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An integrated detoxification process with electrodialysis and adsorption from the hemicellulose hydrolysates of yellow poplars

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HIGHLIGHTS

- Integrated detoxification process with ED and adsorption was performed.
- Integrated detoxification process efficiently removed fermentation inhibitors.
- Fermentation performance increased due to high fermentation inhibitor removal.
- Acetic acid showed high removal efficiency and transport rate in ED process.

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ABSTRACT

An integrated detoxification process with electrodialysis (ED) followed by adsorption was performed to remove fermentation inhibitors from hemicellulose hydrolysates. The hydrolysates were prepared by oxalic acid pretreatment of yellow poplars at different temperatures. Of fermentation inhibitors, acetic acid showed high removal efficiency of about 90% and high transport rate during the ED process without membrane fouling. The integration of the detoxification processes increased up to the ethanol yield of 0.33 g/g sugar, the ethanol production of about 9 g/L, and the productivity of 0.12 g/L h, while the fermentation of non-detoxified hydrolysates did not produce bioethanol. The influence of inhibitor concentration on the fermentability showed that HMF had the highest inhibition effect. The results clearly showed that an integrated detoxification process with ED followed by adsorption removed fermentation inhibitors with high efficiency and increased the fermentability of the oxalic acid pretreated hemicellulose hydrolysates.

1. Introduction

Bioethanol is an alternative biofuel to replace fossil fuels that decreases air pollution and greenhouse gas emissions. Sucrose-containing feedstocks, such as sugarcane and other starch-rich materials, can be effectively converted to ethanol by fermentation (Cardona and Sanchez, 2007). However, the production of bioethanol from a sucrose-containing feedstock has led to considerable debates about its sustainability (Yang and Wyman, 2008). Interest in producing ethanol from lignocellulosic biomass has increased since efficient utilization of hemicelluloses and cellulose in lignocellulosic biomass has offered an opportunity to greatly reduce the cost of bioethanol production (Huang et al., 2008; Zhu and Pan, 2010).

Lignocellulosic biomass, which consists of cellulose, hemicelluloses and lignin, is highly recalcitrant to degradation due to the crystallinity of cellulose and its high molecular weight (Himmel et al., 2007). Thus, lignocellulosic biomass requires proper pretreatments to increase the bioethanol fermentability by the improvement of the accessibility of the cellulolytic enzymes to the cellulose (Lloyd and Wyman, 2005). Until now, various pretreatment methods have been studied such as hot water, alkaline, ammonia, dilute inorganic acids, and organic acids (Yang and Wyman, 2008; Kim et al., 2011; Lee and Jeffries, 2011). Among acid pretreatment methods, oxalic acid is considered a possible alternative to sulfuric acid because it is less toxic to yeasts and other microbes. Furthermore, it exhibits a higher catalytic efficiency of hydrolysis than sulfuric acid, showing less production of fermentation inhibitors (Scordia et al., 2011; Zhang et al., 2011; Lee et al., 2011).

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In general, chemical hydrolysis of lignocellulosic materials using acidic catalysts coproduces many different fermentation inhibitors. Several inhibitory compounds from pretreatments have been reported such as furfural, 5-hydroxymethylfurfural (HMF), acetic acid, formic acid, and phenolic compounds (Sainio et al., 2011; Sun and Cheng, 2002). It was reported to be highly toxic to fermenting microbes; thus, decreasing overall biomass-to-ethanol conversion process efficiency (Mussatto and Roberto, 2004; Palmqvist and Hahn-Hägerdal, 2000a). Some fermentation inhibitors, such as furfural and HMF, significantly affected growth of microbes (*Pichia stipitis*, *Saccharomyces cerevisiae*, *Escherichia coli*) and gave negative impacts on bioethanol yield (Sainio et al., 2011; Weil et al., 2002).

Therefore, effective strategies to remove inhibitors from the biomass pretreated solution (hydrolysate) should be developed to reduce toxicity during fermentation. Fermentation inhibitors should be removed effectively from hydrolysates without removing fermentable sugars i.e., monosaccharides and soluble oligosaccharides (Sainio et al., 2011).

Several methods to detoxify hydrolysates have been reported such as physical, chemical, biological methods, and combined treatments (Weil et al., 2002; Weng et al., 2010). Of methods, chemical methods, including neutralization, overliming, alkaline detoxification, and ion exchange, have disadvantages since additional processes such as neutralization and regeneration are required. In addition, biological methods such as enzymatic and microbial detoxification have low rate of detoxification and high cost even though it provides a friendly environment for bioethanol fermentation (Cavka and Jönsson, 2013).

Until now, various processes such as evaporation, extraction, adsorption, and membrane processes have been considered as physical detoxification method, depending on the properties of the fermentation inhibitors. Adsorption is a convenient and effective technique to remove low concentrations of hydrophobic chemicals from water (Ranjan et al., 2009; Xie et al., 2005; Jeong et al., 2014). Membrane processes including nanofiltration, reverse osmosis, and electrodialysis (ED) have been considered for removing fermentation inhibitors, depending on their molecular size and charge properties (Gautam and Menkhaus, 2014; Wei et al., 2014). Among fermentation inhibitors, furfural, HMF, and phenolic compounds can be removed effectively by adsorption due to their hydrophobic properties, while acetic acid and formic acid show low removal efficiencies. However, they have low removal efficiencies high removal efficiencies in ED process because of charge properties. ED is an electrochemical separation process that uses cation and anion exchange membranes and an electric potential as the driving force. ED has been considered for separating and purifying ionic species (Strathmann, 2010; Lee et al., 2013a,b; Huang et al., 2007).

In the previous study, a detoxification process was applied to remove the fermentation inhibitors using an adsorption column packed with polymeric resins as a feasibility study (Jeong et al., 2014). However, the previous study did not provide information on the characteristic properties of equilibrium and the adsorption capacity of the adsorbents, nor the influence of different inhibitor concentrations on the bioethanol fermentability.

The objective of this study was to increase the bioethanol fermentability by detoxification via an integrated process consisting of ED followed by adsorption. Hemicellulose hydrolysates of hardwood biomass with high xylose concentration were prepared by the oxalic acid pretreatment at different temperatures.

The fermentation inhibitors were removed by the integration process consisting of ED followed by adsorption; ED was employed to remove acetic acid and adsorption by the two different adsorbents was used for the ED treated hydrolysates. As a preliminary study, equilibrium and dynamic column experiments were carried out in the synthetic solutions of furfural, a representative non-ionizable inhibitor. Finally, the bioethanol fermentability of the detoxified oxalic acid pretreated hydrolysates was examined to investigate the integrated detoxification process consisting of ED followed by adsorption.

2. Methods

2.1. Preparation of hydrolysates by the oxalic acid pretreatment

In this study, hardwood chips from yellow polars (*Liriodendron tulipifera*) were used as a woody biomass feedstock. The biomass was milled and screened to a size of 40–60 mesh using a J-NCM Wiley mill (JISICO, Seoul, Korea) and stored at 4 °C at lower than 10% moisture until further use. Pretreatments of the hardwood biomass were performed at 160, 170, and 180 °C for 50 min with 0.1 M oxalic acid catalyst solution of pH 1.3. Biomass and oxalic acid solution in 500 mL cylindrical stainless steel vessels were heated to the reaction temperature and then rotated to keep the liquor in contact with a tumbling digester. Each vessel was loaded with 50 g (dry weight basis) of biomass and sufficient oxalic acid/water mixture to give total solid/liquid ratio of 1:4 (w/w). The liquid fraction (hemicellulose hydrolysate) was separated from the pretreated biomass by vacuum filtration and stored at 4 °C for experiments and further analyses.

2.2. Adsorption equilibrium experiments

Two different adsorbents, activated carbons (Ducksan, Seoul, Korea) and Amberlite XAD-4 resin (Sigma–Aldrich, St. Louis, MO, USA), were used for the adsorption equilibrium and dynamic adsorption experiments. The adsorbents were completely dispersed in 100 mL of different concentrations of furfural aqueous solutions for the adsorption equilibrium experiments. The solutions were continuously shaken in a thermostatic oscillator with identical rotational speed (150 rpm) for 24 h at the desired temperature (30 °C).

2.3. Dynamic adsorption experiments of hemicellulose hydrolysates

Detoxification of the fermentation inhibitors was carried out using an integrated process of ED followed by adsorption. Loading and regeneration steps of the adsorption process were studied in a glass column (ID 0.9 cm, height 15 cm) for the dynamic adsorption experiments with the furfural synthetic solution and the ED treated hydrolysate. Adsorbents were packed in the column after soaking in isopropyl alcohol overnight.

A five-step protocol was used to operate the adsorption column at the desired flow rate as follows: (i) water (200 mL) was pumped through the column; (ii) the solution (furfural solutions or hydrolysates) was fed into the column, and the column effluent was periodically collected; (iii) water (200 mL) was pumped through the column for the water washing step; (iv) ethanol (200 mL) was supplied through the column to desorb the furfural adsorbed on the adsorbents; and (v) water was fed to the column to wash the ethanol from the column.

2.4. ED experiments of oxalic acid pretreated hydrolysates

The ED experimental setup was prepared in a CJ-S3 ED stack (Changjo Techno, Seoul, Korea) consisting of 10 cell pairs with two compartments (dilute and concentrate), and a total membrane effective area of 550 cm^2. Commercial cation exchange membranes (NEOSEPTA® CMX) and anion exchange membranes (NEOSEPTA® AMX) (ASTOM Corp., Tokyo, Japan) were used to prepare the ED stack.