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Purification of pentoses from hemicellulosic hydrolysates with sulfuric acid recovery by using electrodialysis

Julien Lemaire *, Claire-Line Blanc, Fanny Duval, Marc-André Théoleyre, Dominique Pareau

LGPM, CentraleSupélec, Université Paris-Saclay, SFR Condorcet FR CNRS 3417, Centre Européen de Biotechnologie et de Bioéconomie (CEBB), Chemin des Sohettes, 51110 Pomacle, France

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ABSTRACT

The valorization of lignocellulosic biomass as a renewable carbon source is growing in chemical industries, particularly in the agro-industrial sector. Many chemicals compounds and bio-based intermediates can be produced but their production needs to be more cost-competitive. The valorization of pentoses in hemicellulosic hydrolysates, obtained by using dilute sulfuric acid, is of growing interest. However, current downstream processes which involve a partial or complete neutralization of the acid are not satisfactory for economic and environmental reasons.

This work presents a method of purification of pentoses with sulfuric acid recovery which reduces water and chemicals consumptions. The results obtained at the laboratory scale with wheat bran hydrolysates are very promising. The process is based on the combination of ultrafiltration, conventional electrodialysis and ion-exchange. A special organic UF membrane (Alpha Laval - UFX10pHt), resistant to acidic conditions, removed totally macromolecules which can damage the electrodialysis unit by precipitation, with good mean permeate flow rate (24 L h^{-1} m^{-2} till VCF = 4.4). Then, conventional electrodialysis was performed to recover most of sulfuric acid (>80%) without losing sugars (<1%) with an acceptable faradic yield (70%). The specific energy consumption of the electrodialysis stack was interesting (0.6 kWh per kg of H_2SO_4 recovered and 4.2 kWh per m^3 of hydrolysate). Finally, the complete demineralization (conductivity <10 μS cm^{-1}) and discoloration (420 nm absorbance <0.01) of the pentoses solution was obtained by ion-exchange with about a 10-fold increase of resins capacity (20 BV) compared to conventional processes with a neutralization step (2 BV).

1. Introduction

Lignocellulosic biomass is an attractive renewable carbon source for agro-industries, such as food or forestry industries. Actually, it generates large amounts of coproducts (wheat straw and bran, sugar beet pulp, wood waste ...) which are often poorly valued [1]. Many chemicals compounds and bio-based intermediates can be produced from these lignocellulosic residues such as sugars, paper pulp, surfactants, polymers or bioethanol. In the frame of sustainable development, the green chemistry and the valorization of these coproducts to produce bio-based molecules is of growing interest [2,3].

Lignocellulosic biomass is mainly composed of cellulose (40–50%$_w$), lignins (10–35%$_w$) and hemicellulose (20–45%$_w$) which is a copolymer of pentoses and hexoses. Generally, the hydrolysis of lignocellulosic biomass is very difficult because of its recalcitrant structure (low porosity, crystallinity, high molecular weights). This treatment aims at extracting cellulose fibers by solubilizing lignins and hemicellulose. Three main processes are used at industrial scale: Kraft process using alkaline solution like caustic soda in paper industry, "Organo-solv" processes using organic solvents such as acetone, ethanol or acetic acid, and hydrolysis with dilute inorganic acids [4,5]. However, others methods using steam, hot water or a combination of enzymes can also be used. After treatment, a complex mixture of pentoses, hexoses, lignins and mineral salts must be separated to value them.

The present article deals with the valorization of pentoses in hydrolysates obtained by using dilute inorganic acids, more particularly sulfuric acid. Indeed, pentoses have found many applications recently (xylitol, bio-based building blocks, surfactants and biopolymers). Currently, the industrial methods begin with a partial or complete neutralization of the inorganic acid in order to precipitate lignins, proteins and eventually metal residues by using caustic soda or lime. Then pentoses are purified by ion-exchange [6–8], adsorption, chromatography or crystallization [9–11]. This

* Corresponding author.
E-mail address: julien.lemaire@centralesupelec.fr (J. Lemaire).

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process is not satisfactory for economic and environmental reasons. Indeed, large amount of base is required, resulting in greatly increased amount of salts, needing more water and chemical reagents to separate them. Moreover it generates large volume of effluent and the acid catalyst cannot be recycled to the hydrolysis step.

For a decade, the use of electrodialysis (ED) has been growing because of its efficiency to separate ions without consuming chemical reagents or water. ED is an electrochemical separation technique which uses an electric potential as driving force to move ions through selective ion-exchange membranes in order to separate them from others molecules present in solution [12,13]. ED has been applied to demineralize aqueous solutions, desalinate seawater and purify wastewater [14–16]. Besides, ED has been widely used in bioprocesses to separate organic acids (lactic, citric, acetic, succinic oxalic) and amino acids [17–20]. Within the framework of pentoses purification in hemicellulosic hydrolysates, ED proved to be an alternative promising demineralization method but partial or complete neutralization was still required [2,21,22] so as to eliminate macromolecules (lignins and proteins) which could precipitate during ED. Indeed, ED membranes are quite expensive and are dramatically damaged by clogging.

The objective of this study was to investigate the feasibility of sulfuric acid recovery from lignocellulosic hydrolysates in the frame of pentoses valorization. The present process combines ultrafiltration (UF), conventional electrodialysis and ion-exchange (IE) and does not need neutralization step, that is a significant advantage in terms of economy and environment. First, the influence of the nature (mineral or organic) and the cut-off of UF membranes on the elimination of macromolecules precipitating during ED, due to a pH increase, were studied. Then the ED performances were investigated for acid recovery and demineralization. Finally, a polishing treatment by IE was performed to get a solution of sugars with very low conductivity (<10 $\mu S\ cm^{-1}$) and totally discolored. This work proposes an eco-efficient process to purify pentoses from hemicellulosic hydrolysates.

2. Materials and methods

2.1. Hemicellulosic hydrolysate

The lignocellulosic hydrolysate was produced from wheat bran milled then mixed with a dilute sulfuric acid solution (≈10 $g\ L^{-1}$). Its main properties are given in Table 1. Before performing ultrafiltration, centrifugation was required to remove suspended matter, whose content is about 1.5 $g\ L^{-1}$.

Table 1
Physico-chemical properties and composition of the lignocellulosic hydrolysate treated.

Dry weight	8.2	$\%_w$
pH	1.1	–
Conductivity	34.5	$mS\ cm^{-1}$
Absorbance at 420 nm	2.2	–
H_2SO_4	8.7	$g\ L^{-1}$
Glucose	12.8	$g\ L^{-1}$
Xylose	21.3	
Arabinose	10.6	
Sodium	1.9	$mEq\ L^{-1}$
Potassium	4.7	
Ammonium	14.8	
Magnesium	2.8	
Calcium	4.6	
Total cations	28.8	
Chlorure	2.0	
Nitrate	0.9	
Phosphate	24.3	
Sulfate	175.2	
Total anions	202.4	

2.2. Ultrafiltration device

Our pilot device can perform cross-flow filtration through different kinds of membrane with various cut-offs for microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) or reverse osmosis (RO). Two ceramic tubular membranes in series (TAMI) and up to 40 organic flat sheet membranes (Alpha-Laval), composed of polysulfone and polypropylene, in a plate-and-frame module can be used (Table 2).

The centrifugal pump could reach 60 bars and the cross-flow rates were generally comprised between 5 and 100 $L\ h^{-1}\ m^{-2}$ with operating conditions recommended by suppliers. The temperature was controlled between 20 and 80 °C by using a heat exchanger combined with a thermostat. The volume of the UF tank containing the retentate was about 8 L.

2.3. Conventional electrodialysis unit

Our conventional ED unit (Eurodia Industrie) is composed of one stack with 10 unit cells, a voltage generator, three tanks (capacity = 2 L) containing the brine, the product and the electrolyte and three pumps ensuring the flow of each solution through the corresponding compartment (Table 3). Conventional ED was used to transfer acids and salts from the product to the brine. The conductivity, pH, acid concentration, sugar concentration and ion concentration of the brine and the product were monitored as well as the current intensity.

This unit was optimized for demineralization by the manufacturer. Operating conditions (flow rates, current, voltage, electrolyte and initial brine composition) were fixed according to manufacturer's recommendations. Conventional ED is generally performed with a constant tension so the limiting current density is not a constant and decreases during demineralization. Tension (12 V) was determined to work always under the limiting current density so as to optimize energy consumption and faradic yield.

2.4. Ion-exchange system

The polishing treatment by ion-exchange (IE) was performed at laboratory scale in two vertical double jacket glass columns operating in series, filled respectively with 350 mL of a strong anionic resin (LEWATIT S7468) in the OH form and a strong cationic resin (LEWATIT S2528) in the H form. Their inner diameter was 25 mm and the bed height 70 cm. A thermostat was used to maintain the water jacket at 40 °C while the product was injected at room temperature at 4 $BV\ h^{-1}$. BV is a common unit used to express volumes or flow rates as a function of the bed volume.

The flow rate was controlled by a peristaltic pump and the mobile phase flew from the top to the bottom of glass columns. An automatic sampling system was used at the output in order

Table 2
Characteristics of UF ceramic membranes and UF organic flat sheet membranes.

	UF ceramic	UF organic
Surface (cm^2)	50	180
Length (cm)	25	–
Diameter (mm)	6	100
pH	0–14	1–13
Pressure (bar)	1–15	1–10
Temperature (°C)	<120	<75
Cut-off (kD)	8 (TAMI)	10 (UFX10pHt)
	15 (TAMI)	20 (GR61PP)
		50 (GR51PP)