg L^{-1} HMF or 5 mg L^{-1} HMF in 100 g L^{-1} glucose was chosen as this is the concentration range of the targeted industrial processes. The column was reconnected and the HMF solution was pumped through the column in recycle mode. The total volume of the system, including the feed container, was

17 mL. When HMF was adsorbed from the water, the HMF concentration was monitored over time using the UV detector connected to the Äkta system. When a HMF/glucose solution was used as feed, analysis was performed by taking small samples from the feed container (0.05 mL) that were analyzed using HPLC. In the first 2 min, samples were taken every min, then for 15 min every 5 min and then for 30 min every 15 min, followed by samples taken every 30 min to the end of the experiment. The ZLC experiments were conducted at a flow rate of 10 mL min⁻¹ and 20 mL min⁻¹ for HMF from water and at 20 mL min⁻¹ for HMF from aqueous glucose.

Figure 1 Schematic representation of experimental zero length column (ZLC) set-up.

Breakthrough experiments

Adsorption

The breakthrough curves for HMF adsorption were determined with the set-up shown in Fig. 2. Optipore resin was packed in an Omnifit column (length 100 mm, diameter 6.6 mm, or length 450 mm, diameter 20 mm). The experiments were thus performed with a bed volume (BV) of 5 or 50 mL. The reason for this difference was practical column availability and number of BV necessary for completion of the breakthrough curve. The number of BV necessary for the determination of a low concentration (5 mg L⁻¹) breakthrough curve is very high, so we use a small column and therefore small BV. Validation experiments to see if the results from both columns were comparable were performed. The breakthrough curves were determined at a flow rate of 8 bed volumes per hour (BV h⁻¹) with HMF (5 mg L⁻¹ and 5000 mg L⁻¹) from water and HMF (5000 mg L⁻¹) from 100 g L⁻¹ aqueous glucose. The effect of flow rate on column performance was evaluated by varying the flow rate (4, 8 and 12 BV h⁻¹) for HMF from water. All experiments were conducted at 20°C. The outflow of the column was fractionated in fractions with a volume of 0.5 BV. The concentration of every other fraction was analyzed with UV-VIS (HMF from water) or with HPLC with a UV detector (HMF from glucose).

The HMF column capacity (%) was presented as the HMF adsorption capacity at 100% breakthrough of the inlet concentration ($q_{100\% \text{ breakthrough}}$) (determined by measuring the surface area above the breakthrough curve from 0 BV to 100% breakthrough) over the equilibrium adsorption capacity (q_{eq}) as determined earlier:³

$$\text{HMF column capacity} = \frac{q_{100\% \text{ breakthrough}}}{q_{eq}} \cdot 100\% \quad (8)$$

The HMF column adsorption efficiency (%) was presented as the HMF adsorption capacity at 10% breakthrough of the inlet concentration ($q_{10\% \text{ breakthrough}}$) (determined by measuring the surface area above the breakthrough curve from 0 BV to 10% breakthrough) to the column capacity:

$$\text{HMF column efficiency} = \frac{q_{10\% \text{ breakthrough}}}{q_{100\% \text{ breakthrough}}} \cdot 100\% \quad (9)$$

Desorption

Desorption experiments were performed after the columns were loaded with 5000 mg L⁻¹ HMF at 20°C for 30 BV. For this experiment the same set-up was used as for the breakthrough curves (Fig. 2). Water was pumped through the pre-loaded column at 8 BV h⁻¹ at 20°C and 60°C. The outflow of the column was fractionated in fractions with a volume of 0.5 BV. The concentration of every other fraction was analyzed with UV-VIS (HMF from water) or with HPLC with a UV detector (HMF from glucose).

Figure 2. Schematic representation of the breakthrough set-up.

RESULTS AND DISCUSSION

Zero length column experiments

The effective diffusion coefficient of HMF in Optipore is determined from ZLC experiments, both for HMF adsorption from water and from an aqueous glucose solution. Figure 3 shows the HMF concentration in time (normalized for the initial HMF concentration at $t = 0$) for both solutions. The experimental data were modelled with the HSDM to determine D_{eff} and k_f (Table 2).

The HMF concentration in the solution decreases due to adsorption on the Optipore resin until it reaches equilibrium in ~4000 s for HMF in water. The curve of 10 mL min⁻¹ and 20 mL min⁻¹ coincide, indicating that external mass transfer through the liquid film boundary layer, represented by k_f does not limit the adsorption. When the flow rate is increased, the more turbulent flow pattern enhances the external mass transport by reducing the stagnant film layer around the particles.¹⁶ If the external mass transfer was the limiting factor for the adsorption kinetics, higher flow rates would result in faster decline of the HMF concentration. Since the adsorption graphs overlap we can conclude that this is not the case and that internal mass transfer is the rate limiting step.

The experimentally determined HMF reduction in the solution is modelled with the HSDM to obtain D_{eff} and k_f . The effect of k_f is most visible on the first part of the graph, while D_{eff} determines the shape of the graph. The model values are represented by the lines in Fig. 3. The HSDM follows the measured data well for $k_f > 8 \times 10^{-5}$ m s⁻¹ and $D_{eff} \sim 8 \times 10^{-12}$. This means that for

Figure 3. HMF concentration normalized for initial HMF concentration (C_0) in time (symbols) and relative HMF concentration calculated by HSDM (lines).¹⁰

$D_{eff} \sim 8 \times 10^{-12}$, all solutions with $k_f > 8 \times 10^{-5} \text{ m s}^{-1}$ give a good fit to the experimental data. Although k_f is higher than $8 \times 10^{-5} \text{ m s}^{-1}$, its exact value cannot be determined from these data, as the adsorption kinetics are no longer sensitive to k_f at these flow rates and this D_{eff} value. This shows that the external mass transfer indeed does not limit the adsorption, as was already observed from the experimental data. The effective diffusion coefficient in the particle is, as expected, equal for both flow rates, because the diffusion coefficient inside the particle is independent of the flow rate outside the particle.

The theoretical diffusion coefficient of HMF in stagnant water (D_{AB}^0) estimated with the Wilke–Chang correlation¹⁷ is $1.1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ (Table 2). The coefficient is reduced by a factor $\sim 10^2$ when HMF diffuses into the particles. This is due to hindrance of the HMF diffusion by the walls of the pores as well as by adsorption to the walls of the pores.¹⁸

Equilibrium of HMF adsorption from aqueous glucose is reached later, at $\sim 5000 \text{ s}$. This is caused by several factors. When glucose is added to the water, the viscosity increases, reducing the mixing around the particle, thereby increasing the stagnant film layer thickness around the particle. Also the higher viscosity reduces the diffusion through the thicker stagnant film layer as is also indicated by the increased D_{AB}^0 (the by Wilke–Chang correlated diffusion coefficient of HMF in a stagnant liquid) (Table 2). This is also observed from the theoretically determined value of the external mass transport factor ($k_{f,th}$), which is calculated with the Gnielinski

correlation;¹⁹ it is lower for a glucose solution (Table 2). The data obtained from the modelling of our experimental data confirm this: D_{eff} also shows that the diffusion inside the particle is reduced in the presence of glucose. Table 2 shows that the effective diffusion coefficient determined with the HSDM of HMF in glucose is approximately three times lower than when HMF is adsorbed from water. In previous research³ we measured that glucose does not adsorb on the styrene matrix of Optipore. Furthermore, we found that glucose does not alter the solubility of HMF and that the adsorption capacity of Optipore for HMF remains constant, independent of the presence of glucose. This suggested that glucose does not have any thermodynamic effect on HMF diffusion (weaker or stronger binding to the resin). The reduced D_{eff} indicates that HMF diffuses into the particle, probably not only by surface diffusion over the walls of the pores, as is the case in small pores of microporous materials, but probably also by pore diffusion when the HMF is out of the range of the attractive force field of the pore surface, which is possible in the larger pores of macroporous materials.²⁰ Glucose also increases the viscosity of the solution in the pores and this would explain the lower effective diffusion coefficient in the particle.

In the presence of glucose the HSDM model only fits with the experimental data when k_f is $7 \times 10^{-5} \text{ m s}^{-1}$, indicating that the process is, next to restriction from the internal mass transport, also limited by external mass transport. This is also indicated by the Biot number, which is 26, indicating that the process is limited by internal as well as external mass transport.

Breakthrough experiments

The breakthrough curve of HMF on an Optipore packed column was investigated because the breakthrough time and the slope of the breakthrough curve indicate the effectiveness of the adsorption at the chosen conditions.

Breakthrough curve at low HMF concentration

The breakthrough curve of 5 mg L^{-1} HMF in water was determined with a column with a volume of 5 mL . The breakthrough curve is shown in Fig. 4. The breakthrough curve was measured only once. We believe this is allowed since validation experiments performed later (Fig. 5) show that the breakthrough curves are reproducible.

Figure 4 shows that breakthrough starts at $\sim 95 \text{ BV}$ and is complete after $\sim 400 \text{ BV}$. The column adsorption capacity is determined by measuring the adsorbed HMF when the breakthrough curve shows 100% breakthrough of the inlet concentration. The adsorption capacity of the resins in the packed bed is 1.4 mg g^{-1} , this is 99% of the equilibrium adsorption capacity of the resins as determined from the adsorption isotherm in earlier work

Table 2. Effective diffusion coefficients (D_{eff}), kinetic parameter (k_f) and Biot number (Bi) of HMF adsorption in Optipore

		Water		Aqueous glucose
		10 mL min ⁻¹	20 mL min ⁻¹	20 mL min ⁻¹
HSDM	D_{eff} (m ² s ⁻¹)	8.0 × 10 ⁻¹²	8.3 × 10 ⁻¹²	3.0 × 10 ⁻¹²
	k_f (m s ⁻¹)	>8 × 10 ⁻⁵	>8 × 10 ⁻⁵	7 × 10 ⁻⁵
	Bi (—)	>13	>11	26
Theroretical correlations ^{17,19}				
	D_{AB}° (m ² s ⁻¹)	1.1 × 10 ⁻⁹	1.1 × 10 ⁻⁹	0.7 × 10 ⁻⁹
	$k_{f,th}$ (m s ⁻¹)	6 × 10 ⁻⁵	8 × 10 ⁻⁵	6 × 10 ⁻⁵

Figure 4. HMF breakthrough curve at 20°C, 5 mg L⁻¹ HMF in water, BV: 5 mL, 8 BV h⁻¹.

at 5 mg L⁻¹.³ Consequently packing of the resins in a packed bed does not change the adsorption capacity as the equilibrium capacity is similar to that earlier determined in batch experiments. The column adsorption efficiency at 10% breakthrough is 80% of the column adsorption capacity. Hand *et al.*²¹ defined three categories of breakthrough curves depending on the Biot number, For $Bi < 0.5$, the process is controlled by the liquid-phase mass transfer rate, for $0.5 < Bi < 30$ the process is controlled by liquid-phase and solid-phase mass transfer, while for $Bi > 30$, the solid-phase mass transfer rate controls the adsorption process. The calculated Bi number at 5 mg L⁻¹ is 1.67 which makes the process dependent on both liquid and solid phase mass transfer. In the ZLC experiments the process was limited by internal diffusion only, in a packed bed the operating flow rate is much lower resulting in a process that is also controlled by external transport.

At these operating conditions (e.g. flow rate, HMF concentration, residence time), the adsorption capacity of the bed is very effective and breakthrough only occurs after treatment of ~100 BV. These results make the resin Optipore a very promising candidate for HMF removal.

Due to the long experimental time and the high number of BV needed to determine the breakthrough curves at this concentration, the other breakthrough curves, investigating the effect of flow rate and the presence of glucose, were determined at a higher HMF concentration (5000 g L⁻¹) to decrease the experimental time and the number of BV treated.

Investigation of breakthrough curves at high HMF concentration

The experimental time and number of treated BV is reduced by increasing the HMF concentration (5000 mg L⁻¹) during the breakthrough experiments (Fig. 5). This breakthrough curve is shown twice determined with a BV of 50 mL to show the reproducibility of the experiments and once with a BV of 5 mL to show that the data obtained with a column of 5 mL and 50 mL are comparable.

Figure 5 shows that the two curves determined with a 50 mL column coincide and that the reproducibility of the measurements is very good. This reproducibility is representative for all other breakthrough experiments. The curve obtained with the 5 mL column also coincides with the other curves, showing that the data obtained with the two columns are comparable.

Figure 5. HMF breakthrough curves 20°C, 5000 mg L⁻¹ HMF in water, 8 BV h⁻¹: ■ experiment 1 (BV: 50 mL); □ experiment 2 (BV: 50 mL); ⊕ experiment 3 (BV: 5 mL).

Breakthrough starts at ~13 BV and is completed at ~23 BV. The curve is steep and has a regular S-shape indicating efficient HMF adsorption. This is also reflected by the column efficiency of 87% at 10% breakthrough. A steep slope of the breakthrough curve indicates that the mass transfer zone is small and that axial diffusion through the bed is negligible.

The column adsorption capacity at 100% breakthrough of the inlet concentration is only 52% of what was found in earlier batch experiments³ and much lower than the column adsorption capacity achieved with 5 mg L⁻¹. This is unexpected and not understood. Usually packed beds (especially at higher concentrations) establish higher adsorption capacities compared with batch experiments, due to their higher concentration gradient and therefore larger driving force at the adsorption zone, while batch experiments experience a decreasing concentration gradient in time reducing the driving force.^{22,23}

Effect of flow rate

Figure 6 shows that the breakthrough is at ~12 BV for 12 BV h⁻¹, ~13 BV for 8 BV h⁻¹ and ~14 for 4 BV h⁻¹. The curves show the lowest slope for 12 BV h⁻¹ while the slope increases when the flow rate is reduced to 8 and 4 BV h⁻¹. The slightly earlier breakthrough as well as the shallower slope and the tailing indicate a little less efficient adsorption. At low flow rates the residence time in the column is longer and HMF has more time to adsorb. Although this research shows that longer adsorption times affect the breakthrough time and slope, this effect is only marginal. The residence time shows only a small effect on the adsorption efficiency indicating that the internal adsorption is very efficient.

A much larger effect of flow rate on adsorption efficiency was seen with Amberlite XAD4, an adsorbent with a comparable chemical structure.²⁴ Gupta *et al.*⁸ investigated the effect of flow rate on the breakthrough of 5000 mg L⁻¹ furfural in a column packed with Amberlite XAD4. The breakthrough times of furfural on Amberlite XAD4 were much shorter than measured for Optipore at comparable flow rates. At the selected flow rates of 5, 7 and 12 BV h⁻¹, the breakthrough times were 7.7, 6.9 and 4.5 BV, respectively for Amberlite XAD4. These much earlier breakthrough times occur

Figure 6. HMF (5 g L⁻¹) breakthrough curves at different flow rates at 20°C, BV: 5 mL: ○ 4 BV h⁻¹; ■ 8 BV h⁻¹; △ 12 BV h⁻¹.

Figure 7. HMF (5 g L⁻¹) and glucose (100 g L⁻¹) breakthrough curves at 20°C, BV: 50 mL: ○ HMF in water; ■ HMF from glucose; □ glucose (from HMF aqueous glucose solution).

for two reasons. Optipore has a higher adsorption capacity than Amberlite XAD4 due to the much higher surface area.³ Furthermore, the large effect of the flow rate on the breakthrough times and the adsorption capacity, which are both reduced with increasing flow rates indicate that, in contrast to Optipore, at these conditions, adsorption in Amberlite XAD4 is controlled by internal particle diffusion.

Weil *et al.*⁴ could only establish comparable breakthrough times (~13 BV) with 5000 mg L⁻¹ furfural on a column packed with Amberlite XAD4 by reducing the flow rate ~6 times compared to the flow rate used for Optipore to 2.3 BV h⁻¹. And although the breakthrough time at these low flow rates was comparable with that of Optipore, the slope of the curve was very shallow, which is another indication that internal diffusion limits adsorption in Amberlite XAD4 at these conditions. So far Amberlite XAD4 has been identified as a good adsorber for furan derivate removal. This research shows that throughput and capacity are even better and improved enormously when Optipore is used.

Optipore is a hypercrosslinked polymer.^{15,25} These polymers are prepared by emulsion polymerization and are further crosslinked while swollen in a good solvent to increase the adsorption capacity. Previous research showed that due to this treatment the polymer also swells much more in water than resins with similar chemical structures.^{3,26} We assume that this swelling is also responsible for good connectivity of the pores and therefore the higher solute diffusion in the particle.

Effect aqueous glucose on HMF breakthrough

ZLC experiments showed that the diffusion coefficient is reduced when HMF is adsorbed from an aqueous glucose solution compared with adsorption from pure water. Breakthrough experiments of HMF in aqueous glucose solutions were performed to examine the effect of the presence of glucose on the column adsorption efficiency. Figure 7 shows the breakthrough curves of both HMF and glucose from a HMF/aqueous glucose solution. The breakthrough curve of HMF from water is added as reference. The small dip in the glucose breakthrough curve at 15 BV is probably due to an inaccurate correction for the presence of HMF during HPLC analysis.

Glucose is detected at the end of the column after 1.5 BV and HMF breakthrough in aqueous glucose is observed at 12 BV. The glucose retained in the column is by approximation equal to the void volume in the bed. The fast breakthrough of glucose shows that glucose indeed does not adsorb on Optipore, as was shown earlier.³ In the presence of glucose, an earlier breakthrough of HMF is observed than in the presence of pure water and also the slope of the curve is less steep and more tailing is observed. This is explained by the higher viscosity of the glucose solution. This affects the kinetics of adsorption in two ways. As in the ZLC experiments, a higher viscosity increases the stagnant film layer, thereby increasing the resistance to mass transport towards the particle. This is also seen in the correlated k_{fth} numbers; when glucose is present, the k_{fth} decreases from 1.65×10^{-5} m s⁻¹ to 1.19×10^{-9} m s⁻¹ indicating a higher resistance to mass transfer from the bulk solution to the particle. Secondly, ZLC experiments showed that the effective diffusion coefficient is also reduced by the presence of glucose (Table 2).

Weil *et al.*⁴ performed breakthrough experiments on Amberlite XAD4 with furfural in water and furfural from aqueous glucose. The breakthrough curve (breakthrough time and slope of the curve) was unaffected by the presence of glucose in that case. However, the concentration of glucose was 20 times lower (5 g L⁻¹) than in our experiments and therefore the viscosity was very similar to that of water. This support the hypothesis that the faster breakthrough and reduced slope we observe when glucose is present is caused by the viscosity increase of the solution and not by HMF–glucose interactions.

Desorption

Desorption of HMF and HMF and glucose from the column was performed with water at 20°C and 60°C (Fig. 8). Desorption at the elevated temperature of 60°C was chosen to study whether the reduced capacity of the resin observed earlier at this temperature³ also results in faster release of HMF in desorption. The outlet concentration is normalized based on the feed concentration when the column was loaded (c_{out}/c_{ads}).

Figure 8 shows that glucose is released from the column almost immediately, hardly any glucose is present in the permeate after 3

Table 3. Percentage HMF desorbed after 10 and 30 BV at 20°C and 60°C, without and with glucose as percentage loading of the column

	Desorption after 10 BV (%)	Desorption after 30 BV (%)
20°C	50	81
20°C with glucose	46	68
60°C	70	94
60°C with glucose	67	90

Figure 8. HMF and glucose desorption of the column with water, BV: 50 mL: ▲ glucose desorption 20°C; △ glucose desorption 60°C; ● HMF desorption with glucose 20°C; □ HMF desorption without glucose 60°C; ○ HMF desorption with glucose 60°C.

BV only. The 100 g L⁻¹ aqueous glucose solution has a viscosity of 1.3 MPa s at 20°C and of 0.6 mPa s at 60°C.²⁷ A bit more glucose is released from the column at 60°C, due to the reduced viscosity of the solution at this temperature, but this effect is rather small. Glucose release from the column is so fast because glucose is not adsorbed to the column but only present in the void volume of the column and pores of the adsorbent Optipore.³

Figure 8 also shows the outlet concentration of HMF (without and in the presence of glucose) from the column at 20°C and at 60°C. The relative concentration of released HMF reaches a value higher than 1 because the capacity of Optipore is much lower at 60°C than at the loading temperature of 20°C.³ The percentage desorption expressed as percentage of the loading is given in Table 3. In the first 10 BV ~1.5 times more HMF is released from the column rinsed with water at 60°C compared with the column rinsed with water at 20°C. From 10 BV onwards the amount of HMF desorbing from the column is equal for both temperatures. Still the desorption at 60°C is much more efficient, as the amount of HMF still adsorbed to the column at that temperature is less than that adsorbed to the column at 20°C. The total amount of HMF desorbed after 30 BV is 81% at 20°C and 94% at 60°C. A better release of HMF at higher temperature was expected since the capacity of Optipore for HMF is lower at higher temperature.³

Desorption of HMF is a bit faster when glucose is not present (Fig. 8, Table 3). HMF desorption is lower when glucose is still present in the permeate (up to ~3 BV). This is due to the increased viscosity of the glucose solution. As discussed earlier, this lowers

the diffusion rate in the particle as well as the diffusion rate outside the particle in the stagnant boundary film layer.

Although HMF is released from the column by rinsing it with water, desorption requires a high amount of water. Other authors studied the desorption using different solvents (e.g. methanol, ethanol, n-propanol and n-butanol, acetone).^{4,28} Although these solvents removed HMF effectively, their strong interaction with the resin, thus introducing another component in the system, is a major drawback. Increased desorption of HMF at higher temperature indicates that desorption with steam could offer a solution for HMF removal.

CONCLUSION

This study shows that, compared with often-used resins, Optipore is a very efficient resin for HMF removal. Its fast kinetics and high capacity make it possible to efficiently remove HMF from glucose solutions.

The diffusion coefficients of HMF (5 mg L⁻¹) were $\sim 8 \times 10^{-12}$ m² s⁻¹ in water and 3.0×10^{-12} m² s⁻¹ in a glucose (100 g L⁻¹) solution. The reduced diffusion coefficient in the particle when glucose is present is caused by the higher viscosity of the glucose solution and indicates that diffusion is not only at the surface of the pore but that pore diffusion also plays a role in HMF adsorption.

The breakthrough curves of HMF on Optipore showed that the column is very efficient at the conditions tested. At 5 mg L⁻¹, the adsorption is dependent on internal as well as external mass transport parameters. At 5000 mg L⁻¹ the breakthrough curves showed external transport limitations. The desorption of HMF using water is improved when the temperature is increased, which would make desorption with steam an option for desorption. The results clearly show that at the operating conditions investigated (e.g. flow rate, HMF concentration, residence time), the adsorption capacity and kinetics of the resin Optipore are very effective, making it a very promising candidate for HMF removal.

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