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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)$^{\beta}$
$C_{eq,i}$	concentration of component i in a multi-component mixture at equilibrium (mg/L)
$C_{eq,j}$	concentration of component j in a multi-component mixture at equilibrium (mg/L)
C_{lignin}	concentration of lignin in the liquid phase (g/L)
K_F	parameter in Freundlich model (mg/g)/(mg/L)$^{1/n}$
$K_{F,i}$	parameter in extended Freundlich model for component i (mg/g)/(mg/L)$^{1/n}$
K_L	Langmuir constant (L/g)
$K_{L,i}$	parameter in extended Langmuir model for component i (L/g)
K_{RP}	parameter in Redlich-Peterson model (L/g)
n	parameter in Freundlich model
$n_{L,j}$	interaction term in modified Langmuir model for component j
$n_{RP,j}$	interaction term in modified Redlich-Peterson model for component j
Q_0	adsorption capacity of one adsorbate when present alone (mg/g)
Q_0	parameter in Langmuir model (mg/g)
$Q_{0,i}$	parameter in extended Langmuir model for component i (mg/g)
Q_{mix}	adsorption capacity of one adsorbate in mixture (mg/g)
q_e	equilibrium adsorption capacity (mg/g)
q_t	adsorption capacity at time t (mg/g)
t	time (s)
x_i, y_i, z_i	parameter in extended Freundlich model for component i
β	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. Heinonen 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 ≥99.5%) and/or 4.2 g/L xylose (provided by Carl Roth, purity ≥98.5%) in 0.5 L de-ionized