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## Separation of lignin from beech wood hydrolysate using polymeric resins and zeolites – Determination and application of adsorption isotherms

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## ABSTRACT

Separation of lignin from hemicellulose sugar out of beech wood hydrolysate (BWH) by four polymeric and one zeolitic adsorbents was investigated. First, by means of single and binary model solutions (MS), consisting of 3.1 g/L phenol and/or 4.2 g/L xylose, the two most suitable adsorbents were chosen and single- and multi-component isotherms were determined. Second, the isotherm model parameters from the MS were applied to the equilibrium measurements of BWH and statistically evaluated regarding their adaptability. All experiments were carried out in batch mode. Of the five tested adsorbents, Amberlite XAD7HP and SEPABEADS SP700 were found to be the most efficient. Phenol and lignin removal was 100% and over 93% respectively and xylose and hemicellulose sugar recovery was greater 92% at an adsorbent-to-solution ratio of 1:5 w/v (g/mL). Phenol adsorption agreed best to Freundlich equation and xylose adsorption to Langmuir equation for XAD7HP and SP700 in the single-component experiments. In a multi-component system, adsorption behavior of both phenol and xylose for the two adsorbents can be fitted best to an extended Freundlich isotherm. For practical applications, it is reasonable to use Freundlich and extended Freundlich isotherms for xylose adsorption onto XAD7HP and SP700. Application and evaluation of the isotherm model parameters determined by the MS to the equilibrium data from adsorption experiments of BWH onto XAD7HP and SP700 showed that the valid isotherm type and thus the predominant adsorption mechanisms can be predicted accurately. However, the isotherm model parameters of the MS do not adequately describe the specific adsorption process of the BWH onto the resins. Hence, they have to be determined individually. More than 90% of adsorbed lignin and 95% of adsorbed hemicellulose sugar were desorbed using 50 wt% ethanol solution.

## 1. Introduction

The utilization and conversion of lignocellulosic biomass to bioenergy, biofuels and biochemicals can help to cope with energy shortage, decreasing petroleum reserves and increasing climate change. By means of biorefineries, lignocellulosic raw material, e.g., straw or wood, can be fractionated in its three main constituents cellulose, hemicellulose and lignin. Beech wood was identified as one of the most available and suitable biomasses for these purposes in Germany. An appropriate process for the fractionation of beech wood forest residues is the organosolv process, i.e. pulping with ethanol-water [1,2]. The resulting suspension of the organosolv process is separated into a solid cellulose fraction and a liquid fraction containing dissolved hemicelluloses, lignin as well as other wood extractives. The solid cellulose fraction is separated and can be further processed into pulp or rather hydrolyzed to sugar. From the liquid phase, dissolved lignin is precipitated and can

either be used as a direct additive for binding agents or be depolymerized into its phenolic mono-, di- and oligomers [3]. The residual liquid fraction after solvent recovery, so-called beech wood hydrolysate (BWH), contains oligo- and mono-sugars from hemicellulose as well as organic acids, furan derivatives and remaining lignin or rather phenolic compounds [4]. Material usage of the BWH, especially of the oligo- and mono-sugars to high value-added chemical products, fuels and/or food additives can have a great economic and environmental benefit for a biorefinery [5,6]. For this reason impurities and inhibitors, especially phenolic compounds, have to be removed from the BWH for effective subsequent refining and conversion processes [7–10]. This study aimed for the removal of lignin at minimal losses of the hemicellulose sugar in the BWH by means of adsorption using polymeric resins and zeolite.

Commonly used techniques for the removal of lignin from hydrolysate solutions include membrane filtration [11,12], extraction with solvents [8,13], ion exchange [14], precipitation [15,16], coagulation

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Nomenclature			
$a_{RP}$	parameter in Redlich-Peterson model (L/mmol) <sup><math>\beta</math></sup>	$n_{L,j}$	interaction term in modified Langmuir model for component $j$
$C_{eq,i}$	concentration of component $i$ in a multi-component mixture at equilibrium (mg/L)	$n_{RP,j}$	interaction term in modified Redlich-Peterson model for component $j$
$C_{eq,j}$	concentration of component $j$ in a multi-component mixture at equilibrium (mg/L)	$Q_0$	adsorption capacity of one adsorbate when present alone (mg/g)
$C_{lignin}$	concentration of lignin in the liquid phase (g/L)	$Q_0$	parameter in Langmuir model (mg/g)
$K_F$	parameter in Freundlich model (mg/g)/(mg/L) <sup>1/<math>n</math></sup>	$Q_{0,i}$	parameter in extended Langmuir model for component $i$ (mg/g)
$K_{F,i}$	parameter in extended Freundlich model for component $i$ (mg/g)/(mg/L) <sup>1/<math>n</math></sup>	$Q_{mix}$	adsorption capacity of one adsorbate in mixture (mg/g)
$K_L$	Langmuir constant (L/g)	$q_e$	equilibrium adsorption capacity (mg/g)
$K_{L,i}$	parameter in extended Langmuir model for component $i$ (L/g)	$q_t$	adsorption capacity at time $t$ (mg/g)
$K_{RP}$	parameter in Redlich-Peterson model (L/g)	$t$	time (s)
$n$	parameter in Freundlich model	$x_b, y_b, z_i$	parameter in extended Freundlich model for component $i$
		$\beta$	parameter in Redlich-Peterson model

[17], centrifugation [8] and adsorption [7,11,14,18,19]. These techniques exhibit various disadvantages, such as high energy and chemical requirements, low efficiency and relatively high costs. Adsorption is preferred, due to its high efficiency and selectivity regarding the fractionation of complex systems [14]. Possible adsorption materials are activated carbons, inorganic adsorbents (e.g., silica gel, activated alumina, zeolites) and polymeric resins.

The utilization of activated carbons has been extensively investigated. Venkata Mohan and Karthikeyan [20] studied the sorptive uptake of lignin and tannin from diluted aqueous solutions by activated charcoal. Moreover, as one of the few, they presented the desorption of lignin from activated carbon with 1 N NaOH solution yielding no desorption and 1 N HCl solution yielding less than 7% desorption. Montané et al. [21] studied the removal of ligneous impurities from an oligosaccharides rich almond shell hydrolysate by three commercially available activated carbons. The average retention for lignin products was around 64% and for carbohydrates 21%. Liu et al. [22], Shen et al. [23] and Gütsch and Sixta [24] investigated the adsorption of ligneous material from a prehydrolysis liquor on activated carbons. An overall lignin removal of 75–85% was obtained, while that of oligo and mono sugars was between less than 20% and 33%. In addition, Gütsch and Sixta [24] evaluated regeneration possibilities of the spent carbons: solvent treatment was not sufficient for removing lignin, thermal treatments regenerated the spent carbons at temperatures exceeding 800 °C. The strong interactions between the adsorbent and the adsorbed compounds make activated carbon to an efficient adsorption material. At the same time, these are the major drawbacks. The regeneration and recovery and thus the potential use of the adsorbed components is challenging or even impossible. In addition, a material loss of approximately 10% is associated with each thermal regeneration step [25].

The use of inorganic adsorbents, especially zeolites, appears to overcome the mentioned disadvantages, in particular the relatively high loss of sugars. However, very few studies have investigated the removal of phenolic compounds from hydrolysate solutions by inorganic adsorbents. Ranjan et al. [25] examined the adsorption of phenolics from biomass hydrolysates on zeolites: 97% removal of phenolics and a minimal loss of sugars was obtained. It was also found, that zeolites with high silica content adsorb phenolics more efficiently from hydrolysates.

Polymeric resins have become a promising choice for the efficient removal of aromatic impurities. Especially the possibility to recover adsorbed substances by solvent washing is beneficial in comparison to activated carbon and inorganic adsorbents [14]. Chen et al. [19] investigated the separation of phenolic compounds from aqueous phase products of hydrothermal liquefaction of rice straw by modified XAD4 resins. Optimal desorption of all adsorbed components was achieved

with 55 wt% of aqueous ethanol solution. Schwartz and Lawoko [27] removed 90% of acid-soluble lignin from acid hydrolyzed hemicelluloses using XAD4 resin. Regeneration was performed with 75% acetone with an efficiency of 85% with respect to acid-soluble lignin. Lehto and Alén [28] studied the adsorption of phenolic compounds from hardwood autohydrolysates by XAD4 resins, too. Koivula et al. [7] used XAD7HP and XAD16N adsorbents for the removal of foulants from wood autohydrolysates aiming at the reduction of membrane fouling. By means of the XAD7HP resin approximately 50% ligneous material could be removed, but also 30% of the hemicelluloses in the hydrolysate. For XAD16N the results were 70% and 50%, respectively. Heinen et al. [29] studied the separation and recovery of lignin from monosaccharide rich hydrolysates of lignocellulose on six commercial polymeric adsorbents. The XAD16N resin was proven the most efficient. Removal of 80% of ligneous material was achieved simultaneously with 95% monosaccharide recovery. All of the adsorbed lignin could be recovered using 50 wt% aqueous ethanol.

As presented in the brief review, the removal of lignin and phenolic compounds from various aqueous solutions by adsorption on activated carbons, zeolites and polymeric resins, has been investigated to a certain extent. However, the adsorption isotherms regarding the uptake of lignin versus hemicellulose sugar are insufficiently described and BWH from organosolv pulping as feed solution has never been used. Thus, the aim of this study is to develop generic single- and multicomponent isotherm models for the adsorption of lignin on polymeric resins and zeolite and to assess their applicability in a BWH. Isotherm models were developed based on experimental data from adsorption of model solutions (MS) to reduce the complexity and work with well-defined compositions. The direct use of BWH can result in high statistical uncertainties, due to non-constant compositions in each trial and unknown components. In the MS phenol was chosen to represent lignin and xylose the hemicellulose sugar (mono-sugars and oligo-sugars) in the BWH. At first the adsorbents were screened regarding the potential uptake of phenol and xylose at different adsorbent-to-solution ratios and contact times. From these surveys, the two most suitable adsorbents were chosen and single- and multi-component isotherm models were determined. Then, the application of the obtained models from MS to the adsorption process of lignin and hemicellulose sugar from BWH was statistically evaluated.

## 2. Materials and methods

### 2.1. Chemicals

Single- and binary-component MS were prepared by dissolving 3.1 g/L phenol (provided by Carl Roth, purity  $\geq 99.5\%$ ) and/or 4.2 g/L xylose (provided by Carl Roth, purity  $\geq 98.5\%$ ) in 0.5 L de-ionized

water. For the adjustment of the pH value, 5 N NaOH (provided by VWR Chemicals) or 1 N HCl (provided by Carl Roth) solution were prepared.

BWH was supplied by Fraunhofer CBP (Leuna, Germany). Conditions and composition are presented in Table 1. The BWH was collected from one batch and filtered through a 4 µm filter paper (Macherey-Nagel) to remove suspended solids from the liquid fraction. Afterwards it was stored at 4 °C up to its utilization. The pH was adjusted using 5 N NaOH or 1 N HCl solution, too.

The concentrations of mono- and oligo-sugars and lignin in the BWH, shown in Table 1, represent the mean values out of 30 samples. The standard deviations of the measurements are ± 15% for the mono-sugars, ± 20% for the oligo-sugars and ± 9% for the lignin. In the MS, the standard deviations, determined from 60 samples, are ± 3% for xylose and ± 1.8% for phenol. Hence, equilibrium modelling with BWH is associated with relevant statistical uncertainties, which can lead to results that are difficult to interpret and differentiate.

## 2.2. Adsorbents

Studied resins are the hydrophobic styrene-divinylbenzene based (PS-DVB) Amberlite XAD4 and XAD16N supplied by Sigma Chemical Corporation and SEPABEADS SP700 supplied by Resindion S.R.L. (Mitsubishi Chemical Corporation) as well as the uncharged polyacrylate based (PA) Amberlite XAD7HP supplied by Sigma Chemical Corporation. XAD4 is applicable for the adsorption of small hydrophobic molecules from polar solvents, e.g., organics of relatively low to medium molecular weight. XAD16N can be used to adsorb hydrophobic compounds up to molecular weight of 40,000 g/mol. SP700 is recommended for the recovery of materials from fermentation broths, in particular the extraction and concentration of small oligomers. XAD7HP can be used to adsorb organic compounds up to molecular weight of 60,000 g/mol. The studied zeolitic adsorber HiSiv1000, supplied by Honeywell UOP Molecular Sieve, has a crystalline, inorganic silica–alumina structure (Si/Al ratio less than 20), also referred to as “high silica zeolite”. HiSiv1000 has strong adsorption characteristics to larger molecules (approx. 100 g/mol) with hydrophobic character. Physicochemical characteristics of the adsorbents are listed in Table 2.

The adsorbents were initially cleaned or activated before their utilization in batch experiments. Resins were rinsed with de-ionized water to remove preservatives like sodium chloride and sodium carbonate salts and other contaminants. As long as these preservatives and contaminants are present, the conductivity of the rinsing water increases. Hence, the rinsing was continued until the conductivity of the rinsing water no longer increased (typical adsorber-to-water ratio: 1:55). After the rinsing of the resins, they were dried for 24 h at 80 °C. Pretreatment of the zeolite was performed at 360 °C in air atmosphere for 16 h to remove any organic contamination in the adsorbent pores. The prepared adsorption materials were stored in oven-dried flasks up to their utilization.

## 2.3. Experimental procedure

Single-component and binary-component batch experiments were performed in 800 mL round bottom beaker with a working volume of 500 mL. The beaker was placed in a water bath at 25 °C and agitated with a magnetic stirrer at 500 rpm for 180 min. Except during the sampling, the beaker was covered. The pH was adjusted to 6.0 as several studies have shown, that this leads to preferred uptake of phenols, due to the predominant existence as neutral molecules. Hence, the interaction between the adsorbents and phenols are mainly physical van der Waals forces [30–32]. After the temperature of the adsorbate solutions was stabilized, the adsorbents were added with the adsorbent-to-solution ratios (A:S) of 1:5, 1:10, 1:15, 1:20, 1:25 and 1:33 w/v. Thereby, the weight-to-volume ratios (w/v) correspond in the following to the measure g/mL. The moment at which the adsorbents were added

to the adsorbate solution was considered as time zero for the experiments. In order to identify equilibrium time and concentration, small-volume liquid samples of 3 mL were collected during the trials at pre-determined time intervals.

Equilibrium time and concentration were reached after no change in the concentration of adsorbate in solution was detected. The samples were filtered by vacuum filtration using filter paper Whatman No. 2 (pore size = 8 µm). Thereafter, the concentration of phenol and/or xylose in the filtrate was analyzed. These experiments were carried out to study the effects of adsorbent dose and contact time as well as to identify the most suitable adsorbent materials. Furthermore, to calculate the model parameters of single- and multi-component adsorption isotherms.

The experimental procedure of batch adsorption studies for BWH was identical to that for MS. Filtered samples were analyzed regarding their concentration of lignin and hemicellulose sugar.

## 2.4. Chemical analysis

For the analysis of phenol uptake in MS and lignin uptake in BWH UV/VIS spectrophotometer (VWR, Model: UV-6300PC) was used with a 1 cm diameter quartz cuvette. For the analysis of phenol, the sample was diluted with ultrapure water in a ratio of 1:10 v/v. The measurement was carried out at 254 nm. Absorbance of lignin was detected at 280 nm [7,12], after diluting the sample with ultrapure water, so that the absorbance was between 1.0 and 0.3. Thereby, it has to be mentioned that some wood extractives and carbohydrate degradation products (e.g., furfural and 5-HMF) also absorb UV light at 280 nm [29]. This can lead to an overestimation of the lignin content in the BWH. Since the use of the absorption rate is unpractical for further calculations, the values were converted into a mass concentration by means of Eq. (1).

$$C_{\text{lignin}} = \frac{A_{280} \cdot D}{\alpha \cdot l} \quad (1)$$

$A_{280}$  is the absorbance value at 280 nm,  $\alpha$  is the absorptivity factor (110 L/g cm as an average value for several wood species [34]),  $l$  is the length of the cuvette (cm) and  $D$  is the dilution factor. All UV/VIS spectrophotometer measurements were conducted with ultrapure water as blank sample and at least in duplicate.

Xylose and hemicellulose sugar (mono-sugars and oligo-sugars) removal in MS and BWH respectively, were analyzed using high performance liquid chromatography (HPLC) by Agilent Technology system 1200 series equipped with a degasser, binary pump system, auto sampler, column oven, refractive index detector (RID) and diode array detector (DAD). The samples for xylose in MS and mono-sugars in BWH were prepared as follows: The sample was transferred to a 1.5 mL centrifugation tube with a filter inlet (pore size: 0.2 µm) and centrifuged for 10 min at 10 °C and 15,000 rpm. The filtrate was then

**Table 1**

Conditions and composition of beech wood hydrolysate from organosolv pulping.

Raw material	Beech wood
<i>Hydrolysis conditions</i>	
Temperature	170 °C
Time	130 min
Pressure	20 bar
Catalyst (96% H <sub>2</sub> SO <sub>4</sub> solution)	0.8% based on dry wood
Lignin precipitation	Dilution with water
<i>Hydrolysate composition</i>	
Mono-sugar	2.6 g/L
Oligo-sugar	1.6 g/L
Lignin*	3.1 g/L
pH	2.7

\* All components that contribute to the UV absorbance at 280 nm.

**Table 2**  
Physicochemical characteristics of the studied polymeric resins and zeolite.

Adsorbent	Structure	Surface area (m <sup>2</sup> /g)	Pore diameter (Å)	Porosity (mL/g)	Particle size (mm)	Density (g/mL)
XAD4	PS-DVB	750	100	0.98	0.25–0.84	1.02
XAD7HP	PA	450	90	1.14	0.25–0.84	1.05
XAD16N	PS-DVB	800	100	1.82	0.25–0.84	1.02
SP700	PS-DVB	1200	90	2.20	0.25–0.70	1.01
HiSiv1000	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	353	8	–	Powder < 0.1	0.53

diluted with ultrapure water in a ratio of 1:10 and transferred to a 1.5 mL tube with 1 mL inlet, closed with a PTFE septum cap and stored at 4 °C. Preparation of the oligo-sugars in BWH is in principle identical, but includes a previous hydrolysis step (based on [33]). For the hydrolysis, samples were mixed with 72% sulfuric acid in a ratio of 28:1 v/v. Afterwards they were heated for 40 min at 121 °C and then cooled down to 30 °C for 30 min. The pH of the resulting acid-hydrolysate was adjusted to 5.0 with CaCO<sub>3</sub>. Subsequently the sample was prepared as already described for mono-sugars. For the detection of xylose in MS and mono- and oligo-sugars in BWH, the RID signal was used. All other analytes, i.e. furans, were detected using the DAD signal at 280 nm. The auto sampler was set at 15 °C, 10 µL of a sample were injected and separated by a Metacarb 87P column (300 mm × 7.8 mm) equipped with a precolumn (50 mm × 4.6 mm) at 80 °C. The analytical conditions used were as follows: flow 0.35 mL/min, isocratic mode, mobile phase millipore water. All HPLC measurements were conducted at least in duplicate.

2.5. Calculations

2.5.1. Fundamentals

The removal rate of phenol and xylose from MS and lignin and hemicellulose sugar from BWH onto the adsorbents was calculated according to Eq. (2):

$$\%Removal = \frac{C_0 - C_t}{C_0} \times 100 \tag{2}$$

where C<sub>0</sub> refers to the initial concentration (mg/L) and C<sub>t</sub> to the pollutant concentration at time t (mg/L).

The equilibrium adsorption capacity q<sub>e</sub> (mg/g) was calculated from the mass balance equation according to Eq. (3):

$$q_e = \frac{(C_0 - C_{eq}) \cdot V_0}{m} \tag{3}$$

where C<sub>eq</sub> refers to the equilibrium concentration (mg/L), V<sub>0</sub> to the volume of adsorbate solution (L) and m to the mass of used adsorbent (g).

2.5.2. Single- and multi-component isotherm models

Bonding mechanisms and enthalpies, which are predominant during the adsorption of an adsorbate on a particular adsorbent, can be predicted using equilibrium isotherm models. In this study, single- and multi-component models for adsorption isotherms were applied (Table 3).

In single-component systems, the non-competitive isotherm equations Freundlich (Eq. (4)), Langmuir (Eq. (5)) and Redlich-Peterson (Eq. (6)) were used. The Freundlich isotherm is an empirical equation employed to describe a non-ideal and reversible adsorption. The model can be adopted to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface [36]. The Langmuir isotherm, also an empirical model, assumes monolayer adsorption, which can only occur at a fixed number of definite localized sites that are identical, with no lateral interactions and steric hindrance

between the adsorbed molecules. Each molecule possesses constant enthalpy and equal affinity [37,36]. The Redlich-Peterson (RP) isotherm incorporates three parameters into an empirical equation. The isotherm model combines elements from both the Langmuir and Freundlich equation and the mechanism of adsorption is a hybrid one and does not follow ideal monolayer adsorption. The limits of the isotherm are predetermined by the exponent β<sub>RP</sub>. When β<sub>RP</sub> tends to zero, RP approaches Freundlich isotherm model, and when β<sub>RP</sub> is close to one, RP approaches Langmuir condition [39].

When more than one potential adsorbate is present in the aqueous solution, there can be interaction and/or competition for adsorption on same active sites between the various components. Hence, there is a possibility, that adsorption of one component may effect the adsorption of other components. For the characterization of multi-component systems, the equivalent models of the applied single-component isotherms were used. That means, extended Freundlich, non-modified competitive Langmuir, modified competitive Langmuir, extended Langmuir, non-modified competitive Redlich-Peterson and modified competitive Redlich-Peterson were applied [32,40].

Model parameters of single- and multicomponent isotherm equations were determined by nonlinear regression method by means of the open source software GNU Octave. The nonlinear least-squares solver “lsqcurvefit” using the optimization package was used.

2.5.3. Model validation and evaluation

For the validation and statistical evaluation of the various single- and multi-component equilibrium models, the error function Marquardt’s percent standard deviation MPSD was calculated.

$$MPSD = 100 \times \sqrt{\frac{1}{N-P} \sum_{i=1}^n \left( \frac{q_{e,i}^{exp} - q_{e,i}^{cal}}{q_{e,i}^{exp}} \right)^2} \tag{14}$$

N is the number of data points, P is the degree of freedom of the isotherm equations, q<sub>e,i</sub><sup>exp</sup> is the experimentally determined equilibrium

**Table 3**  
Studied single- and multi-component isotherm models of adsorption (model equations and model parameters).

Isotherm model	Model equation	Model parameters	Eq.
<i>Single-component</i>			
Freundlich	q <sub>e</sub> = K <sub>F</sub> C <sub>eq</sub> <sup>n</sup>	K <sub>F</sub> ; n	(4)
Langmuir	q <sub>e</sub> = Q <sub>0</sub> $\frac{K_L C_{eq}}{1 + K_L C_{eq}}$	K <sub>L</sub> ; Q <sub>0</sub>	(5)
Redlich-Peterson	q <sub>e</sub> = $\frac{K_{RP} C_{eq}}{1 + a_{RP} C_{eq}^{\beta_{RP}}}$	K <sub>RP</sub> ; a <sub>RP</sub> ; β <sub>RP</sub>	(6)
<i>Multi-component</i>			
Extended Freundlich	q <sub>e,i</sub> = $\frac{K_{F,i} C_{eq,i}^{n_i + x_i}}{C_{eq,i}^{x_i} + y_i C_{eq,i}^{z_i}}$	x <sub>i</sub> ; y <sub>i</sub> ; z <sub>i</sub>	(7)
	q <sub>e,j</sub> = $\frac{K_{F,j} C_{eq,j}^{n_j + x_j}}{C_{eq,j}^{x_j} + y_j C_{eq,j}^{z_j}}$	x <sub>j</sub> ; y <sub>j</sub> ; z <sub>j</sub>	(8)
Non-modified competitive Langmuir	q <sub>e,i</sub> = $\frac{Q_{0,i} K_{L,i} C_{eq,i}}{1 + \sum_{j=1}^N K_{L,j} C_{eq,j}}$	–	(9)
Modified competitive Langmuir	q <sub>e,i</sub> = $\frac{Q_{0,i} K_{L,i} C_{eq,i}}{1 + \sum_{j=1}^N K_{L,j} \left( \frac{C_{eq,j}}{n_{L,j}} \right)}$	n <sub>j</sub>	(10)
Extended Langmuir	q <sub>e,i</sub> = $\frac{Q_{0,i} K_{L,i} C_{eq,i}}{1 + \sum_{j=1}^N K_{L,j} C_{eq,j}}$	K <sub>L,i</sub> ; Q <sub>0,i</sub>	(11)
Non-modified competitive Redlich-Peterson	q <sub>e,i</sub> = $\frac{K_{RP,i} C_{eq,i}}{1 + \sum_{j=1}^N a_{RP,j} C_{eq,j}^{\beta_{RP,j}}}$	–	(12)
Modified competitive Redlich-Peterson	q <sub>e,i</sub> = $\frac{K_{RP,i} C_{eq,i}}{1 + \sum_{j=1}^N a_{RP,j} \left[ \frac{C_{eq,j}}{n_{RP,j}} \right]^{\beta_{RP,j}}}$	n <sub>j</sub>	(13)

adsorption capacity (mg/g) and  $q_{e,i}^{cal}$  is the calculated equilibrium adsorption capacity (mg/g). The model, which fits the best to the experimental data, is the one with lowest *MPSD*.

### 3. Results and discussion

In Section 3.1 results of adsorbent screening and in Section 3.2 results of single- and multi-component isotherm modelling using MS are presented and discussed. Sections 3.3 and 3.4 illustrates the results of the adsorption processes with BWH and discuss the applicability of the generic isotherm models to real and complex solutions. Finally, Section 3.5 is a brief excursus regarding desorption of lignin and hemicellulose sugar.

#### 3.1. Adsorbent screening with model solution

##### 3.1.1. Effect of adsorbent-to-solution ratio

The effect of the adsorbent dose was determined using A:S ratios of 1:5, 1:10, 1:20, 1:25 and 1:33 w/v. Comparison of the five adsorbents and A:S was done based on phenol and xylose removal from binary-component solutions according to Eq. (2). The relative removal rate of phenol and xylose increases with increasing A:S ratio (Fig. 1). This increase can be explained with the increase in surface area and number of active sites of the adsorbents. Typically, at one A:S ratio the removal rate of the sorbates becomes constant due to the aggregation of adsorption sites and thus a decrease in total available adsorbent surface area and an increase in diffusion path length. Except for XAD4, the phenol removal become constant between an A:S ratio of 1:10–1:5 w/v. Thus, even higher removal rates appear to be possible for higher dosage of XAD4 (Fig. 1). XAD7HP and SP700 were able to remove phenol almost completely from the binary MS. SP700 has an aromatic PS-DVB matrix, hence phenol as an aromatic molecule has a strong affinity. XAD4 and XAD16N adsorbents are also PS-DVB based, but show lower surface areas and porosities and are, therefore, most probably less efficient. XAD7HP is an uncharged polyacrylate based adsorbent with an aliphatic surface and has naturally higher hydrophilicity compared to PS-DVB adsorbents, and thus lower affinity towards aromatic molecules. Nevertheless, in contrast to other studies [7,29,35] XAD7HP was the most efficient resin regarding the adsorption of phenol during the batch experiments. One reason might be the much better distribution and thus higher wetting of the adsorbent particles in the MS, due to the weakly polar characteristics. Another explanation could be the better uptake of materials with low molecular weights. The  $\text{SiO}_2/\text{Al}_2\text{O}_3$ -based HiSiv1000 adsorbent has a hydrophobic character and is distinguished by 12-member oxygen rings. The zeolite has free diameters of 7–7.4 Å. Aromatic phenol molecules have a molecular size of approx. 6 Å and can thus be recovered easily by HiSiv1000. However, the zeolite is much less selective and efficient compared to the resins.

The removal rate of xylose can be considered as constant for the polymeric adsorbents at an A:S ratio of 1:10 w/v (Fig. 1). SP700 showed the lowest removal of xylose with 4.42% at A:S = 1:5 w/v and XAD7HP the highest removal rate with 7.83% at A:S = 1:5 w/v. The removal of xylose using zeolite HiSiv1000 did not become constant at the maximum A:S ratio of 1:5 w/v. However, maximum removal of 16.91% was detected at A:S = 1:5 w/v. These results can be explained by the previously shown chemical structures and characteristics of the adsorbents.

##### 3.1.2. Effect of contact time

The effect of contact time was evaluated for all five adsorbents at an A:S ratio of 1:5 w/v. The phenol removal and the xylose removal were determined at predefined time intervals from 0 to 180 min. Fig. 2 illustrates, that within the first 8 min the adsorption rate was very fast and afterwards it gradually decreased. This is due to the initially high difference in concentration between the adsorbate solution and adsorbent surface, which decreases with adsorption time until reaching

the equilibrium concentration. The experimental conditions, that means mixing of the solutions using a magnetic stirrer, may cause abrasion of the adsorbent materials. This would increase the adsorption rate over time due to smaller particle sizes. However, for the polymeric resins no apparent abrasion could be observed and the zeolite was already powdery (Table 2). The equilibrium time for the removal of phenol by the studied adsorbents was found to be between 15 and 90 min and for the removal of xylose between 60 and 90 min, under the experimental conditions. XAD7HP and SP700 were the two fastest adsorbents.

#### 3.1.3. Selection of adsorbents

The above presented results and the separation factor  $R_L$  were used to select the two most appropriate adsorbents regarding the separation problem. The separation factor  $R_L$  is expressed in Eq. (15) and determined from single-component MS.

$$R_L = \frac{1}{1 + K_L C_0} \quad (15)$$

$K_L$  is one constant of the non-competitive Langmuir-Isotherm (Eq. (5)).  $R_L$  values between 0 and 1 indicating a favorable adsorption process. The closer the value is to 0, the more favorable is the process. For  $R_L$  values smaller than 0 or greater than 1, the adsorption can be described as unfavorable for a certain pollutant.

The studies on the A:S ratio have shown, that the most efficient phenol uptake was reached at a ratio of 1:5 and lowest xylose uptake at a ratio of 1:33 (Fig. 1). However, since the focus is the maximum removal of phenol from the aqueous solutions and xylose uptake increased only very slightly with increasing A:S ratio, the A:S ratio of 1:5 was chosen for further studies. The studies on the effect of contact time have shown that for all adsorbents equilibrium was reached after 90 min at the latest (Fig. 2). The  $R_L$  values (Table 4) of phenol uptake for all adsorbents were in the range of 0.078–0.713, indicating that adsorption of phenol on the studied adsorbents is a favorable process. Lowest  $R_L$  values can be observed for XAD7HP and SP700 with 0.078 and 0.083, respectively. For xylose the  $R_L$  values were either smaller than 0 or greater than 1. Hence, the adsorption of xylose is unfavorable. In the following, the two polymeric adsorbents XAD7HP and SP700 were further considered.

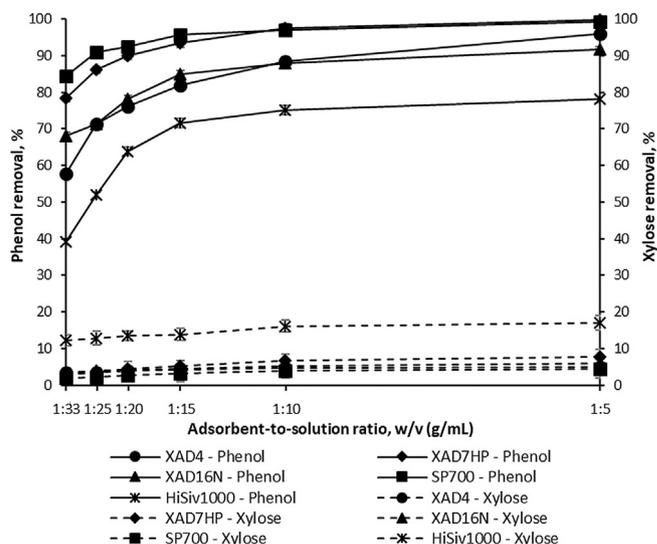
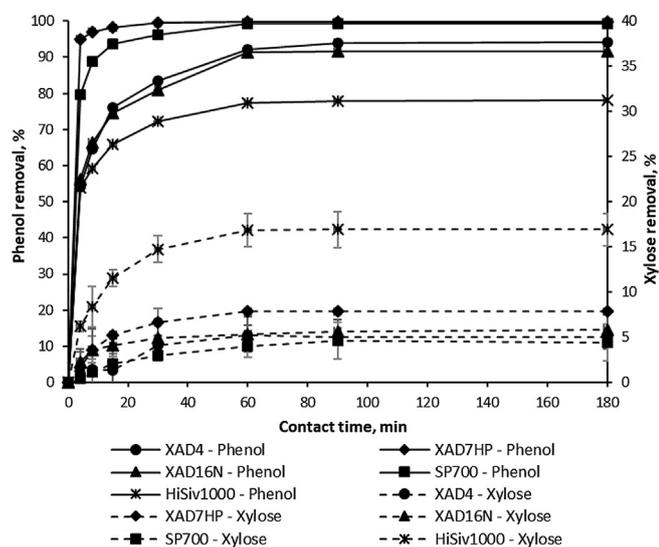


Fig. 1. Effect of adsorbent-to-solution ratio on the removal rate of phenol and xylose from binary-component phenol-xylose solution (Experimental details:  $T = 25^\circ\text{C}$ ,  $\text{pH} = 6$ ,  $t = 180$  min,  $V = 0.5$  L,  $\text{rpm} = 500$ ). Error bars represent the standard deviation.



**Fig. 2.** Effect of contact time on the removal rate of phenol and xylose from binary-component phenol-xylose solutions (Experimental details:  $T = 25\text{ }^{\circ}\text{C}$ ,  $\text{pH} = 6$ ,  $A:S = 1:5\text{ w/v (g/mL)}$ ,  $t = 180\text{ min}$ ,  $V = 0.5\text{ L}$ ,  $\text{rpm} = 500$ ). Error bars represent the standard deviation.

**Table 4**  
Separation factors  $R_L$  and Langmuir constants  $K_L$ .

	$K_L$ (L/g)	$R_L$
<b>XAD4</b>		
Phenol	1.127	0.223
Xylose	-0.244	-39.52
<b>XAD7HP</b>		
Phenol	3.835	0.078
Xylose	-0.217	11.29
<b>XAD16N</b>		
Phenol	0.130	0.713
Xylose	-0.239	-234.6
<b>SP700</b>		
Phenol	3.585	0.083
Xylose	-0.230	29.41
<b>HiSiv1000</b>		
Phenol	0.448	0.418
Xylose	-0.262	-10.13

### 3.2. Isotherm modelling with model solution

#### 3.2.1. Single-component models

Single component models were applied on the one hand to get the best-fit model and thus to interpret the mechanisms during the adsorption process. On the other hand they were used for the determination of the multi-component models. The calculated parameters of the isotherms are presented in Table 5. According to the *MPSD* the uptake of phenol by XAD7HP and SP700 can be fitted best by the Freundlich equation (Fig. 3(a)). Hence, multilayer adsorption, with non-uniform distribution of adsorption heat and affinities, seems to be predominant. Nevertheless, Langmuir and Redlich-Peterson equations also provide satisfactory graphical fit to the experimental data points. For the uptake of xylose by XAD7HP and SP700, the Langmuir equation exhibits the best fitting according to *MPSD* (Fig. 3(b)). This would suggest that monolayer adsorption, with constant enthalpy and equal affinity, is predominant. However, the similarity in standard deviations of the adsorption capacities of xylose illustrate, that Freundlich and Redlich-Peterson isotherm models could be applicable too.

Moreover, the Freundlich parameter  $n$  is for phenol in the range between 0 and 10, indicating favorable adsorption, and for xylose greater than 10, indicating unfavorable adsorption. The Langmuir

parameter  $K_L$  can be used for the quantification of the interaction between adsorbate and adsorbent. The  $K_L$  values for phenol are higher than for xylose, consequently interactions between phenol and adsorbents are more stable than interactions between xylose and the adsorbents. XAD7HP and SP700 show very similar results for  $K_L$  regarding the adsorption of phenol and xylose [32].

#### 3.2.2. Multi-component models

The simultaneous adsorption data of phenol and xylose onto the studied resins were applied to the multi-component isotherm models extended Freundlich, non-modified competitive Langmuir, modified competitive Langmuir and extended Langmuir as well as non-modified competitive Redlich-Peterson and modified competitive Redlich-Peterson (Eqs. (7)–(13)). The resulting model parameters of all multi-component adsorption isotherms are given in Table 6. Comparison of the experimental and calculated equilibrium adsorption capacities ( $q_e$ ) of phenol and xylose uptake by XAD7HP and SP700 is presented in Fig. 4(a)–(d). Thereby, the bisecting line represents the measured adsorption process and the 10%, 20% and 30% error lines indicate the deviation of the calculated results from the experiments. Hence, the closer the calculated results are distributed around the bisecting line, the better fits the model.

The extended Freundlich model was best fitted to the experimental data and had the lowest *MPSD* for the uptake of phenol by both resins in a binary mixture with xylose. This is also illustrated in Fig. 4(a) and (c), where most of the data points calculated with the extended Freundlich model are falling within the 10% error lines around the bisecting line. The multi-component non-modified competitive Langmuir model shows poor fit to the experimental data and high values for the *MPSD*. The use of the interaction term  $n_{L,j}$  clearly improves the fit. The extended Langmuir model shows no improvement in fitting and has a larger *MPSD* than the modified Langmuir model. The non-modified competitive Redlich-Peterson model shows suitable fitting and a low *MPSD* for the uptake of phenol by XAD7HP. By introducing the interaction term  $n_{RP,j}$  in the modified Redlich-Peterson model, the fitting changed for the worse. For phenol uptake by SP700 the contrary was observed: modified Redlich-Peterson provided suitable fitting and non-modified Redlich-Peterson was worse.

The multi-component extended Freundlich isotherm gives the best results for the uptake of xylose on XAD7HP and SP700 in a binary mixture with phenol. This is exemplified in Fig. 4(b) and (d) and by the lowest *MPSD* in Table 6. However, it must be taken into account that some calculated data points of the extended Freundlich model are distributed around the 10% and 20% error line compared to experimental data. This is because of higher standard deviations due to a more unstable adsorption process compared to the phenol uptake. This instability is due to the initially high concentration difference between

**Table 5**

Parameters of the single-component isotherm models Freundlich, Langmuir and Redlich-Peterson for adsorption of phenol and xylose by Amberlite XAD7HP and SEPABEADS SP700.

Single component isotherm model	Parameter	XAD7HP		SP700	
		Phenol	Xylose	Phenol	Xylose
Freundlich	$K_F$	0.095	5.97E-10	0.135	9.01E-15
	$n$	0.436	10.92	0.562	18.46
	<i>MPSD</i>	<b>18.99</b>	9.270	<b>8.015</b>	14.28
Langmuir	$Q_0$	0.108	-3.54E-04	0.137	-1.07E-04
	$K_L$	3.835	-0.216	3.585	-0.229
	<i>MPSD</i>	43.87	<b>6.317</b>	17.76	<b>13.38</b>
Redlich-Peterson	$K_{RP}$	113.5	7.4E-05	0.985	1.83E-05
	$\alpha_{RP}$	1184	-0.231	6.887	-0.339
	$\beta_{RP}$	0.542	0.958	0.619	0.736
	<i>MSPD</i>	25.55	9.876	11.28	20.13

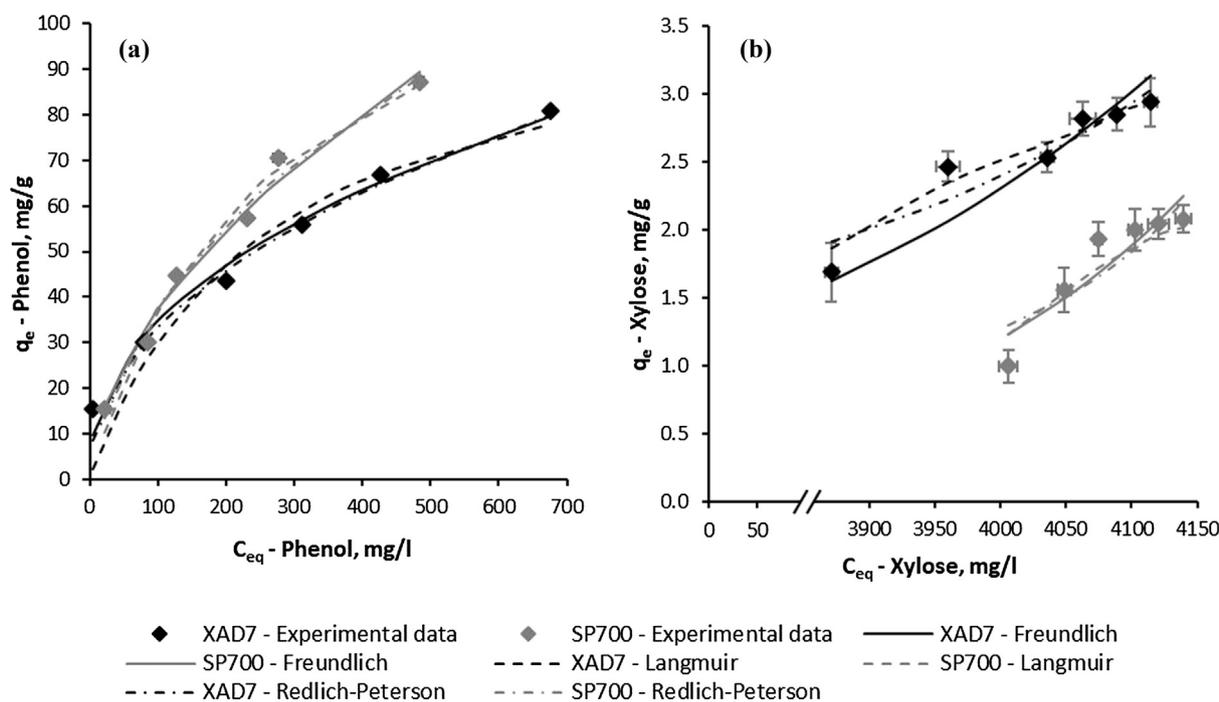


Fig. 3. Freundlich, Langmuir and Redlich-Peterson isotherms (a) for phenol uptake by XAD7HP and SP700 and (b) for xylose uptake by XAD7HP and SP700 (Experimental details:  $T = 25\text{ }^\circ\text{C}$ ,  $\text{pH} = 6$ ,  $t = 90\text{ min}$ ,  $V = 0.5\text{ L}$ ,  $\text{rpm} = 500$ ,  $C_{\text{phenol}} = 3.1\text{ g/l}$  respectively  $C_{\text{xylose}} = 4.2\text{ g/l}$ ). Error bars represent the standard deviation.

Table 6

Parameters of the multi-component isotherm models of the adsorption of phenol and xylose by Amberlite XAD7HP and SEPABEADS SP700.

Multi-component isotherm model	Parameter	XAD7HP		SP700	
		Phenol	Xylose	Phenol	Xylose
Extended Freundlich	$x_i$	-0.062	-2.438	-0.748	-4.311
	$y_i$	1.228	8.86E-03	1.736	0.021
	$z_i$	-6.889	3.678	-9.623	6.703
	$MPSD$	14.36	6.527	6.058	10.37
Non-modified competitive Langmuir	$MPSD$	69.86	65.64	163.5	69.71
Modified competitive Langmuir	$n_{L,j}$	16.47	0.938	33.87	0.974
	$MPSD$	37.18	39.04	27.91	32.37
Extended Langmuir	$Q_{0,i}$	0.280	1.74E-03	0.752	1.29E-03
	$K_{L,i}$	26.80	10.13	13.01	9.589
	$MPSD$	51.51	35.00	29.61	29.79
Non-modified competitive Redlich-Peterson	$MPSD$	16.70	87.72	54.98	89.68
Modified competitive Redlich-Peterson	$n_{RP,j}$	0.704	0.149	1.788	1.053
	$MPSD$	23.06	90.15	27.45	105.2

the adsorbate solution and the adsorber surface, which only changed slightly during the adsorption of xylose onto XAD7HP and SP700. In contrast to the adsorption of phenol, the determined single- and multi-component isotherms for the uptake of xylose, namely Langmuir and extended Freundlich, differ in their characteristics. However, when transferring the results from the batch adsorption experiments to a continuous fixed-bed column, the adsorption process should be described using equivalent models and parameters. This is because in columns regions exist where the pure component is predominant and regions where component profiles overlap. Hence, in this case as multi-component isotherm extended Freundlich is approved due to the above mentioned facts and as single-component isotherm Freundlich equation

due to low  $MPSD$  values too (Table 5).

These results support the theory, that the multi-component extended Freundlich isotherms apply to those systems where each component individually follows the single-component Freundlich isotherm (Section 3.2.1). The extended Freundlich equation assumes that the adsorption of each component in a multi-component system has an exponential distribution of adsorption energy and that the coverage by each adsorbate molecule at each energy level is given by the extended Langmuir isotherm [41].

In binary or in general in multi-component solutions, three types of effects on the adsorption can occur [42]:

- (i) Synergism: Effect of the mixture is greater than that of each of the individual effects of the components in the mixture.
- (ii) Antagonism: Effect of the mixture is less than that of each of the individual effects of the components in the mixture.
- (iii) Non-interaction: Effect of the mixture is neither more nor less than that of each of the individual effects of the components in the mixture.

The effect of interaction between phenol and xylose in a binary mixture could be interpreted by the ratio of the adsorption capacity of one adsorbate ( $Q_{mix}$ ) in the binary mixture to the same adsorbate when present alone ( $Q_0$ ). Thus defined [43]:

$$\begin{aligned}
 Q_{mix}/Q_0 > 1, & \text{ synergism} \\
 Q_{mix}/Q_0 = 1, & \text{ non-interaction and} \\
 Q_{mix}/Q_0 < 1, & \text{ antagonism.}
 \end{aligned}$$

In this study  $Q_{mix}/Q_0$  was calculated as 1.00 and 1.11 for phenol and xylose with XAD7HP, as well as 0.99 and 0.62 for phenol and xylose with SP700. Hence, the binary mixture shows no effect on the phenol adsorption in both adsorbents, whereas it showed a slightly synergistic effect on the xylose adsorption with XAD7HP and an antagonistic effect with SP700.

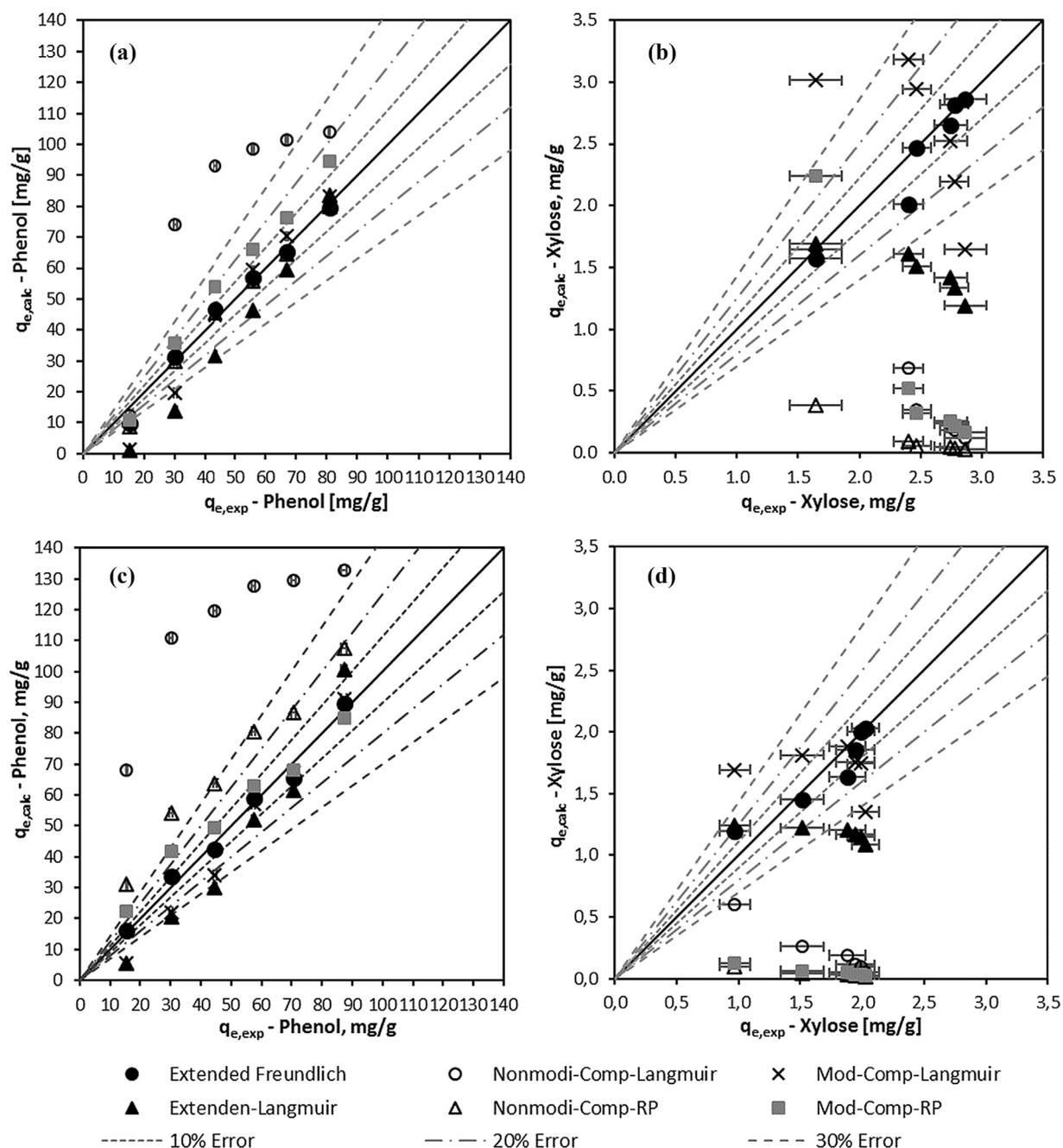


Fig. 4. Comparison of experimental and calculated equilibrium adsorption capacity ( $q_e$ ) of (a) phenol uptake by XAD7HP in phenol-xylose mixture, (b) xylose uptake by XAD7HP in phenol-xylose mixture, (c) phenol uptake by SP700 in phenol-xylose mixture and (d) xylose uptake by SP700 in phenol-xylose mixture (Experimental details:  $T = 25^\circ\text{C}$ ,  $\text{pH} = 6$ ,  $t = 90$  min,  $V = 0.5$  L,  $\text{rpm} = 500$ ,  $C_{\text{Phenol}} = 3.1$  g/l respectively  $C_{\text{Xylose}} = 4.2$  g/l). Error bars represent the standard deviation.

### 3.3. Adsorbent screening with beech wood hydrolysate

In order to validate the selection of adsorbents using MS, all five adsorbents were tested again using BWH at an A:S ratio of 1:5 w/v for 180 min – see Fig. 5. Equilibrium for the removal of the lignin was reached after 90 min at latest. Again, the adsorbents Amberlite XAD7HP and SEPABEADS SP700 showed the best separation characteristics. This means, 93.4% and 94.8% of lignin could be removed. Decrease in adsorption capacity compared to phenol removal in MS experiments can be explained with the presence of furans. Furans also have a strong affinity for adsorption. Total furans (furfural + 5-hydroxymethylfurfural) are present in the BWH with a concentration of 0.6 g/L. By their adsorption, active sites on the adsorbents are occupied, which then are no longer accessible to the lignin. Uptake of the furans

was greater than 99% for both resins. The maximum removal or rather losses of hemicellulose sugar amounted 6.9% for XAD7HP and 8.0% for SP700. These results are similar to those using MS. Hence, by means of a binary phenol-xylose MS the appropriate adsorption materials can be selected regarding their application in the uptake of lignin from beech wood hydrolysate. However, the adsorption capacities have to be determined individually for each solution or rather wood hydrolysate.

As mentioned in Section 2.3, the pH value of the BWH was adjusted from 2.7 to 6.0 using 5 N NaOH solution, in order to enable comparability between MS and BWH experiments. Lignin in BWH is a highly complex macromolecule (molecular weight  $\sim 1000$  g/mol [8,44]) consisting of several phenolic compounds such as phenol ( $\text{p}K_a = 9.99$ ), syringol ( $\text{p}K_a = 9.98$ ), catechol ( $\text{p}K_a = 9.48$ ), guaiacol ( $\text{p}K_a = 9.93$ ) and vanillin ( $\text{p}K_a = 7.40$ ) linked together by hydrogen bonds formed

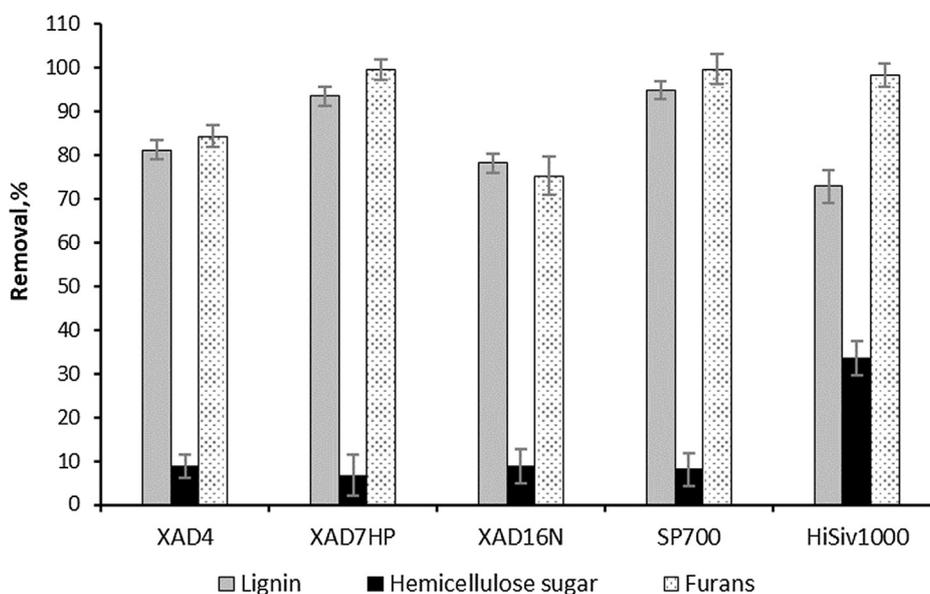


Fig. 5. Adsorbent screening for the removal of lignin from beech wood hydrolysate (Experimental details:  $T = 25\text{ }^{\circ}\text{C}$ ,  $\text{pH} = 6$ ,  $A:S = 1:5\text{ w/v (g/mL)}$ ,  $t = 180\text{ min}$ ,  $V = 0.5\text{ L}$ ,  $\text{rpm} = 500$ ). Error bars represent the standard deviation.

mainly by carboxylic acids ( $\text{p}K_a = 3\text{--}4$ ) [8]. Hence, when the pH is increased the carboxylic acids are dissociated, which results in a partial breakup of the hydrogen bonds thus destabilizing the lignin network. The phenolic compounds are still predominant as molecular species. Accordingly, it is to be expected that at a pH of 6.0 the adsorption rate of the smaller lignin molecules is higher due to a better accessibility and mass transfer within the adsorbent particles. The increased negative charge of the lignin molecules has no or just a minor influence on the adsorption due to the nonpolar characteristics of the adsorbents.

### 3.4. Application and evaluation of isotherm models to beech wood hydrolysate

The isotherm model parameters from MS experiments (Tables 5 and 6) were applied in order to predict and interpret the mechanisms and enthalpies, which are predominant during the adsorption of lignin and hemicellulose sugar from BWH by XAD7HP and SP700. The precision of the prediction and thus interpretation was analyzed by calculating the *MPSD* according to Eq. (14). Thereby,  $q_{e,i}^{exp}$  is the experimentally determined equilibrium adsorption capacity from BWH and  $q_{e,i}^{cal}$  is the calculated equilibrium adsorption capacity determined by experimental data from BWH and isotherm model parameters from MS experiments. Additionally, multi-component isotherm parameters were re-

determined using equilibrium data from BWH experiments. Thereby, the model parameters were calculated directly and not by means of the single-component isotherms due to the character of the mixture. Validation of these isotherm models was executed by calculating the *MPSD*, too. Thereby,  $q_{e,i}^{exp}$  is the experimentally determined equilibrium adsorption capacity from BWH and  $q_{e,i}^{cal}$  is the calculated equilibrium adsorption capacity determined by experimental data and isotherm model parameters from BWH. All *MPSD* values for multi-component equilibrium modelling using isotherm parameters from MS and BWH are displayed in Table 7. Additionally, the multi-component isotherms of lignin and hemicellulose sugar adsorption onto XAD7HP and SP700 using model parameters from BWH are illustrated in Fig. 6.

The application of the multi-component isotherm model parameters determined by MS (Tables 5 and 6) to the adsorption processes in BWH resulted in very high values for *MPSD*. This applies to all model equations as well as for both adsorbents. The re-determined model parameters using BWH resulted in significantly lower values for the *MPSD* (Table 7). In the case of lignin adsorption, these seems to be mainly due to the lower equilibrium concentration compared to phenol. The reason for this may be on the one hand the strong affinity of the adsorbents towards furans and other degradation products with hydrophobic character present in the BWH. These components with typically smaller molecule sizes compared to lignin can lead to a blocking or occupation

Table 7

Comparison of Marquardt's percentage standard deviation (*MPSD*) for the multi-component equilibrium modelling of lignin and hemicellulose sugar uptake by the adsorbents XAD7HP and SP700 using isotherm model parameters determined by model solutions and beech wood hydrolysate.

Multi-component isotherm model	Model parameter source	XAD7HP		SP700	
		Lignin <i>MPSD</i>	Hemi. sugar <i>MPSD</i>	Lignin <i>MPSD</i>	Hemi. sugar <i>MPSD</i>
Extended Freundlich	MS	103	28.3	74.5	49.7
	BWH	0.90	2.35	1.65	0.94
Non-mod. comp. Langmuir	MS	218	46.4	287	53.4
	BWH	30.8	23.1	39.4	21.7
Mod. comp. Langmuir	MS	129	52.4	119	78.3
	BWH	29.8	32.1	37.5	20.6
Extended Langmuir	MS	142	49.2	173	69.1
	BWH	30.8	23.1	39.4	21.7
Non-mod. comp. Redlich-Peterson	MS	222	93.7	295	92.0
	BWH	139	77.4	163	72.0
Mod. comp. Redlich-Peterson	MS	143	61.0	202	89.7
	BWH	189	69.3	209	58.1

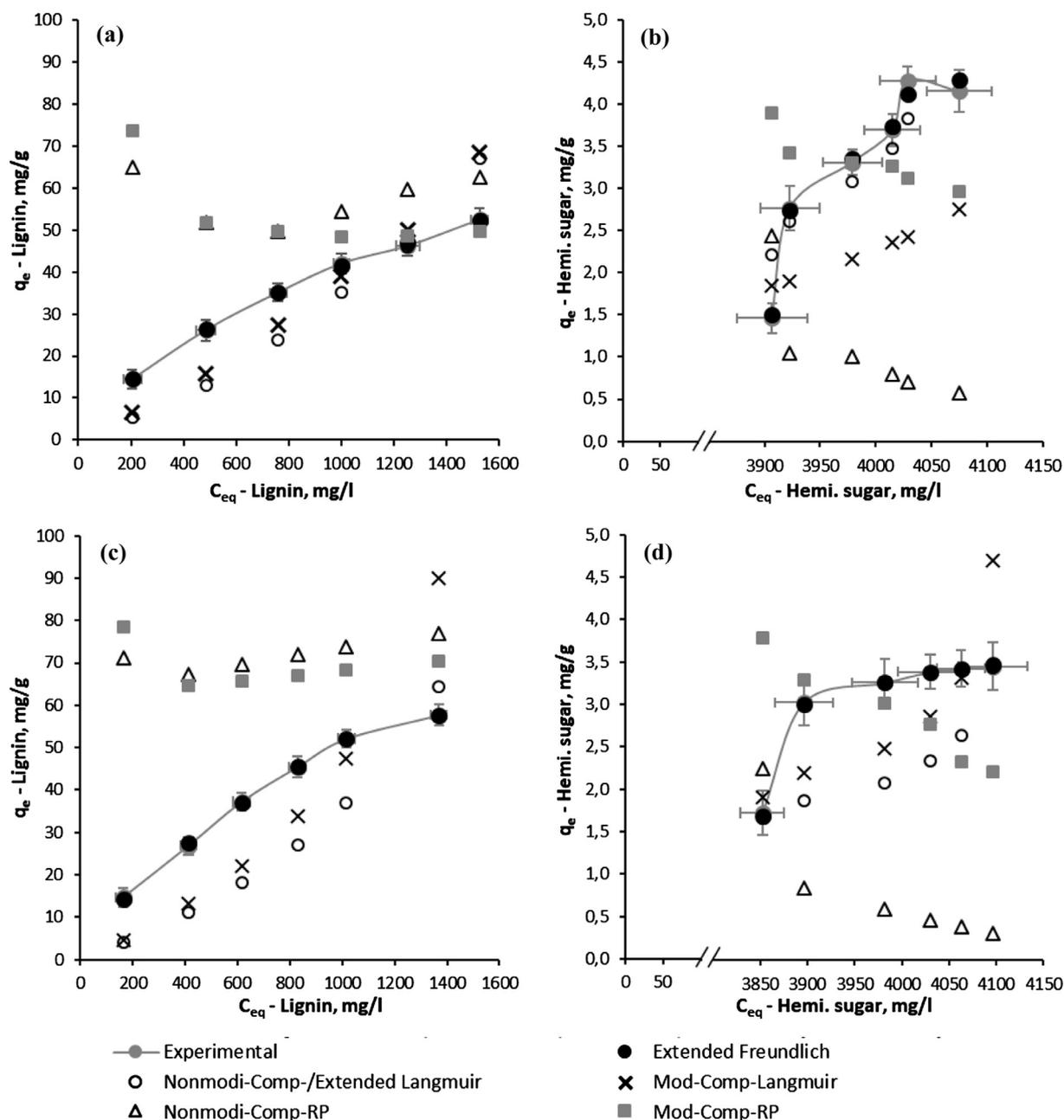


Fig. 6. Comparison of the multi-component isotherms determined by using model parameters from BWH of (a) lignin uptake by XAD7HP in BWH, (b) hemicellulose sugar uptake by XAD7HP in BWH, (c) lignin uptake by SP700 in BWH and (d) hemicellulose sugar uptake by SP700 in BWH (Experimental details:  $T = 25\text{ }^{\circ}\text{C}$ ,  $\text{pH} = 6$ ,  $t = 180\text{ min}$ ,  $V = 0.5\text{ L}$ ,  $\text{rpm} = 500$ ). Error bars represent the standard deviation.

of the particle pores, which are then no longer accessible. On the other hand, lignin is very heterogeneous and consists of a wide range of molecules of different sizes, shapes and functionalities. Hence, the surface groups of the lignin molecules differ, which may have a significant influence on the degree of affinity with the adsorbents. Regarding the adsorption of the hemicellulose sugar, the differences between the  $MPSD$  values of applied MS model parameters compared to BWH model parameters are smaller due to the general low equilibrium concentrations during the uptake of sugars. Nevertheless, the differences in  $MPSD$  could be explained by the variety of the molecular mass distribution of the hemicellulose sugars, which is in a range between 150 and 10,000 g/mol [44,45]. It is believed that mainly the smaller molecules are adsorbed, while the larger ones remain in the fluid phase [21].

Adsorption of lignin onto XAD7HP and SP700 correlates best with

the extended Freundlich model depicted by the lowest  $MPSD$  and Fig. 6(a) and (c). Model parameters for XAD7HP are  $K_F = 0.0562$ ,  $n = 0.7981$ ,  $x_i = -0.8461$ ,  $y_i = 0.6111$  and  $z_i = -0.3923$  and for SP700  $K_F = 0.0523$ ,  $n = 0.7164$ ,  $x_i = -7.2441$ ,  $y_i = 0.0187$  and  $z_i = -0.2199$ . The non-modified competitive Redlich-Peterson model shows a very poor fit to the experimental data and high values for the  $MPSD$ . Despite the introduction of the interaction term  $n_{RP,j}$  of the modified competitive Redlich-Peterson model, the fitting and the  $MPSD$  got even worse. The use of the non-modified competitive Langmuir isotherm, which corresponds to the extended Langmuir equation if the model parameters are determined directly (Table 3), shows considerably lower  $MPSD$  values and a better fitting. The modified competitive Langmuir model with the interaction term  $n_{L,j}$  also shows improvement.

From Fig. 6(b) and (d) and by the lowest  $MPSD$  in Table 7 it can be

seen that the uptake of hemicellulose sugar by XAD7HP and SP700 is best represented by the extended Freundlich model, too. Model parameters are  $K_F = 0.5504$ ,  $n = -2.9731$ ,  $x_j = -3.4311$ ,  $y_j = 0.0115$  and  $z_j = -0.9199$  respectively  $K_F = 0.0523$ ,  $n = -1.8841$ ,  $x_j = -0.6585$ ,  $y_j = 0.0345$  and  $z_j = -1.5606$ . The non-modified and modified competitive Redlich-Peterson model provide very poor fit. Non-modified competitive or rather extended Langmuir and modified competitive Langmuir show a more adequate but still not satisfying correlation to the experimental results.

From these considerations, it can be concluded that by means of MS used in this study the multi-component isotherm models and thus the adsorption mechanisms for the uptake of lignin and hemicellulose sugar from BWH by XAD7HP and SP700 can be predicted relatively accurately. Nevertheless, the isotherm model parameters of the MS do not adequately describe the specific adsorption process of the BWH onto the resins. Hence, they have to be determined individually. An extension of the MS or rather of the model by a third component, e.g., furfural, could still improve the fit of the applied model parameters.

### 3.5. Desorption

For completeness, the desorption of lignin and hemicellulose sugar from the adsorbents XAD7HP and SP700 was investigated. Loaded adsorbents from the BWH experiments with A:S = 1:5 and  $t = 180$  min were used. At first excess hydrolysate was removed by washing the adsorbents with ultrapure water in a ratio of 1:3 w/v at  $T = 25$  °C. No significant lignin and hemicellulose sugar removal was observed. Afterwards, 50 wt% aqueous ethanol was used as desorbate solution [19] in adsorbent-to-desorbate solution ratios (A:D) of 1:1, 1:2 and 1:3 w/v (g/mL) at  $T = 25$  °C. Efficiency of the desorption process was calculated by the desorption ratio according to Eq. (16):

$$\text{Desorption ratio} = \frac{C_d V_d}{(C_0 - C_{eq}) V_0} \times 100\% \quad (16)$$

where  $C_d$  refers to the concentration in the desorbate (mg/l) and  $V_d$  to the volume of desorbate solution (L). Desorption ratios for lignin from XAD7HP and SP700 were 45.07% and 43.75% at A:D = 1:1, 77.95% and 63.18% at A:D = 1:2 and 90.67% and 89.24% at A:D = 1:3. Thus, high removal of lignin from both resins seems possible. Regarding the desorption of the hemicellulose sugar from XAD7HP and SP700 46.87% and 48.62% at A:D = 1:1, 93.74% and 87.25% at A:D = 1:2 and 100% and 95.87% at A:D = 1:3 could be reached. The desorption of adsorbed components from XAD7HP seems to be easier compared to SP700. This is probably due to a stronger adsorption of lignin, as an aromatic macromolecule, onto the PS-DVB matrix of SP700 compared to the polyacrylate based XAD7HP. The separation of lignin from the desorbate solution was not examined.

## 4. Conclusion

Separation of lignin from hemicellulose sugar out of beech wood hydrolysate (BWH) by four polymeric (XAD4, XAD7HP, XAD16N, SP700) and one zeolitic (HiSiv1000) adsorbents was investigated. First, by means of single- and binary-component model solutions (MS), consisting of 3.1 g/L phenol and/or 4.2 g/L xylose, the two most suitable adsorbents were chosen and single- and multi-component isotherm models were determined. Second, the model parameters from the MS were applied to predict and interpret the adsorption mechanisms and enthalpies, which are predominant during the adsorption of lignin and hemicellulose sugar from BWH. The quality of the models was evaluated statistically. All experiments were carried out in batch mode.

Of the five tested adsorbents, the polyacrylate based XAD7HP and the polystyrene based SP700 were found to be the most efficient. Both adsorbents removed phenol almost completely from MS and over 93% of lignin from BWH at an adsorbent-to-solution ratio of 1:5 w/v. At the

same time, xylose and hemicellulose sugar removal was less than 8%. The equilibrium for XAD7HP was reached after 15 min and for SP700 after 30 min. The other adsorbents showed lower adsorption capacities to phenol or lignin and partially high sugar losses.

Adsorption of phenol correlates best to the Freundlich equation and adsorption of xylose correlates best to the Langmuir equation for XAD7HP and SP700 in a single-component adsorption system. In a multi-component system, adsorption behavior of both phenol and xylose for the two adsorbents is best expressed by the extended Freundlich isotherm. However, for practical applications it seems to be reasonable to use Freundlich and extended Freundlich isotherm for xylose adsorption onto XAD7HP and SP700. In the binary MS a slightly synergistic effect on the xylose adsorption with XAD7HP and an antagonistic effect with SP700 were observed. Non-interaction on the phenol adsorption with both adsorbents.

Application and statistical evaluation of the isotherm model parameters determined by the MS to the equilibrium data from adsorption experiments of BWH onto XAD7HP and SP700 showed that the valid isotherm type and thus the predominant adsorption mechanisms can be predicted accurately. However, the isotherm model parameters of the MS do not adequately describe the specific adsorption process of the BWH onto the resins. Hence, they have to be determined individually. An extension of the MS by a third component, e.g., furfural, could allow predictions that are more accurate. In conclusion, the utilization of a MS to describe a “real” problem should always be treated with great caution and checked for applicability.

Lignin adsorbed on XAD7HP and SP700 was desorbed with greater 90% using 50 wt% aqueous ethanol solution in an adsorbent-to-ethanol solution ratio of 1:3 w/v. In addition, almost all adsorbed sugar was recovered.

## Acknowledgement

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**Update**

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## Corrigendum

# Corrigendum to ‘Separation of lignin from beech wood hydrolysate using polymeric resins and zeolites – determination and application of adsorption isotherms’ Corrigendum in Journal ‘Separation and Purification Technology 209 (2019) 491–502’

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## A B S T R A C T

Failures were found in the characterization and determination of the Langmuir isotherm. Moreover, there are mistakable or rather missing information and interpretations concerning the studied adsorption and desorption processes. Within this corrigendum, these failures will be discussed and corrected. The numeration of the sections and subsections in which the corrections are depicted, are equivalent to the original article. The authors would like to apologise for any inconvenience caused.

## 2. Materials and methods

### 2.5.2 Single- and multi-component isotherm models

The authors regret the statement on page 494, that they predicted adsorption enthalpies. No adsorption enthalpies were determined within this study.

The authors regret the statement on page 494, that the Langmuir isotherm is an empirical model. It is correct, that the Langmuir isotherm is based on defined model assumptions and is mathematically derived from those.

## 3. Results and discussion

### 3.1.3 Selection of adsorbents

The authors regret negative results for the Langmuir constant  $K_L$  (Table 4, page 496) for the adsorption of xylose onto the five studied adsorbents. Due to the relation  $K_L = k_A/k_D$ , where  $k_A$  is the rate constant of adsorption and  $k_D$  is the rate constant of desorption, it is physico-chemical not possible that  $K_L$  becomes negative using fresh adsorbents.

Selected measuring points were repeated in duplicate. Based on the new database, the Langmuir constant  $K_L$  was redetermined for each adsorber. The new and correct version of Table 4 can be found below.

The  $R_L$  values of xylose uptake for all adsorbents were between 0.886 and 0.944, indicating insignificant adsorption of xylose on the studied adsorbents. The highest  $R_L$  values can be determined for XAD4 and SP700 with 0.940 and 0.944, respectively. Nevertheless, the two polymeric adsorbents XAD7HP and SP700 were further considered, since the focus is the maximum removal of phenol from the aqueous solutions.

### 3.2.1 Single-component models

The authors regret in Table 5 and Fig. 3(b) (page 496 and 497) incorrect Freundlich, Langmuir and Redlich-Peterson model parameters and thus adsorption isotherms for the uptake of xylose by XAD7HP and SP700. These isotherm parameters were recalculated using the new equilibrium database. The new and correct version of Table 5 and Fig. 3(b) can be found below.

The determination of the adsorption isotherms for the uptake of xylose by XAD7HP and SP700 is associated with distinct uncertainties due to the high liquid phase concentrations at all investigated A:S ratios. These high liquid phase concentrations are related to the very low adsorption rates. According to MPSD, it seems to be that Langmuir equation exhibits the best fitting for XAD7HP and SP700. However, the high standard deviations of the experimental data illustrate, that Freundlich and Redlich-Peterson isotherm models could be applicable too. It must be noted that due to the very narrow sections of the adsorption isotherms, the model parameters can only be derived to a limited extent.

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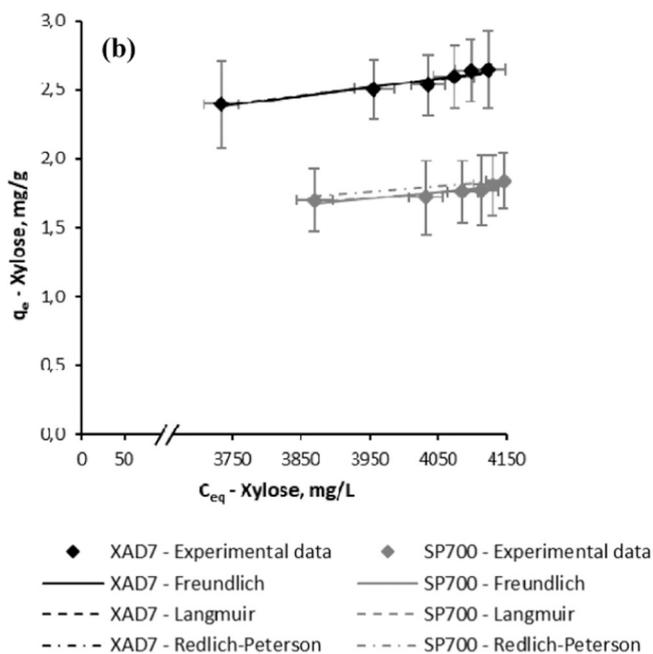
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**Table 4**  
Separation factors  $R_L$  and Langmuir constants  $K_L$ .

	$K_L$ (L/g)	$R_L$
XAD4		
Phenol	1.127	0.223
Xylose	0.015	0.940
XAD7HP		
Phenol	3.835	0.078
Xylose	0.018	0.928
XAD16N		
Phenol	0.130	0.713
Xylose	0.020	0.924
SP700		
Phenol	3.585	0.083
Xylose	0.014	0.944
HiSiv1000		
Phenol	0.448	0.418
Xylose	0.031	0.886

**Table 5**  
Parameters of the single-component isotherm models Freundlich, Langmuir and Redlich-Peterson for adsorption of phenol and xylose by Amberlite XAD7HP and SEPABEADS SP700.

Single component isotherm model	Parameter	XAD7HP		SP700	
		Phenol	Xylose	Phenol	Xylose
Freundlich	$K_F ((g/g)/(g/L)^{1/n})$	0.095	6E-04	0.135	4E-04
	$n$	0.436	1.023	0.562	1.072
	$MPSD$	18.99	1.067	8.015	1.701
Langmuir	$Q_0$ (g/g)	0.108	0.036	0.137	0.032
	$K_L$ (L/g)	3.835	0.018	3.585	0.014
	$MPSD$	43.87	1.060	17.76	1.690
Redlich-Peterson	$K_{RP}$ (L/g)	113.5	0.006	0.985	0.006
	$\alpha_{RP}$ (L/g) <sup><math>\beta</math></sup>	1184	8.100	6.887	9.790
	$\beta_{RP}$	0.542	0.008	0.619	0.158
	$MSPD$	25.55	1.234	11.28	3.569



**Fig. 3.** Freundlich, Langmuir and Redlich-Peterson isotherms (b) for xylose uptake by XAD7HP and SP700 (Experimental details:  $T = 25^\circ\text{C}$ ,  $\text{pH} = 6$ ,  $t = 90$  min,  $V = 0.5$  L,  $\text{rpm} = 500$ ,  $C_{\text{xylose}} = 4.2$  g/L). Error bars represent the standard deviation.

### 3.2.2 Multi-component models

The authors regret in Table 6 and Fig. 4(a) – (d) (page 497 and 498) incorrect model parameters for the investigated multi-component adsorption isotherms. The model parameters of these isotherms were re-determined using the new results of the single-component model parameters from Table 5. The new and correct version of Table 6 and Fig. 4(a) – (d) can be found below.

The extended Freundlich model was best fitted to the experimental data and had the lowest  $MPSD$  for the uptake of phenol by both resins in a binary mixture with xylose. This is also illustrated in Fig. 4 (a) and (c), where most of the data points calculated with the extended Freundlich model are falling within the 10 % error lines around the bisecting line.

The determination of the multi-component adsorption isotherms for the uptake of xylose in a binary mixture with phenol is associated with distinct uncertainties due to the high liquid phase concentrations at all investigated A:S ratios. Furthermore, it must be noted that because of the very narrow sections of the adsorption isotherms, the model parameters can only be derived to a limited extent. The multi-component extended Freundlich isotherm gives the best results. This is exemplified by very low  $MPSD$  values in Table 6 and in Fig. 4(b) and (d) where all data points are on the bisecting line.

### 3.4 Application and evaluation of isotherm models to beech wood hydrolysate

The authors regret in Table 7 (page 499) incorrect  $MPSD$  values when using isotherm model parameters determined by the MS to the

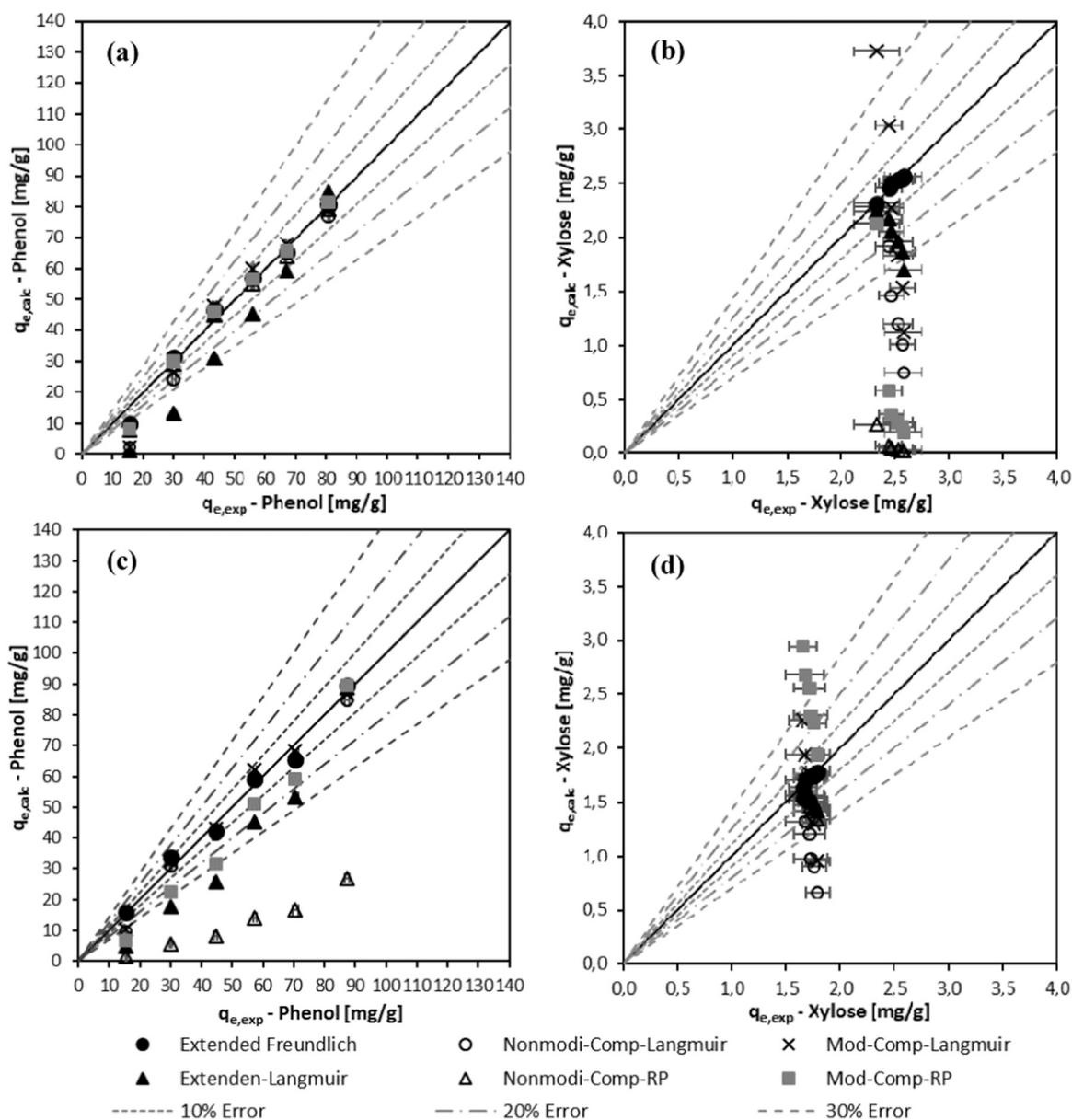


Fig. 4. Comparison of experimental and calculated equilibrium adsorption capacity ( $q_e$ ) of (a) phenol uptake by XAD7HP in phenol-xylose mixture, (b) xylose uptake by XAD7HP in phenol-xylose mixture, (c) phenol uptake by SP700 in phenol-xylose mixture and (d) xylose uptake by SP700 in phenol-xylose mixture (Experimental details:  $T = 25^\circ\text{C}$ ,  $\text{pH} = 6$ ,  $t = 90 \text{ min}$ ,  $V = 0.5 \text{ L}$ ,  $\text{rpm} = 500$ ,  $C_{\text{phenol}} = 3.1 \text{ g/L}$  respectively  $C_{\text{xylose}} = 4.2 \text{ g/L}$ ). Error bars represent the standard deviation.

equilibrium data from adsorption experiments of BWH onto XAD7HP and SP700. The new results of the multi-component model parameters from MS in Table 6 were applied and MPSD values were recalculated. The new and correct version of Table 7 can be found below.

### 3.5 Desorption

The authors regret the imprecise explanation of the adsorption experiments on page 501. In the following, the experimental procedure is explained more in detail in order to be able to interpret the obtained results.

Loaded adsorbents from the BWH experiments with  $A:S = 1:5$  and  $t = 180 \text{ min}$  were used. At first excess BWH was removed by washing the adsorbents with ultrapure water in a ratio of 1:3 w/v (g/mL). This washing step was done continuously via a suction filter using filter paper Whatman No. 2 (pore size = 8  $\mu\text{m}$ ). From the used washing water, samples were taken. In a second step, an ethanol-water solution (50:50 w/w), which was used as desorbate solution, was given in a 500 mL round bottom beaker placed in a water bath at  $25^\circ\text{C}$  and agitated with a magnetic stirrer at 500 rpm. After the temperature of the desorbate solution was stabilized, the loaded adsorbents were added with the adsorbent-to-desorbate solution ratios (A:D) of 1:1, 1:2 and 1:3

**Table 6**  
Parameters of the multi-component isotherm models of the adsorption of phenol and xylose by Amberlite XAD7HP and SEPABEADS SP700.

Multi-component isotherm model	Parameter	XAD7HP		SP700	
		Phenol	Xylose	Phenol	Xylose
Extended Freundlich	$x_i$	-2.419	1.729	-0.546	-3.414
	$y_i$	-5E-07	0.003	1.317	-0.002
	$z_i$	7.803	0.023	-5.381	3.925
	<i>MPSD</i>	14.35	0.806	6.054	1.036
Non-modified competitive Langmuir	<i>MPSD</i>	29.75	38.89	12.83	32.72
Modified competitive Langmuir	$n_{L,j}$	0.855	0.586	0.917	0.653
	<i>MPSD</i>	32.89	37.33	13.30	26.20
	$Q_{0,i}$ (g/g)	0.344	0.002	0.854	0.002
Extended Langmuir	$K_{L,j}$ (L/g)	21.39	10.48	20.37	20.24
	<i>MPSD</i>	54.15	17.70	37.27	10.22
	<i>MPSD</i>	19.12	89.59	73.16	13.85
Non-modified competitive Redlich-Peterson	$n_{RP,j}$	0.945	0.122	0.197	0.454
Modified competitive Redlich-Peterson	<i>MPSD</i>	21.96	86.86	31.65	53.02

**Table 7**  
Comparison of Marquardt's percentage standard deviation (*MPSD*) for the multi-component equilibrium modelling of lignin and hemicellulose sugar uptake by the adsorbents XAD7HP and SP700 using isotherm model parameters determined by model solutions and beech wood hydrolysate.

Multi-component isotherm model	Model parameter source	XAD7HP		SP700	
		Lignin <i>MPSD</i>	Hemi. sugar <i>MPSD</i>	Lignin <i>MPSD</i>	Hemi. sugar <i>MPSD</i>
Extended Freundlich	MS	112	32.4	33.3	36.5
	BWH	0.90	2.35	1.65	0.94
Non-mod. comp. Langmuir	MS	147	36.7	173	44.9
	BWH	30.8	23.1	39.4	21.7
Mod. comp. Langmuir	MS	136	46.7	106	67.4
	BWH	29.8	32.1	37.5	20.6
Extended Langmuir	MS	135	44.9	128	54.5
	BWH	30.8	23.1	39.4	21.7
Non-mod. comp. Redlich-Peterson	MS	172	93.5	193	227
	BWH	139	77.4	163	72.0
Mod. comp. Redlich-Peterson	MS	139	65.9	151	82.2
	BWH	189	69.3	209	58.1

w/v (g/mL). The respective amounts of desorbate solution were adjusted to the available quantity of loaded adsorbents. The residence time for each trial was 90 min. Except during the sampling, the beaker was covered.

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