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Removal of inhibitors from a hydrolysate of lignocellulosic biomass using electrodialysis

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ABSTRACT

In this study, the transport and removal of inhibitors from the hydrolysate of a waste mushroom medium and the fouling phenomena were investigated in the electrodialysis (ED), an electrochemical process using ion exchange membranes in the electric field. In the preliminary study, the influence of pH and potential on the process performance was investigated using synthetic solutions containing acetic acid and glucose. The removal of acetic acid, a weak acid inhibitor, was especially high when the process was operated at higher solution pH values and potentials. In the electrodialytic experiments of the hydrolysate of a waste mushroom medium as lignocellulosic biomass, the high removal efficiency of formic acid and acetic acid was measured due to the electrotransport in the electric field. Furthermore, non-ionizable inhibitors, furfural and HMF (5-hydroxymethylfurfural), were removed due to diffusion and adsorption through ion exchange membranes. During the ED experiments, the deposition of organics decreased the process performance. However, the process performance was not changed as reversible fouling by chemical cleaning methods. It was clearly shown that the inhibitors could be removed effectively without any significant fouling effect in the ED process of the hydrolysate of a lignocellulosic biomass.

1. Introduction

Concerns on the use of lignocellulosic biomass for the second generation bioethanol production have increased due to the anticipated oil shortage, increasing oil prices and global warming [1]. Bioethanol is accepted as one of the alternative biofuels due to the replacement of oil-derived fuels and decrease in air pollution and greenhouse gas emission. Currently, the production of bioethanol from sucrose-containing feedstocks has led to considerable debate about its sustainability.

Lignocellulosic biomass, which consists of cellulose, hemicelluloses and lignin, is accepted as renewable and abundant source in the natural world. It has been considered as an attractive raw material for biofuel production because of its availability in large quantities at low cost [2]. Efficient utilization of hemicelluloses and cellulose in lignocellulosic biomass offers an opportunity to reduce greatly the cost of bioethanol production [3–5]. However, lignocellulosic biomass is highly recalcitrant to the degradation due to the crystallinity of cellulose and its high molecular weight. Lignocellulosic biomass requires pretreatment to improve the accessibility of the cellulose to the cellulolytic enzymes prior to its fermentation [6–8].

Various pretreatment methods have been studied such as hot water, alkaline, ammonia, dilute inorganic acids, and organic acids [9]. Generally, acid pretreatment of lignocellulosic biomass produces fermentable sugars and a great amount of chemical species, which can inhibit the subsequent fermentation. Several inhibitory compounds are reported such as furfural, 5-hydroxymethylfurfural (HMF), acetic acid, and phenolic compounds. These compounds inhibit the activity of yeast cells, thus decreasing the growth rate of the microbes, ethanol production rate, and ethanol yield [10–12].

Inhibitory chemicals should be removed at a low concentration level to avoid these inhibition problems to microorganisms prior to fermentation. Various detoxification methods have been proposed to overcome inhibitory effects on the yeast and bacterial metabolism, such as physical methods (evaporation, extraction, and adsorption), chemical methods (neutralization, overliming, alkaline detoxification, ion exchange), biological methods (enzymatic and microbial detoxification) and combined treatments [13–15].

Electrodialysis (ED), an electrochemical separation process using an electric potential, has been considered for the separation and purification containing ionic species in liquid phase [16–18]. ED employs cation and anion exchange membranes to remove ions from an electrolyte solution or to concentrate ionic species in the

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solution. It has been used in the area of the mineralization of water, desalination of saline solution, production of table salt, and wastewater treatment. Recently, ED has been widely applied in the separation of organic acids, such as lactic acid, citric acid, acetic acid and their salts [19,20].

Even though interests on the lignocellulosic biomass have increased in the production of biofuels, the transport and removal of weak acidic inhibitors (acetic acid and formic acid) was not widely considered using electrodialysis even though inhibitors affect fermentation process performance [4,21]. The objective of this research is to study the removal of inhibitors in order to increase the fermentation performance for the ethanol production from the hydrolysate of a lignocellulosic biomass. The influence of the operating conditions on the electrodialytic performance was investigated and the proper operating condition was determined in the preliminary study. And the transport of sugars and inhibitors through ion exchange membranes was investigated in the ED process of the hydrolysate of a lignocellulosic biomass, waste medium obtained after cauliflower mushroom cultivation.

2. Experimental

2.1. Hydrolysate from the oxalic acid pretreatment of lignocelluosic biomass

In the present study, the waste medium obtained after cauliflower mushroom (*Sparassis crispa*) cultivation was used as lignocellulosic biomass. The medium used for the cultivation of the cauliflower mushroom consists of 80% Douglas fir sawdust, 10% wheat powder, 10% corn powder and oligosaccharide. The lignocellulosic biomass, supplied by the Jeonnam Forest Resources Research Institute (Naju, Jeonnam, Korea), was milled and screened to a mesh size of 40–60 using a Wiley mill J-NCM (Jisco, Seoul, Korea) and stored at 4 °C with the moisture content of less than 10%.

For the acid pretreatment of lignocellulosic biomass, oxalic acid pretreatment was conducted at 130 °C for 25 min and the temperature was rapidly increased to 170 °C with 0.064 g/g of biomass (dry weight of biomass) in a cylindrical stainless steel reaction vessel [22]. The liquid fraction (hydrolysate) was separated from the pretreated biomass by vacuum filtration and stored at 4 °C for experiments and further analyses.

2.2. Characterization of anion exchange membranes

In the present study, the properties of three different anion exchange membranes, NEOSEPTA® AMX, AM-1, and ACM (ASTOM Corp., Japan), were characterized to select proper anion exchange membrane for the stack preparation. The transport number of a counter-ion through the anion exchange membrane was estimated based on the membrane potential measurement using Ag/AgCl electrodes in KCl solution [23]. Electrical resistance measurements were carried out at 100 kHz using a clip cell connected to a LCZ meter, NF 2321 (NF Electronic Instruments, Japan) in both solutions. The exchange capacity of the anion exchange membrane was estimated by determining the functional groups in the membrane structure by the titration method with 0.05 N HCl after soaking in 0.1 N NaOH for 24 h [24]. The thickness of anion exchange membranes was measured using a thickness gauge (Mitutoyo, Japan).

2.3. Electrodialytic experimental setup

A stack consisting of ten cell pairs (diluate and concentrate) was assembled in a CJ-S3 electrodialysis stack with total membrane effective area of 550 cm^2 (Changjo Techno, Korea). The stack was prepared using common commercial cation exchange membrane, NEOSEPTA® CMX (ASTOM Corp., Japan), and anion exchange membrane which was selected based on the characteristic properties.

The electrodialytic experiments were carried out to investigate the influence of pH and electrical potential on the process performance. Synthetic solutions containing glucose (representative of fermentable sugars) and acetic acid (representative of weak acid inhibitors) in 0.25 M K_2SO_4 were used as diluate. As initial concentrate, a solution of 0.05 M K_2SO_4 was circulated during the electrodialytic experiments. The initial volume of the diluate and concentrate was set to 500 mL. Five hundred milliliters of 3% Na_2SO_4 was used as electrode rinse solution.

The ED experiments were performed using a hydrolysate from the pretreatment of waste mushroom medium. The hydrolysate was supplied to the stack as the initial diluate in the study. Distilled water was used as the initial concentrate for the ED experiments. The volume of three solutions (diluate, concentrate, and electrode rinse solution) was set to 300 mL each.

For all the ED experiments, the flow rate of the solution maintained at 1.56 L/min. The electrical power was supplied in the ED experiments with a constant electrical potential. Cleaning procedures were carried out between runs with cleaning solutions, distilled water and then base solution (1.0 wt% NaOH) and distilled water. After cleaning, the electrodialytic performance was investigated using 500 mL of 0.1 M NaCl and 0.05 M NaCl as diluate and concentrate, respectively, to investigate fouling effect on the process performance. Throughout the ED experiments, the pH value of the solutions was measured using a pH meter (Eutech Instruments, USA) and the conductivity of the solutions was measured using a conductivity meter (Eutech Instruments, USA).

2.4. Analysis of sugars and inhibitors

Concentrations of sugars, oxalic acid, and various inhibitors were determined using an HPLC (Waters 2695 system) with an Aminex HPX-87H column (300 × 7.8 mm, Bio-Rad, Hercules, CA) and a refractive index detector (Waters 2414 system). The analysis was performed with 5 mM H_2SO_4 as the mobile phase at 0.3 mL/min for 55 min in the isocratic mode. All of the samples were properly diluted and filtered through a 0.45 μm filter before analysis to remove the particles.

3. Results and discussion

3.1. Characteristic properties of anion exchange membranes

In the present study, the properties of three anion exchange membranes were characterized and the results are shown in Table 1. As shown in the table, water content, exchange capacity, and transport number were measured to be similar among examined anion exchange membranes except electrical resistance. Among characteristic properties, a membrane with a high electrical resistance increases the power consumption [24]. AMX has the lowest electrical resistance among the anion exchange membranes. The stack consisting of a ten cell pair of CMX and AMX was prepared for the ED experiments.

3.2. Influence of the solution pH on the electrodialytic performance

In this study, the electrodialytic experiments were carried out in a system of acetic acid (10 g/L) and glucose (20 g/L) in common electrolyte solution (0.25 M K_2SO_4) to investigate the influence of the potential and pH on the ED performance. Firstly, the influence