



## Separation and recovery of lignin from hydrolysates of lignocellulose with a polymeric adsorbent



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### ARTICLE INFO

#### Article history:

Received 1 March 2017

Received in revised form 17 May 2017

Accepted 1 June 2017

Available online 2 June 2017

#### Keywords:

Lignocellulose

Hydrolysate

Lignin

Adsorption

Scale up

### ABSTRACT

Separation and recovery of lignin from monosaccharide rich hydrolysates of lignocellulose by adsorption was investigated. Six polymeric adsorbents were compared by batch equilibrium experiments. XAD-16N was found to be the most efficient. Use of XAD-16N was studied in more detail in a column. A good separation efficiency could be obtained: with 95% monosaccharide recovery yield limit, the lignin removal level was 80%. Organic acids and furans were not adsorbed on XAD-16N. Practically all of the adsorbed lignin could be recovered efficiently with 50 wt.% aqueous ethanol solution. The lignin fraction had 99% purity with respect to the other solutes in the hydrolysates. Applicability of the process on large scale was demonstrated successfully by scaling up the process using data obtained with a laboratory scale unit (scale-up factor: 420). A 76% lignin removal (target: 70%) was achieved with higher than 95% monosaccharide recovery yield (target: 95%).

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### 1. Introduction

Lignin is the second most abundant polymeric material after cellulose and the most abundant aromatic polymer on Earth [1–3]. It is found in lignocellulosic biomasses where it accounts for as much as 30% of weight and 40% of energy content [1,4,5]. Lignin is an amorphous three dimensional polymer network consisting of repeating randomly branched phenylpropanoid (C9) units bound together by carbon–carbon or ether bonds [1,4,6]. The structure of lignin depends on its origins [1,3]. Similarly as the other main components of lignocellulosic biomasses, cellulose and hemicelluloses, lignin is a valuable platform chemical for the production of a wide and continually expanding range of products. Lignin can be used as raw material for aromatic fine chemicals such as phenols, vanillin, and syringaldehyde, dispersing agents, aromatic polymers, activated carbon, carbon fibers, composites, polyphenolic glues, ion exchangers, biofuels, low cost fillers, and additives [1,2,4–8].

Lignin is liberated from lignocellulosic biomasses during pulp production and during other biomass valorization processes such as hydrolysis [8–13]. In hydrolysis, the polysaccharides in the biomass are cleaved into monosaccharides with mineral acids (e.g. sulfuric acid) or enzymes as the catalysts. However, lignin is resilient towards chemical and enzymatic degradation and thus it

remains mostly unchanged [6,14]. Thus, recovery of lignin and lignin derivatives from lignocellulose derived solutions would create a huge renewable source for aromatic compounds. In addition, lignin removal from these solutions might be necessary due to limitations set by the downstream processing. Lignin is known, for example, to inhibit fermentation monosaccharides [15–17].

A number of methods for the separation of lignin from aqueous solutions has been presented. These include precipitation (change in pH, temperature or ionic strength of the solution) [12,18–20], membrane filtration (ultrafiltration and nanofiltration) [10,21,22], centrifugation [23], ionic liquids [13,19], coagulation [24], bacteria [25], and adsorption [9,11,26–31]. Adsorption is an efficient and highly selective method for the purification of complex mixtures. Removal of lignin by adsorption on activated carbon has been investigated considerably. Liu et al. [28] studied removal of lignin from pre-hydrolysis liquor in a two-step adsorption process. Over 80% of lignin was removed with approximately 30% hemicellulose losses [28]. Montané et al. [29] studied the use of three commercially available activated carbons for the removal of lignin from a xylo-oligosaccharide rich solution produced by autohydrolysis of almond shells. Removal of lignin from dilute aqueous solutions by adsorption on activated carbon has been investigated by Venkata Mohan and Karthikeyan [30] and Andersson et al. [31]. Gütsch and Sixta [27] investigated the removal of lignin from Kraft pulping prehydrolysate solutions with activated carbon at high temperature (150–170 °C): 75% lignin removal was obtained. Shen et al.

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## Nomenclature

$C_{\text{lignin}}$	concentration of lignin in liquid phase, g/L
$D$	dilution factor, –
$d_{\text{bed}}$	adsorbent bed diameter, cm
$h_{\text{bed}}$	adsorbent bed length, cm
$l$	length of the cuvette, cm
$q_{\text{lignin}}$	concentration of lignin in solid phase, g/L
$V_{\text{bed}}$	adsorbent bed volume, mL or L
$V_{\text{desorbent}}$	desorbent volume, mL
$V_{\text{hydrolysate}}$	hydrolysate volume, mL
$m_{\text{adsorbent}}$	mass of wet adsorbent, g

## Greek letters

$\alpha$	absorptivity factor, L/(mg cm)
$\varepsilon_{\text{b}}$	bed porosity, –
$\varepsilon_{\text{p}}$	porosity of the adsorbent, –
$\rho_{\text{ads}}$	density of the wet adsorbent, g/mL

## Subscripts and superscripts

0	initial
ads	adsorption step
des	desorption step
eq	equilibrium

[9] have also studied the removal of lignin from pre-hydrolysis liquors by adsorption on activated carbon: 85% lignin removal was obtained with less than 20% and 0% losses of oligosaccharides and monosaccharides, respectively [9]. Strand et al. [11] obtained lignin removal of 68% and 85% for spruce and birch based pre-hydrolysis liquors, respectively, by adsorption on activated carbon. The sugar losses were 20% and 14%, respectively [11].

Activated carbon is an efficient adsorbent, however, the strong interactions between the adsorbent and the adsorbed compounds make the regeneration of the adsorbent, *i.e.* the recovery of the adsorbed compounds challenging. Desorption of lignin from activated carbon has been presented only by Venkata Mohan and Karthikeyan [30] with 1 N NaOH and 1 N HCl solutions with little success: only approximately 7% desorption ratio was obtained. Regeneration of activated carbon by heat was studied by Gütsch and Sixta [27]: lignin is converted into activated carbon at 950 °C temperature.

Polymeric adsorbents are also efficient for removal of aromatic compounds (*e.g.* lignin and furans). On the contrary to activated carbon, desorption of compounds from these can be done more efficiently (*e.g.* [32]). Use of XAD-8 polyacrylate adsorbent for the removal of aromatic substances including lignin from dilute water suspensions of thermo-mechanical pulps was investigated by Pranovich et al. [33]. Efficient desorption of the adsorbed compounds was achieved with methanol. Koivula et al. [34] have investigated the use of polyacrylate based XAD-7HP and polystyrene based XAD-16 adsorbents for the adsorption of foulants in wood based autohydrolysates as a pretreatment step for ultrafiltration process. XAD-16 adsorbent removed at maximum 70% of lignin from birch autohydrolysate (lignin amount as UV absorbance), but also 50% of hemicelluloses present in the solution. The corresponding values for XAD-7 were 50% and 30%. Desorption of lignin from the adsorbents was not investigated in [34]. XAD-16 and XAD-7 have also

been used to remove lignin and lignans from a spruce based galactoglucomannan fraction [35] and pulp mill process water [36], respectively. Schwartz and Lawoko [37] achieved 90% removal of acid-soluble lignin from hemicellulose rich hardwood extracts with polystyrene based XAD-4 adsorbent. 85% of the adsorbed lignin could be recovered with 75% acetone [37].

Although lignin removal from various aqueous solutions by activated carbon and polymeric adsorbents has been investigated to some extent, authentic hydrolysates of lignocellulose have never been used as the feed solution. Here we present a study in which the recovery of lignin from such hydrolysates by adsorption on polymeric adsorbents is investigated. Both the adsorption and desorption steps are taken into account in order to properly evaluate the separation efficiency. The aim of this work is to present an adsorption based process that allows the separation and recovery of lignin from these monosaccharide rich solutions for further processing. However, it is not an aim of this work to present a method for the production of pure monosaccharides from the hydrolysates as further purification of the hydrolysates (separation of organic acids and furans) after the lignin removal can be accomplished using methods presented in [32,38–41]. The applicability of the lignin separation and recovery process on a large scale is demonstrated by scaling up the separation process using data obtained with a laboratory scale adsorption unit.

## 2. Experimental

### 2.1. Materials and methods

Authentic pentose (from here on C5) and hexose (C6) rich hydrolysates of lignocellulose were used as feed solutions. These were produced in a demonstration scale production plant using hardwood as raw material. C5 hydrolysate was produced during

**Table 1**  
Compositions of the C5 and C6 hydrolysates used in this work.

Component	Concentration, g/L		
	"C5 hydrolysate" <sup>a</sup>	"C6 hydrolysate" <sup>a</sup>	"Mix hydrolysate" <sup>b</sup>
Lignin	13.98	3.39	6.67
Glucose	10.59	74.94	75.26
Xylose	83.47	17.95	25.50
Galactose	6.32	0.88	1.90
Mannose	10.85	2.46	3.70
Total monosaccharides	111.23	96.23	106.36
Formic acid	1.33	0.52	n.a.
Acetic acid	22.89	6.18	n.a.
Furfural	5.51	2.2	n.a.
5-hydroxymethyl furfural	0.48	0.35	n.a.

<sup>a</sup> Used in laboratory scale experiments.

<sup>b</sup> Used in pilot scale experiments.

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