

Article

Hydrothermal Liquefaction (HTL) of Lignin: The Adsorption Separation of Catechol Guaiacol and Phenol

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Abstract: The complex nature of the hydrothermal liquefaction (HTL) of lignin product downstream requires an effective separation strategy. In this study, the use of adsorption separation was undertaken using deep eutectic solvent (DES)-modified amberlite XAD-4 adsorbents to achieve this goal. XAD-4 was modified with a choline chloride: ethylene glycol DES and characterized using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and the Brunauer–Emmett–Teller (BET) test. In addition, the HTL product was characterized using Gas Chromatography with Flame Ionization Detection (GC-FID). The performance of unmodified and DES-modified adsorbents was initially tested on the model compounds of guaiacol, phenol and catechol, followed by the HTL product in a batch adsorption system. The Freundlich model best described the model compound adsorption system with a preferential affinity for guaiacol ($k_f = 12.52$), outperforming phenol and catechol. Adsorption experiments showed an increase in capacity and selectivity for all species when the DES-modified adsorbents were used at all mass loadings. GC-FID analytics showed the DES-modified XAD-4 (300 mg) as having the highest selectivity for guaiacol, with an equilibrium concentration of 121.45 mg/L representing an 85.25% uptake, while catechol was the least favorably adsorbed. These results demonstrate the potential of DES-functionalized XAD-4 adsorbents in selectively isolating high-value aromatics from the HTL of the lignin product stream.

Keywords: hydrothermal liquefaction; lignin; adsorption; deep eutectic solvents; amberlite XAD-4



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1. Introduction

With increasing global concern about climate change and the environmental pollution hazards brought about with the combustion of fossil fuels, alternative ‘green’ energy sources are earnestly being sought to replace fossil fuels as the dominant source of world energy supplies [1]. In addition, the growing number of urban dwellers and rapid global industrialization are leading to the fast exploitation of fossil fuel reserves, which take a long time to replace. Therefore, renewable sources like lignocellulosic biomass are now looked upon as being an abundantly available, ‘green’ and renewable potential sources of alternative energy, which do not necessarily compete with conventional food crops [2].

Lignocellulose represents the matter of plants in general terms, and it is the most abundant sustainable carbon source on the planet. It is estimated that 181.5 billion tons are produced annually, of which 8.2 billion tons are currently in use [3]. Its composition is quite complex, consisting of three polymers, namely, cellulose (40–60%), hemicellulose (20–40%), lignin (10–25%) and other minor components [4,5]. These polymers can be fractionated into their components, thus having the potential to be upgraded into value-added materials

and platform chemicals capable of replacing those conventionally obtained from fossil fuel sources [5].

Lignin is the most abundant, naturally occurring source of aromatic compounds. Depending on its source, it constitutes between 10 and 40% of biomass [6,7], and it is in plentiful supply as a by-product of the paper and pulp industries, where it is utilized as a source of energy [6]. In fact, as a by-product of the pulping and other biorefinery industries, it is estimated that about 50 million tons are produced annually, with less than 2% being utilized as precursor chemicals with upgrade potential [7]. However, as an aromatic heteropolymer, the lignin structure needs to be deconstructed and separated into its constituent molecules if it is to be upgraded into the high-value-added chemicals widely used in the chemical, pharmaceutical, cosmetic and fuel industries today.

Hydrothermal liquefaction (HTL) is a thermochemical process that employs the deconstruction of biomass or lignin via hydrolysis usually in an aqueous environment [8]. Water can serve a dual role as a solvent and catalyst in the process because as it reaches its supercritical point (above 375 °C), its properties, such as polarity, flow and solubility, are enhanced [8,9]. The process involves subjecting lignin to a high-temperature and -pressure regime, usually 150–400 °C and 100–220 bar in the presence of a catalyst, resulting in the cleavage of the β -O-4 linkages holding the monolignol units together [9,10]. The resulting product includes organic (bio oil), aqueous and gaseous phases. This technique has a unique advantage over biomass-processing technologies as it sidesteps the need for moisture removal, which requires extra energy and cost [11].

The organic/bio-crude phase of the HTL of lignin consists of a complex mixture of aromatic compounds, among which phenol, catechol and guaiacol are prominent. Due to their similar physicochemical properties, the challenge therefore arises of devising an effective strategy for their selective separation. Various methods have been proposed to overcome this problem, with adsorption technology emerging as being quite effective [12]. Activated carbons, owing to their large specific surface areas, are widely employed in this process, as they can readily adsorb various aromatic compounds from aqueous solutions, but they have a few drawbacks, such as high costs, difficulty in regeneration and adsorption of undesired species [13]. In contrast, synthetic polymeric adsorbents like Amberlite XAD-4 can overcome such limitations, as they are cheaper, more easily regenerated and selective [14,15]. However, as previously mentioned, the HTL of lignin target molecules possesses similar properties, and as such they will readily compete with each other for the active sites on the adsorbent surface and thus impede selective adsorption. This competition has an effect on both the rate and equilibrium adsorption capacity of the system, which is of vital interest in adsorption process design [16,17]. In order to overcome this limitation, it is proposed that some form of adsorbent surface modification (functionalization) is required by the introduction of certain functional groups on the surface/pore structure of the adsorbent.

Deep eutectic solvents (DESs) are a mixture of two or more pure compounds for which the eutectic point temperature is below that of an ideal liquid mixture, presenting significant negative deviations from the ideal, where the difference between the ideal and real eutectic point (temperature depression) is greater than zero [18]. One or more of the compounds which make up these solvents must have hydrogen bond donor (HBD) or hydrogen bond acceptor (HBA) ability. They exhibit several desirable characteristics, such as low cost, low melting point, low volatility, high thermal stability, high conductivity, high surface tension, non-toxicity, ease of preparation and biocompatibility [19]. Some in the scientific community call them ‘green solvents’. It has been suggested that their capacity to engage in hydrogen bonding might confer on them the ability to serve as modification agents for adsorbents via the introduction of functional groups to the adsorbent surface

structure. In recent years, various authors have put forward works on the functionalization of adsorbents with DESs for selective molecular adsorption.

Chen et al. studied the separation of phenolic compounds from the aqueous-phase products of the HTL of rice straw. They introduced a benzene ring, α , α' -dichloro-p-xylene (DCX), as a modification agent into the structure of Amberlite XAD-4 in order to attach hydrogen bonds and thus improve selectivity in the adsorption of aromatic compounds from the product solution. They also compared the performance of the modified and unmodified adsorbents and reported a marked increase in the adsorption capacity of about 50% for the modified adsorbent compared with the unmodified one [13]. Lawal and co-workers prepared a low-cost biochar–clay hybrid adsorbent and thereafter modified it with a 1M glycerol: 2M hexadecyltrimethylammonium bromide DES. Their aim was to evaluate the effectiveness of the adsorbents in adsorbing dye (acid blue 74) and pharmaceuticals (ciprofloxacin and acetaminophen) in both batch and dynamic adsorption systems. The results showed a ‘tremendous’ increase in adsorption capacity when the hybrid adsorbent was modified with the DES, with acid blue 74 having the highest sorption capacity followed by ciprofloxacin and acetaminophen. In conclusion, they stated that their DES-modified adsorbent could effectively be utilized for organic dyes and pharmaceutical removal [20]. Ma and Row worked on a reliable and efficient method for the simultaneous isolation of ciprofloxacin and levofloxacin from milk. To aid in their task, six polyhydric alcohol-based DES-modified phenolic resins were used. All DES-modified resins showed better adsorption capacities for the target analytes over those of the unmodified ones, with the choline-glycerol-based resin performing better than the rest. They attributed this to the extensive hydrogen bonding network and electrostatic interactions brought about by the DESs [21].

Despite extensive research work, a gap in knowledge persists on the use of DES-functionalized adsorbents for the selective separation of aromatic compounds from the organic/bio-crude phase of lignin HTL. Without an effective separation strategy, the goal of achieving an economical and sustainable bio-refinery process might not be achieved. The objective of this study is to evaluate the effectiveness of DES-modified XAD-4 in the selective isolation of high-value aromatics from the organic phase of the HTL of lignin, by (I) characterizing the structural changes brought about by the introduction of the DES into the adsorbent structure, (II) determining a suitable adsorption isotherm model for multicomponent model compound systems and (III) establishing the efficacy of DES-modified adsorbents in selective aromatic compound extraction. In this study, an attempt is made to address the separation problem in the downstream sector of lignin valorization by providing a scalable adsorption separation process with the use of DES-modified XAD-4 adsorbents.

2. Materials and Methods

2.1. Materials

The lignin sample used in this study was sourced from LignoPure GmbH, Hamburg, Germany, while Amberlite XAD-4 was obtained from Purolite Int. Ltd., Ratingen, Germany. The HTL continuous reactor was partly constructed at the Institute for Catalysis Research and Technology (IKFT) Germany. All other reagents, such as anhydrous ethanol, choline chloride and ethylene glycol, were analytical reagents and used as obtained.

2.2. Hydrothermal Liquefaction of Lignin

The lignin sample used in this study is classified as ‘soda lignin’ in the pulping industry as it is a by-product of the ‘soda pulping’ process. To prepare the feedstock, 30 g of KOH was added to 3 kg of soda lignin, and water was used to dissolve the mixture

until reaching a weight of 30 kg. After the solution was rigorously mixed, it was charged into the continuous HTL reactor; a schematic illustration and real reactor are shown in Figures 1 and 2. The reactor was heated at a rate of 5 °C/min and 230 bar until it reached a temperature of 350 °C [9,11]. Once these conditions were obtained, they were held for 19 min before the reactor was shut down, cooled to 20 °C and its product discharged. The aqueous and organic (bio-crude) phases were then separated from the solid phase using a vacuum pump. Organic- and aqueous-phase characterization was carried out by a GC-FID (GC 7820A, Agilent, Santa Clara, CA, USA) Column: Restek RTX-5 (RTX-5, 30 m, 0.32 mm, 0.5 µm, Restek, Bellefonte, PA, USA).

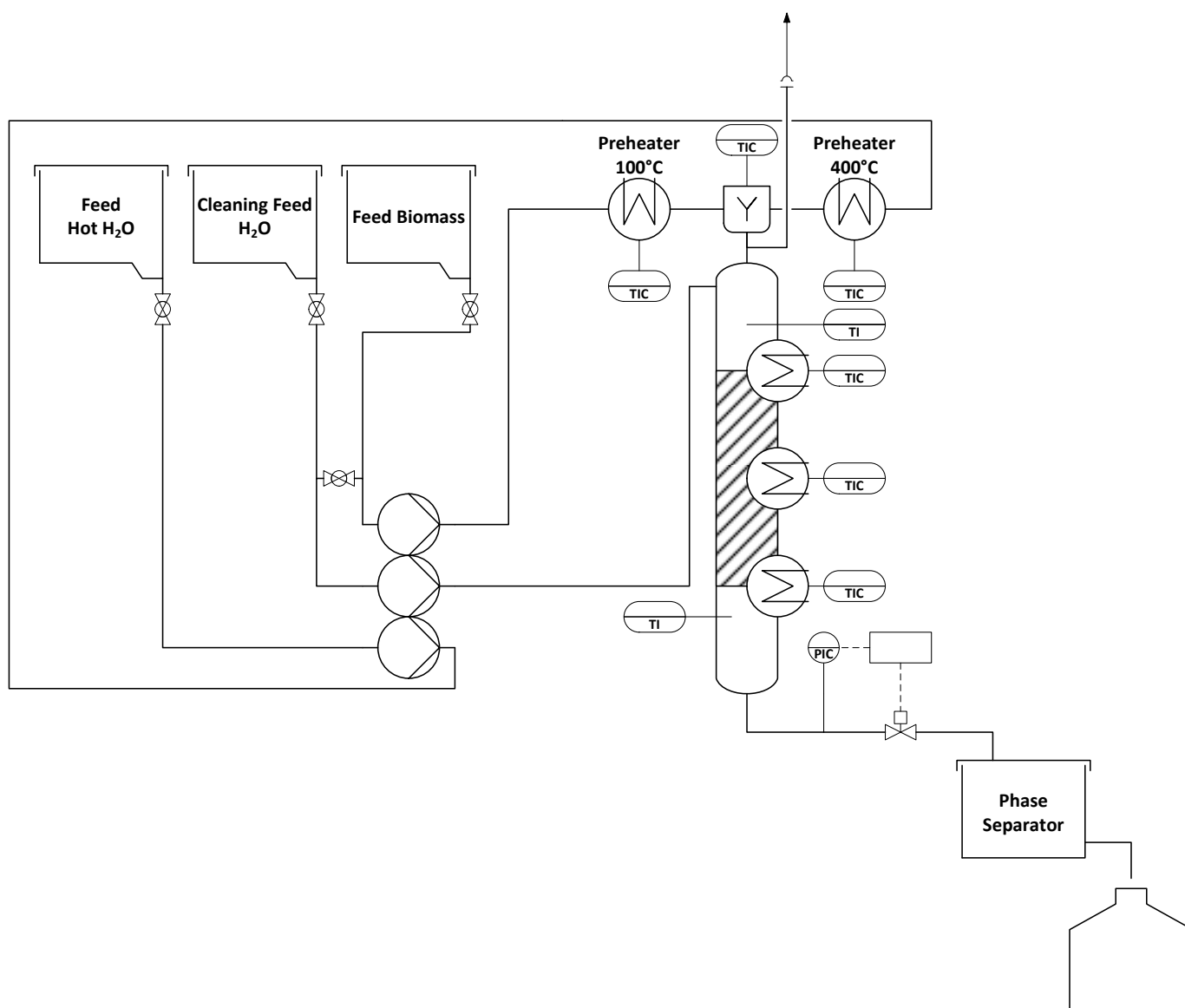


Figure 1. Schematic flowchart of the HTL unit at IKFT.

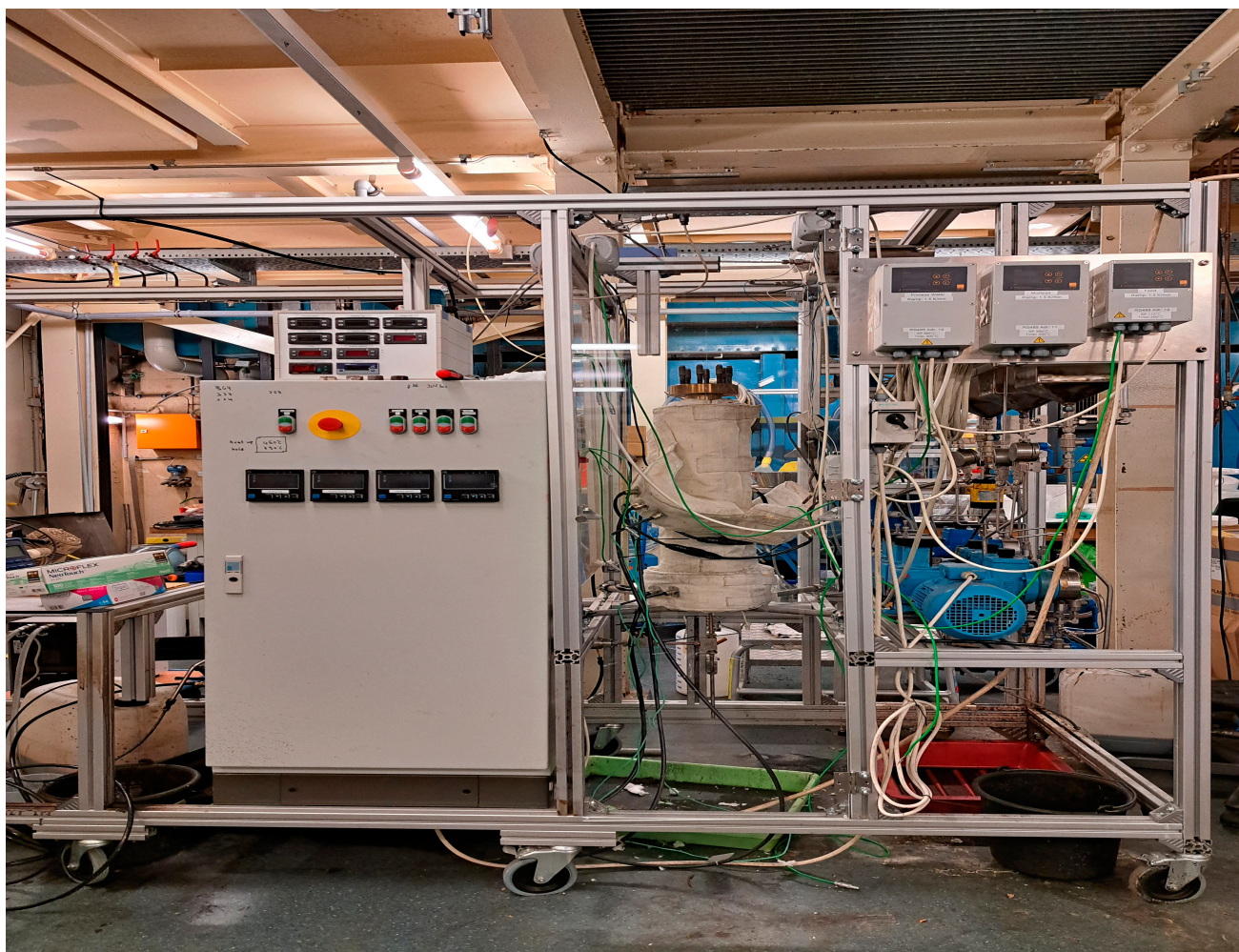


Figure 2. HTL reactor unit developed at IKFT.

2.3. Adsorbent and DES Preparation

A 10 g sample of XAD-4 was soaked in 50 mL of anhydrous ethanol for 24 h. Thereafter, it was thoroughly washed with distilled water to remove any residual organic and ethanol impurities before being oven-dried. All DESs used in this study were prepared using the heating and stirring method, as described by Abbot et al. [22]. Choline chloride (ChCl) and ethylene glycol (EG) DESs of molar ratio 1:2 were combined in a sealed Erlenmeyer flask and stirred continuously at 600 rpm and 70 °C using a magnetic stirrer until a clear homogenous solution was obtained. This DES was labeled ChCl:EG (1:2). The solution was then left to stand for 24 h to observe its stability.

2.4. Adsorption Experiments on Model Compounds

Batch experiments were carried out in a multicomponent system on phenol, guaiacol and catechol, identified as having the highest concentrations in the organic and aqueous phases of lignin-derived HTL. A series of solutions of varying concentrations (100–1000 mg/L) containing all three compounds was prepared. For each experiment, 100 mg of XAD-4 was added to 30 mL of prepared solution and placed in a thermostatic oscillator at 25 °C and 179 rpm for 24 h. Once equilibrium was attained, the samples were removed and filtered and the supernatant analyzed by HPLC. The experimental apparatus is shown in Figure 3.



Figure 3. Batch adsorption separation of HTL of lignin products in the thermostatic oscillator.

2.5. Adsorbent Modification

Adsorbent modification was carried out in Erlenmeyer flasks by the incipient impregnation method, where XAD-4 was combined with the ChCl:EG (1:2) DES at a 2:1 mass ratio (2 g of XAD-4 to 1 g of DES). The mixture was then sonicated for 4 h, followed by mechanical stirring for another 2 h. Samples were then oven-dried at 90 °C for 24 h and washed several times in distilled water to remove any unattached DES. The washed samples were then filtered through a PTFE 0.45 µm filter, followed by drying overnight at 105 °C before being stored in a desiccator until further use [23]. This sample was labeled DES-modified XAD-4.

2.6. Adsorption Experiments on HTL of Lignin Using DES-Modified XAD-4

Batch adsorption experiments were carried out on the HTL of lignin product using DES-modified XAD-4 adsorbents in Erlenmeyer flasks. We added 30 mL of HTL product to varying weights of the functionalized adsorbents (100 and 300 mg), and we placed them in a thermostatic oscillator at 25 °C and 170 rpm for 24 h. After equilibrium was reached, samples were removed and filtered and the equilibrium solution analyzed using GC-FID. As a control sample, the same procedure was carried out using corresponding weights of unmodified adsorbents.

3. Results and Discussion

3.1. Component Analysis of the Organic/Aqueous Phase of the HTL of Lignin Product

After HTL, the products obtained were classified into aqueous, organic, solid and gaseous phases. As the solid- and gaseous-phase products were of no relevance to this study, both phases were excluded from further analysis. Although there were numerous compounds that constituted the organic and aqueous phases, indicating a complex composition, the GC-FID was calibrated to detect only the major components [13,24]. The presence of major phenols, alcohols and including ketones could be detected in these product phases (Table 1), with phenol, catechol and guaiacol present in the highest concentrations, ranging from 189.2 to 823.5 mg/L. The presence of these compounds can be attributed to the cleavage of ether bonds, demethoxylation or side-chain cleavage of the building block units of lignin's structural units [9].

Table 1. Composition of the organic and aqueous phases of major HTL of lignin products.

	Adsorbate	Concentration (mg/L)
1	Phenol	592.7
2	O-cresol	13.6
3	Guaiacol	823.5
4	Catechol	257.4
5	4-Ethylphenol	-
6	4-Methylguaiacol	86.5
7	4-Ethylguaiacol	80.5
8	Syringol	75.1
9	Methanol	-
10	3-Ethylphenol	-
11	2-Methoxy-4-Propylphenol	-
12	4-Ethylcatechol	-
13	3-Methoxycatechol	-
14	3-Methylcatechol	-
15	Resorcinol	-
16	Vanillin	-

3.2. Characterization of XAD-4 and Modified Adsorbent

3.2.1. Brunauer–Emmett–Teller (BET) Parameters

Following modification, XAD-4 was observed to undergo a color change from white to a faint shade of brown, which suggests some chemical interactions and surface functionalization during the modification process. The introduction of oxygen-containing groups in the ethylene glycol of the DES induces color shifts possibly as a result of electron delocalization and/or charge-transfer interactions [24]. The surface areas, pore volumes and pore sizes of the adsorbents and the BJH pore distribution are presented in Table 2 and Figure 4, respectively. These parameters are generally recognized as having an influence on adsorbent capacity and were determined using the Brunauer–Emmett–Teller (BET) test [25].

Table 2. BET parameters of XAD-4 and DES-modified XAD-4.

	XAD-4	DES-Modified XAD-4
BET surface area (m ² /g)	864.52	629.76
Micropore BET (m ² /g)	123.86	107.19
Total pore volume (cm ³ /g)	1.09	0.76
Micropore volume (cm ³ /g)	0.05	0.04
Average pore radius (nm)	5.56	5.59

The surface areas of both adsorbents are relatively high, although that of the modified adsorbent showed a 27% reduction. This reduction may be attributed to pore coverage, partial blockage and/or structural changes arising from DES modification. While some studies report similar observations, for some others, it was to the contrary [12,13,23]. Both materials possess low micropore volumes, indicating that the structures of the materials are dominated by mesopores, and the presence of relatively large pore radii suggests adsorbents are better suited to the adsorption of larger molecules like organic compounds from aqueous solutions [26]. The total pore volume also reduced, probably because of mild etching of the polymer network, and the pore radius showed a slight increase from 5.56 nm to 5.59 nm. A possible reason for this observation is that the slight swelling of the XAD-4 matrix by the DES expands pore walls, which shifts the pore size distribution more towards mesopores during BET N₂ adsorption.

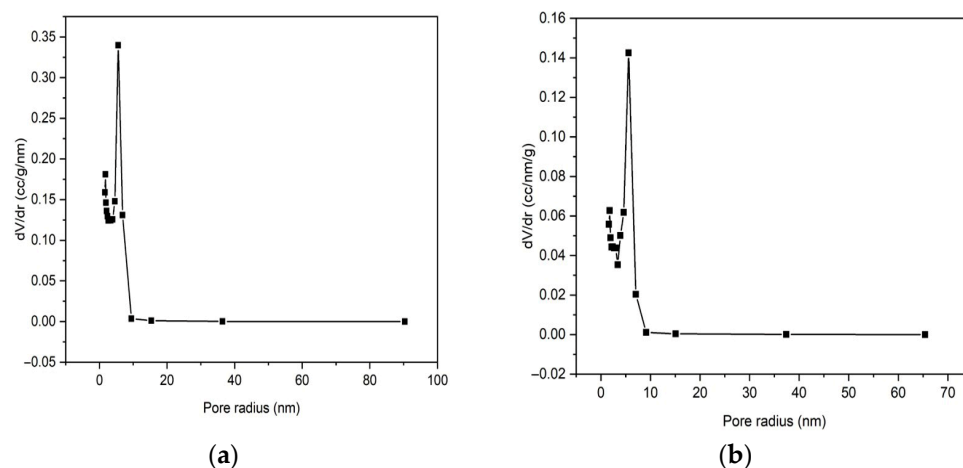


Figure 4. BJH pore size distribution of (a) XAD-4 and (b) DES-modified XAD-4.

3.2.2. Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR spectra of XAD-4 and DES-modified XAD-4 adsorbents were investigated. Noticeable spectral changes can be observed after modification, suggesting the incorporation of the DES into the XAD-4 structure (Figures 5 and 6). The deepening and broadening of the absorption band at 3319 cm^{-1} in the modified adsorbent confirm the appearance of O-H functional groups, indicative of the presence of hydroxyl components belonging to ethylene glycol and/or choline chloride. A shift in peaks from 2922 cm^{-1} to 2874 cm^{-1} also indicates the presence of additional $-\text{CH}_2-$ and $-\text{CH}_3$ groups brought into the polystyrene-divinylbenzene backbone structure of XAD-4 by the DES. The appearance of a distinct band at 1606 cm^{-1} reflect changes corresponding to aromatic $\text{C}=\text{C}$ stretching due to DES incorporation. Notably, a new absorption band at 1078 cm^{-1} , conspicuously absent in the unmodified resin, is assigned to $\text{C}-\text{O}$ and $\text{C}-\text{N}$ stretching vibrations, further evidencing the structural modifications brought about by the DES functional groups. These spectral changes, and especially the addition of hydroxyl groups, confirm the modification of the XAD-4 structure, which confers hydrogen-bonding abilities to the adsorbent upon DES functionalization.

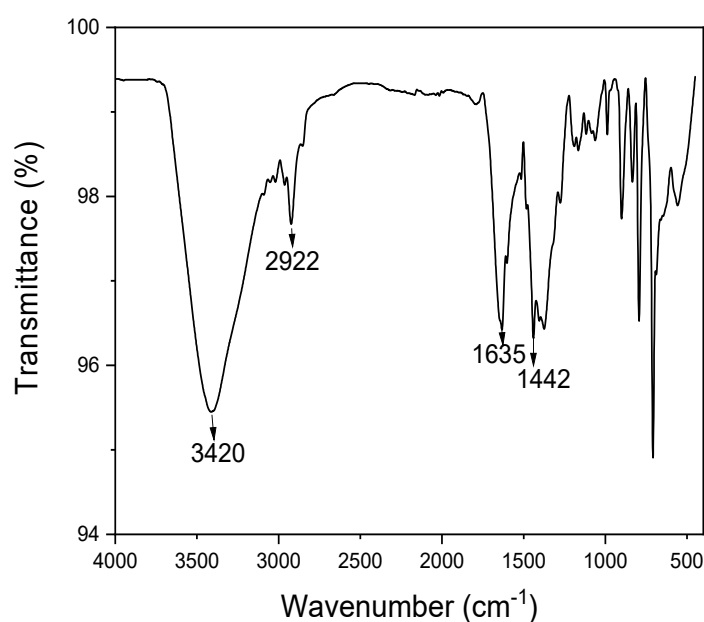


Figure 5. FT-IR spectra for XAD-4.

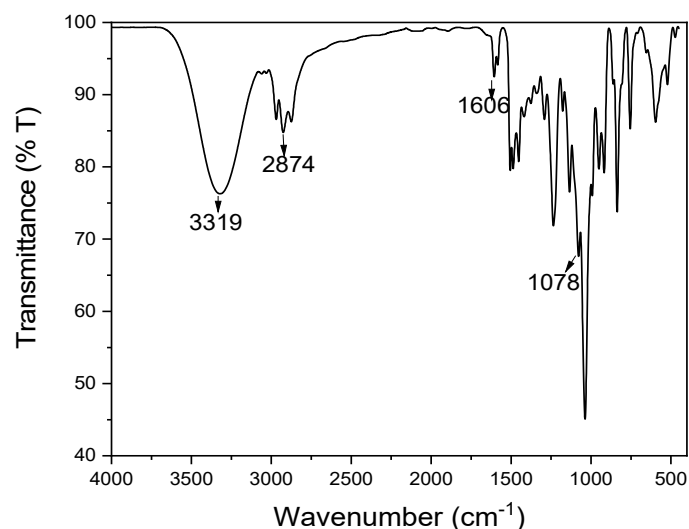
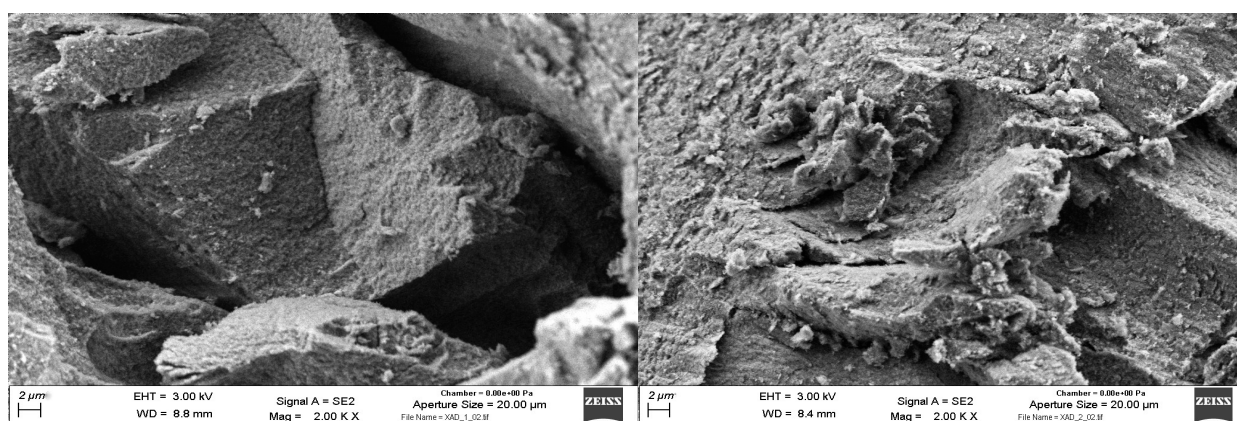


Figure 6. FT-IR spectra for DES-modified XAD-4.

3.2.3. Scanning Electron Microscopy (SEM)

SEM images of the unmodified XAD-4 adsorbent presented in Figure 7A show uniform, continuous segments with few cracks and a regularity suggesting little or no surface modification. In contrast, DES-modified adsorbent has a rougher, irregular fragmented surface with noticeable bulges and clusters, indicating modification possibly induced by structural stress (Figure 7B). This could hint at possible structural modification by the DES [27].



(A)

(B)

Figure 7. SEM images (20 µm) of (A) XAD-4 and (B) DES-modified XAD-4.

3.3. Performance of Unmodified and Modified XAD-4 on Model Compounds

In order to gain a better understanding of the mechanism of the process, the performance of unmodified and modified XAD-4 was tested on three lignin components subject to HTL and found to be present at the highest concentrations in the product stream: catechol, guaiacol and phenol. Although it would be desirable to test all compounds present in the stream, experimental limitations related to cost and time meant we were only able to study these three compounds. For this purpose, solutions containing all three solutes were prepared with the same initial mass concentration for each compound, and the results are presented in Figure 8.

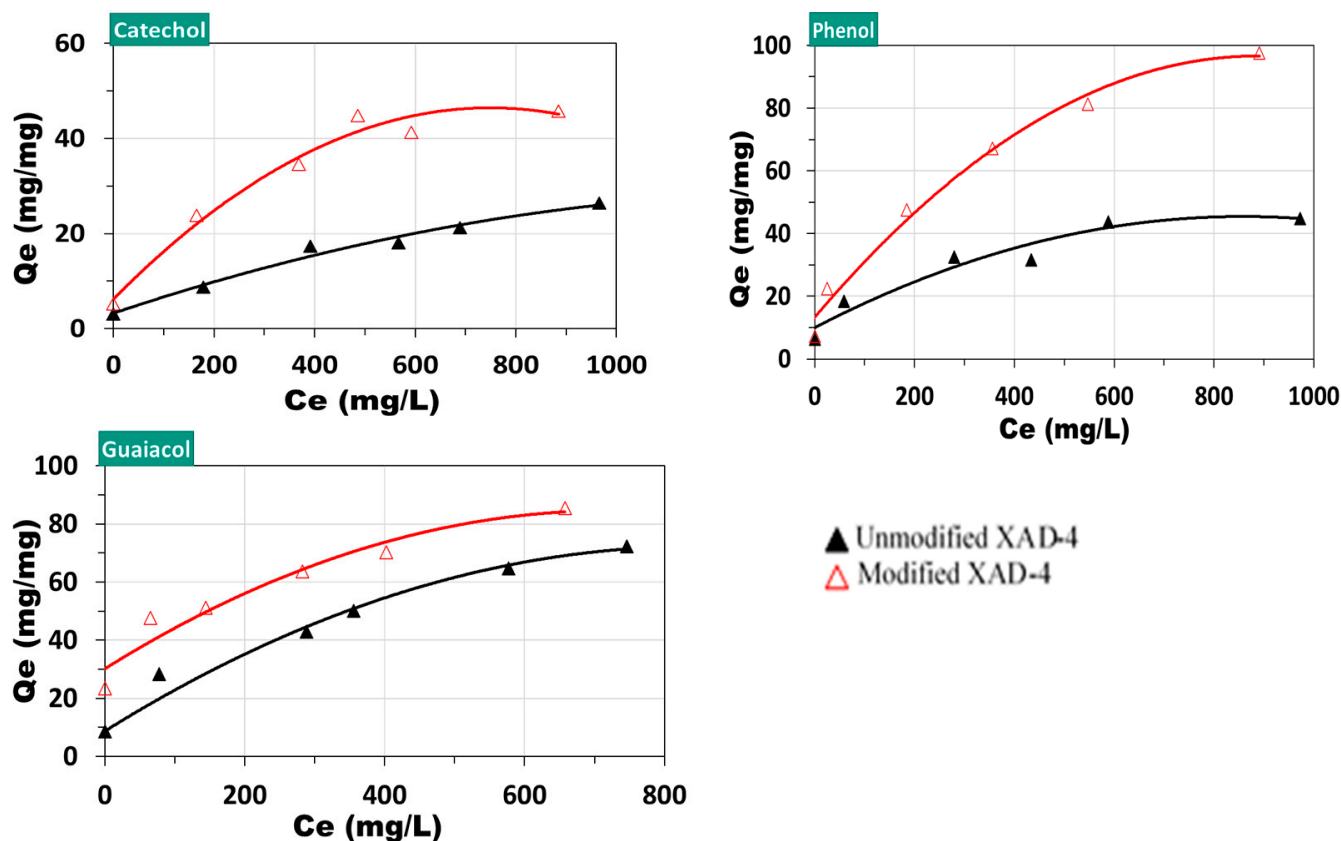


Figure 8. Adsorption isotherms for catechol, phenol and guaiacol model compounds with the Freundlich model fitting.

The values for the isotherms were calculated based on the equation

$$Q_e = \frac{(C_o - C_e)V}{m}$$

where

C_o is initial adsorbate concentration (mg/L);

C_e is the equilibrium concentration;

Q_e is the amount adsorbed at equilibrium (mg/g);

V is the volume of solution (L);

m is the mass of adsorbent (mg).

The Freundlich, Langmuir and Temkin model parameters for the experiments are presented in Tables 3–5, respectively. A close look at these parameters indicates that the model best suited to the isotherms is the Freundlich model, as the data do not fit the Langmuir or Temkin models. This is in agreement with other studies carried out on the adsorption of phenolic compounds with XAD-4 [13,28]. The equilibrium isotherm parameters were modeled using the linearized Freundlich equation

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e$$

where K_f is the Freundlich distribution coefficient, indicating adsorption capacity, and n is the correction factor, which provides an insight into the favorability of adsorption or otherwise.

Table 3. Parameter data for the Freundlich equation.

Adsorbate	Adsorbent	n	K _f	R ²
Phenol	unmodified XAD-4	1.911	3.918	0.9987
Phenol	modified XAD-4	3.042	4.739	0.9967
Guaiacol	unmodified XAD-4	2.538	5.169	0.9985
Guaiacol	modified XAD-4	3.918	12.522	0.9987
Catechol	unmodified XAD-4	1.773	2.257	0.9979
Catechol	modified XAD-4	2.636	3.853	0.9598

Table 4. Parameter data for the Langmuir equation.

Adsorbate	Adsorbent	Q _{max}	K _l	R ²
Phenol	unmodified XAD-4	0.1068	0.1068	0.1068
Phenol	modified XAD-4	0.1113	-1.24×10^{-6}	-4.78×10^{-8}
Guaiacol	unmodified XAD-4	0.1135	2.43×10^{-6}	-2.17×10^{-8}
Guaiacol	modified XAD-4	0.1108	-1.29×10^{-6}	-3.58×10^{-8}
Catechol	unmodified XAD-4	0.0653	-0.117	-1.33
Catechol	modified XAD-4	0.4243	0.00976	0.9024

Table 5. Parameter data for the Temkin equation.

Adsorbate	Adsorbent	B	A	R ²
Phenol	unmodified XAD-4	0.0687	0.041	0.9365
Phenol	modified XAD-4	0.0585	0.0692	0.9036
Guaiacol	unmodified XAD-4	0.0643	0.0616	0.9115
Guaiacol	modified XAD-4	0.0651	0.0533	0.9025
Catechol	unmodified XAD-4	0.0606	0.219	0.9127
Catechol	modified XAD-4	0.0575	0.349	0.8394

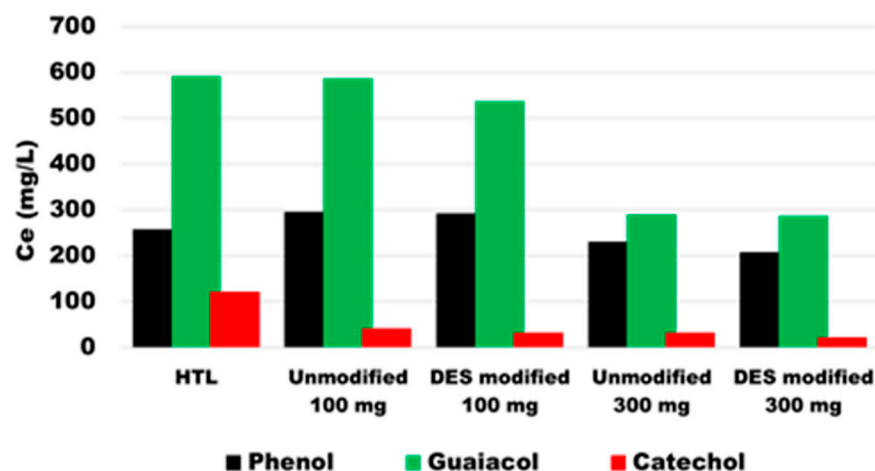
The performance of the DES-modified XAD-4 across all adsorbates showed a significant improvement compared to the unmodified adsorbent, with guaiacol demonstrating the highest affinity for both adsorbents. The reason for this could be guaiacol being the least polar amongst the three, meaning that having the lowest affinity for the aqueous phase produces a greater tendency to be readily adsorbed. The DES-modified adsorbent might interact more favorably with the functional groups introduced into the pore structure of the adsorbent by the DES [29,30]. In addition, guaiacol with its methoxy and hydroxyl groups has a more balanced amphiphilic character, allowing for combined hydrophobic and hydrophilic interactions with the polar and non-polar matrix components of the adsorbent and leading to its selective adsorption over the others [31]. Its greater molecular weight could also provide a steric hindrance to other molecules, leading to its preferential attachment to the adsorbent active sites. Catechol's affinity for both adsorbents was observed to be the lowest. As the compound with the highest solubility in water (43 g/100 mL), it can be inferred that weaker interactions with the adsorbent would result in catechol being more readily retained in the aqueous phase [31,32].

3.4. Performance of Unmodified and Modified XAD-4 on HTL Product

Batch adsorption experiments were conducted on the HTL of lignin products using unmodified and DES-modified adsorbents. The analytics carried out by GC-FID are presented in Table 6 and Figure 9.

Table 6. GC-FID data for HTL using unmodified and modified XAD-4 adsorbents.

	Catechol (mg/L)	Phenol (mg/L)	Guaiacol (mg/L)
HTL product	257.4	592.9	823.5
Unmodified XAD-4 (100 mg)	296.1	587.3	41.9
DES-modified XAD-4 (100 mg)	293.4	538.0	32.7
Unmodified XAD-4 (300 mg)	231.2	295.3	33.8
DES-modified XAD-4 (300 mg)	207.8	287.6	121.5

**Figure 9.** GC-FID comparison data for unmodified and DES-modified adsorbents.

The DES-modified adsorbents outperformed the unmodified adsorbents at both 100 mg and 300 mg dosages across all tested adsorbates on the HTL product. Additionally, both unmodified and DES-modified adsorbents exhibited a higher adsorption affinity for guaiacol compared to the other compounds. DES-modified XAD-4 (300 mg) had the highest percentage uptake (85.25%). A possible explanation for this observation is that the competitive adsorption effects that different species exert on each other in a complex multicomponent solution, such as the HTL of lignin, lead to guaiacol being preferentially adsorbed. In addition, the presence of other species, such as organic acids, esters and salts, in the HTL product could have played a role by altering physicochemical properties such as pH, ionic strength, viscosity and polarity, which have an influence on the adsorption process [33]. Adsorbate molecular orientation and size give rise to a steric hindrance effect, which in turn could lead to an inhibitory effect on the adsorption rates and capacities of all species as they compete for the active sites on the adsorbent surface [33]. Similar effects were also observed in previous studies [33–35]. The introduction of the DES into the XAD-4 matrix is driven mainly by hydrophobic interactions via π - π and Van der Waals force mechanisms between DES alkyl chains and adsorbent aromatic groups. Hydrogen bonding to a lesser extent might also account for interactions between the DES and residual hydroxyl groups deposited on the adsorbent surface during ethanol pretreatment. The higher guaiacol uptake by DES-modified XAD-4 arises from the hydrogen bonding between guaiacol and DES hydroxyl groups on the adsorbent surface and the preferential adsorption owing to its dual amphiphilic nature [31]. Likewise, the hydrogen bonding functional groups introduced through DES modification might also have a role to play in this regard [36].

4. Conclusions

This study reports the adsorption separation of the HTL of lignin product downstream using DES-modified adsorbents. This study reports the adsorption separation in the HTL of lignin products downstream using DES-modified adsorbents, as determined through

experimental analysis. Initial tests were performed on model compounds of phenol, guaiacol and catechol, which are compounds, found in the highest concentrations in the lignin HTL product stream using unmodified and modified XAD-4. The DES-modified XAD-4 adsorbents had an adsorption capacity for the compounds in the order of guaiacol > phenol > catechol, with the DES-modified XAD-4 (300 mg) having a guaiacol percentage uptake of 85.25%, indicating that the modified adsorbent has a higher selective adsorptive capacity for guaiacol than when unmodified. The Freundlich model best explains the adsorption behavior of the compounds in the HTL product stream. They exhibited inhibitive competition for adsorbent active sites when tested on all adsorbents, and the possible reasons for this were identified. The results of this study demonstrate the promising ability of DES-modified XAD-4 adsorbents in the selective adsorption of phenolic compounds from the HTL of the lignin product stream. Further work is required in exploring multicomponent systems including the other compounds derived from the HTL product in order to gain a better understanding of the mechanism underlying the competitive adsorption effects. In addition, computational techniques such as Density Functional Theory (DFT) should be applied in the pre-screening of undesirable DES solvents, thereby reducing the laboratory time and costs.

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Conflicts of Interest: The authors declare no conflicts of interest.

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