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Solute interactions in the nanofiltration of wood hydrolysates

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Abstract

Spent sulfite liquor derived from sulfite pulping is considered as carbon source for bio-based platform chemicals. The spent sulfite liquor containing sugars, hydroxylic acids, furan derivatives and cooking chemicals is currently predominantly combusted to generate energy and to recover the pulping chemicals. In order to improve the economic performance of the whole pulping process a partial material use of the spent sulfite liquor is desirable. The lignosulfonates can be separated by ultrafiltration and be used as concrete plasticizer or as source for phenolic-based hydrogels or performance materials. The carbohydrates and other wood degradation products can be used as energy and carbon source in a fermentation process. In order to improve the fermentation process, the amount of inhibitory compounds, such as furan derivatives and short-chain organic acids needs to be reduced. Intermolecular interactions between different molecules influence the detoxification process by means of nanofiltration. The lignosulfonate interacts with inhibitor components and increase their retention, which is unfavorable for the process efficiency. The interactions between gluconic acid and short-chain organic acids were found to increase the membrane selectivity.

Introduction

Side streams of the wood pulping process are an abundant available carbon source. The lignosulfonate fraction can be used e.g. as concrete additives and plasticizers [1]. Another option is the chemical conversion to phenolic monomers with several reactive sides, which can be further utilized to bio-based hydrogels and foams [2]. For the utilization of lignosulfonate a separation from other wood degradation products and the cooking chemicals need to be done. Ultrafiltration is considered as a feasible method, since the separation and the purification of the lignosulfonate can take place in the process [3].

The ultrafiltration permeate consists of pulping chemicals and wood degradation products such as sugars, aldonic acids, hydroxylic acids, furan derivatives and low molecular weight lignosulfonate fragments. The sugars and aldonic acids can be used as carbon and energy source in a fermentation process to produce platform chemicals. To enhance the efficiency of the fermentation process, inhibitor components like furan derivatives and short-chain (C₁-C₂) organic acids need to be removed [4]. Nanofiltration can be used to separate the fermentation inhibitors and at the same time the fermentable components such as sugar and aldonic acids can be concentrated [5]. A thermodynamically understandable explanation of the negative retention of molecules occurring in this system during the nanofiltration process has not yet been achieved.

We therefore performed studies on mixtures of model compounds as well as with solution from the industrial pulping process to investigate intermolecular interactions and derive transferable understanding of the involved principles. To this end, thermodynamic hypotheses were tested and found to be

suitable to make predictions about negative retentions in model systems and actual process streams.

Material and methods

Membrane

NF270 from Filmtec was used for the nanofiltration experiments. It is a commercial available polymeric thin-film composite membrane. UP005 from Microdyn Nadir was used in the ultrafiltration experiments.

Chemicals

The mixtures of model solutions were prepared from pure chemicals (glucose, xylose, gluconic acid, acetic acid, 5-Hydroxymethylfurfural (HMF), furfural, furfuryl alcohol, tetrahydrofurfuryl alcohol and magnesium sulfate) with a purity higher than 99 %, all derived from Sigma Aldrich. Additionally, process liquors from an industrial acidic spruce sulfite pulping process were used. The mixtures were prepared with deionized water and the pH was set to pH 4 with sodium hydroxide or hydrochloric acid. Table 1 shows the composition of a model solution with a total content (DS) of 100 g L⁻¹.

Table 1: Composition of a model solution with a DS of 100 g L⁻¹.

| Component | c [g L ⁻¹] |
|-------------------|------------------------|
| Acetic acid | 3.5 |
| Furan derivative* | 0.5 |
| Mg – sulfate | 5 |
| Gluconic acid | 22 |
| Glucose | 63 |
| Xylose | 13 |

* Either HMF, furfural, furfuryl alcohol or tetrahydrofurfuryl alcohol or a mixture of all of them

Filtration experiments

The filtration experiments were performed in lab-scale using flat sheet membranes with 80 cm² active filtration area. The experiments were performed in circulation mode to ensure constant feed concentration. The sample volume was kept insignificant low (1 mL) compared to the feed volume of 5 L. All the experiments were carried out between 3 and 35 bar pressure.

Isolation of lignosulfonate

The lignosulfonate added to the model solutions were derived from a magnesium bisulfite pulping liquor. The lignosulfonate was separated and purified from pulping

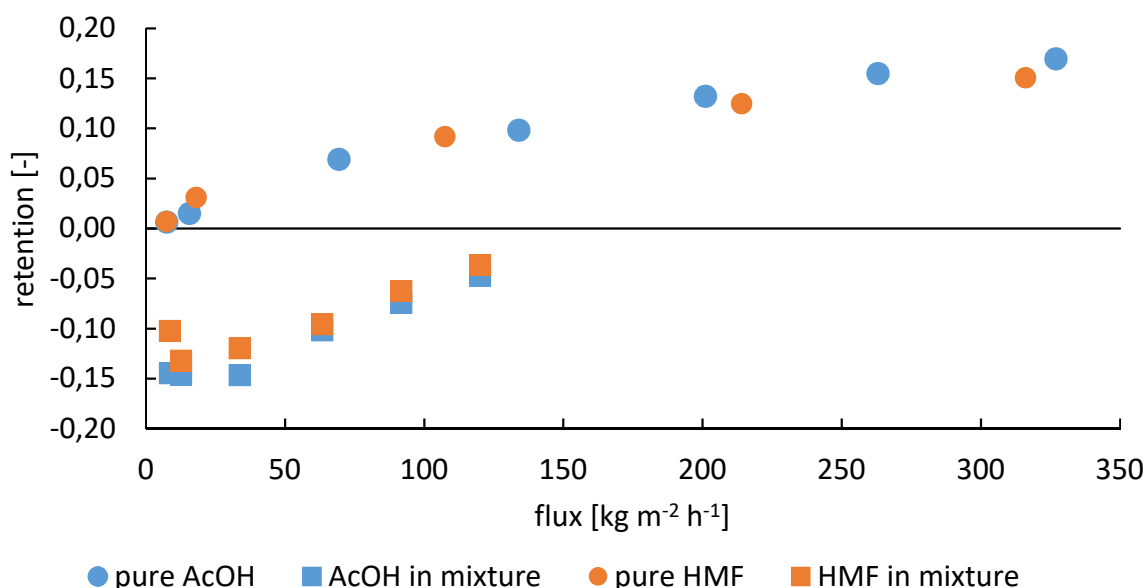


Figure 1: Retention of acetic acid (AcOH) and HMF in pure solution in water (dots) and in synthetic wood hydrolysate mixture [squares].

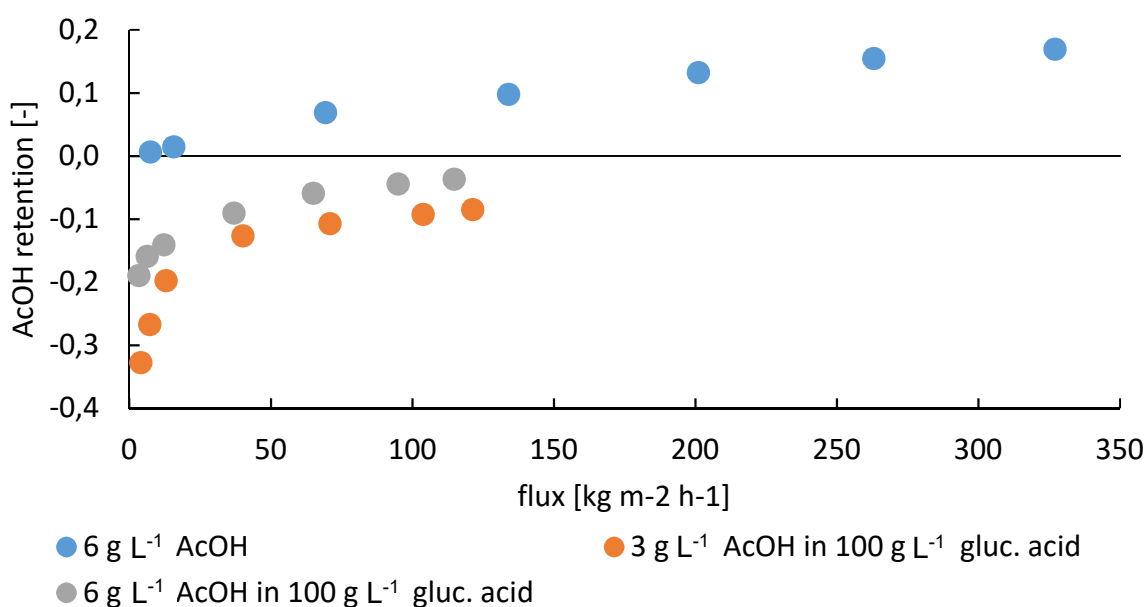


Figure 2: Retention of acetic acid (AcOH) in pure water and in mixtures with gluconic acid (gluc. acid).

chemicals and other wood degradation products via ultrafiltration. Several purification cycles were performed to get lignosulfonate with a purity of higher than 97 w%.

Results and discussion

Negative retention of HMF and Acetic is driven by other liquor components

It is well established, that negative retention of both HMF and acetic acid can occur during membrane separation of biomass hydrolysates. In order to establish an experimental framework we therefore performed experiments with (i) pure HMF, (ii) acetic acid and (iii) mixtures of both compounds with glucose, xylose, gluconic acid and magnesium sulfate at a total concentration of 100 g L⁻¹.

As shown in figure 1, the retention of acetic acid and HMF was slightly positive in pure solutions. The retentions in the mixture was negative. We therefore concluded that the experimental conditions were suitable to establish which

interactions promote negative retention of HMF and acetic acid in spent sulfite liquors. Due to a higher osmotic pressure difference, the permeate flux for the mixture was lower compared to the pure solutions.

Negative retention of acetic acid is required to neutralize electric charges in the permeate

We have previously shown that the negative retention of acetic acid is due to a spontaneously arising electric field, caused by the retention of gluconate ions [6]. Gluconate ions have a higher molecular weight compared to acetate ions and therefore showed a much higher retention. By contrast, hydronium ions distribute almost equally on both sides of the membrane, as their retention is negligible. As gluconate and acetate ions were the only anions in the process, the acetate ions equal the charge balance. This results in a negative retention of acetic acid. As can be seen in figure 2, the higher the ratio between gluconic acid and acetic acid concentrations, the higher the negative retention of acetic acid.

Negative retention of HMF is caused by hydration of salts in the retentate

The above-described principle of charge neutralization is not suitable to explain the negative retention of HMF, because it is an uncharged molecule. We have previously shown that the presence of inorganic salts affects the retention of furan derivatives such as HMF. Magnesium sulfate in aqueous solution forms a hydration shell, including 34 [6] molecules of water, as schematically shown in figure 3. These water molecules were bound to the salt ions and were not accessible for the solution of HMF anymore. Therefore, the concentration of HMF in the “unbound water” was elevated compared to the concentration based on the overall water molecules. Magnesium sulfate showed very high retention. This led to a permeate stream, almost free of magnesium sulfate but enriched with HMF. Due to this unequal distribution of magnesium sulfate and reduction of unbound water, HMF concentration in permeate is increased to establish a new equilibrium of HMF in unbound water. To test this hypotheses experiment with other salts (magnesium chloride and sodium chloride) as well as with other furan derivatives such as furfural were performed. The observed salting out tendencies of different salts were in correlation with their hydration numbers published in literature.

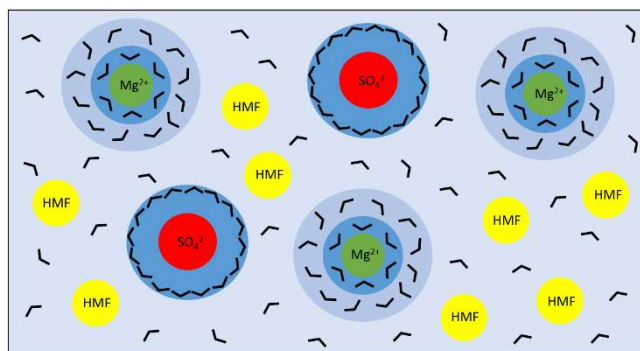


Figure 3: Scheme of water clusters around salt molecules and thus a reduced amount of unbound water for the solution of HMF.

Furthermore, the presence of lignosulfonate increased the retention of acetic acid (figure 5). We hypothesized that the interaction between acetate ions and lignosulfonate takes place via the counter ion of the sulfonate groups. A comparison of magnesium and sodium lignosulfonate indicated this. A more detailed discussion of the mechanism is published in [7].

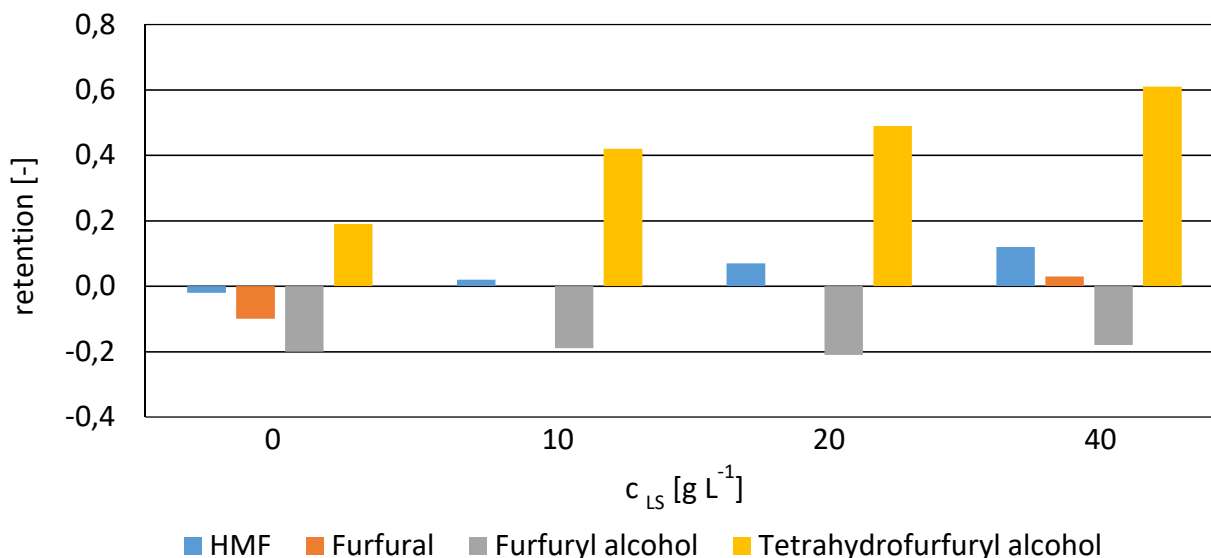


Figure 4: Influence of lignosulfonate concentration on the retention of furan derivatives at 25 bar pressure and 40 °C.

Lignosulfonate increases the retention of HMF and acetic acid

Lignosulfonates are complex molecules, with a variety of functional groups and chemical bonds (including aromatic electron systems, hydroxyl- and sulfonic acid moieties). Consequently, they can interact with other molecules in a number of ways (π -electron interactions, hydrogen bonds and ionic bonds). To clarify which type of bond is responsible for the lignosulfonate interaction with HMF we tested the retention of HMF, furfural, furfuryl alcohol and tetrahydrofurfuryl alcohol in the presence of increasing concentrations of lignosulfonate (figure 4). We found out that the electron configuration of the ring oxygen atom and the aldehyde oxygen plays an important role. The alcohol group of the furan derivatives showed minor impact. [7]

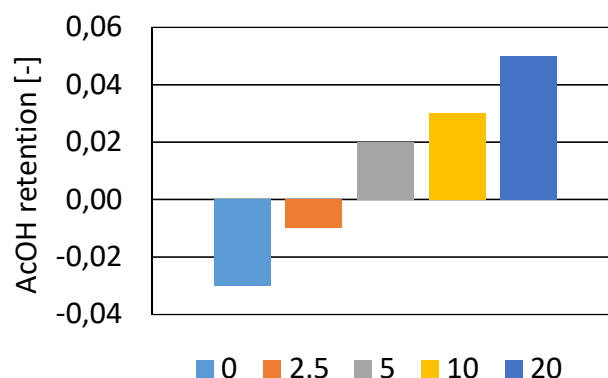


Figure 5: Influence of lignosulfonate concentration (in g L⁻¹) on the retention of acetic acid (AcOH) at 25 bar pressure and 40 °C.

Conclusion

The retention of inhibitor components was affected by several intermolecular interactions. In the case of acetic acid and HMF, additional electrical forces and a lack of free water led to negative retention. The mechanisms can be shown in binary mixtures as well as in multi-component mixtures. The lignosulfonate interactions via hydrogen bonds with different furan derivatives reduce the overall membrane selectivity. Consequently, a high lignosulfonate retention in the ultrafiltration step is required in terms of overall process efficiency. Furthermore, it is shown that the mechanistic description of retention behavior found in experiments with model solutions can be extrapolated to process liquors. In addition, it can be shown that lignosulfonate solute interactions were not directly affected by membrane interactions, thus we conclude that the explained mechanisms can be applied to other separation processes as well.

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