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# 1 Purification of pentoses from hemicellulosic hydrolysates with 2 sulfuric acid recovery by using electrodialysis

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## 6 Abstract

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

14 This work presents a method of purification of pentoses with sulfuric acid recovery which  
15 reduces water and chemicals consumptions. The results obtained at the laboratory scale with  
16 wheat bran hydrolysates are very promising. The process is based on the combination of  
17 ultrafiltration, conventional electrodialysis and ion-exchange. A special organic UF  
18 membrane (Alpha Laval - UFX10pHt), resistant to acidic conditions, removed  
19 totally macromolecules which can damage the electrodialysis unit by precipitation, with good  
20 mean permeate flow rate (24 L.h<sup>-1</sup>.m<sup>-2</sup> till VCF = 4.4). Then, conventional electrodialysis was  
21 performed to recover most of sulfuric acid (>80%) without losing sugars (< 1%) with an  
22 acceptable faradic yield (70%). The specific energy consumption of the electrodialysis stack  
23 was interesting (0.6 kWh per kg of H<sub>2</sub>SO<sub>4</sub> recovered and 4.2 kWh per m<sup>3</sup> of hydrolysate).  
24 Finally, the complete demineralization (conductivity < 10 μS.cm<sup>-1</sup>) and discoloration (420 nm

25 absorbance < 0.01) of the pentoses solution was obtained by ion-exchange with about a 10-  
26 fold increase of resins capacity (20 BV) compared to conventional processes with a  
27 neutralization step (2 BV).

28 **Keywords:**electrodialysis;pentoses; purification;acid recycling; green chemistry.

## 29 **Highlights**

- 30 • A purification process of pentoses from hemicellulosic hydrolysates was developed.
- 31 • Ultrafiltration, electrodialysis and ion exchange were combined.
- 32 • Sulfuric acid can be recycled for the hydrolysis step of lignocellulosic biomass.
- 33 • Less water and reagents were required to demineralize the hydrolysate.
- 34 • Process eco-efficient and economical compared to conventional methods.

35

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40

## 41 1. Introduction

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

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

59 The present article deals with the valorization of pentoses in hydrolysates obtained by  
60 using dilute inorganic acids, more particularly sulfuric acid. Indeed, pentoses have found  
61 many applications recently (xylitol, bio-based building blocks, surfactants and biopolymers).  
62 Currently, the industrial methods begin with a partial or complete neutralization of the  
63 inorganic acid in order to precipitate lignins, proteins and eventually metal residues by using  
64 caustic soda or lime. Then pentoses are purified by ion-exchange [6–8], adsorption,  
65 chromatography or crystallization [9–11]. This process is not satisfactory for economic and  
66 environmental reasons. Indeed, large amount of base is required, resulting in greatly  
67 increased amount of salts, needing more water and chemical reagents to separate them.

68 Moreover it generates large volume of effluent and the acid catalyst cannot be recycled to  
69 the hydrolysis step.

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

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

## 92 **2. Materials and methods**

### 93 **2.1. Hemicellulosic hydrolysate**

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

98 **Table 1 – Physico-chemical properties and composition of the lignocellulosic hydrolysate treated**

Dry weight	8.2	%w
pH	1.1	-
Conductivity	34.5	$\text{mS.cm}^{-1}$
Absorbance at 420 nm	2.2	-
$\text{H}_2\text{SO}_4$	8.7	$\text{g.L}^{-1}$
Glucose	12.8	
Xylose	21.3	$\text{g.L}^{-1}$
Arabinose	10.6	
Sodium	1.9	
Potassium	4.7	
Ammonium	14.8	
Magnesium	2.8	
Calcium	4.6	
<b>Total cations</b>	<b>28.8</b>	$\text{mEq.L}^{-1}$
Chlorure	2.0	
Nitrate	0.9	
Phosphate	24.3	
Sulfate	175.2	
<b>Total anions</b>	<b>202.4</b>	

99 **2.2. Ultrafiltration device**

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

105 **Table 2 – Characteristics of UF ceramic membranes and UF organic flat sheet membranes**

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

106 The centrifugal pump could reach 60 bars and the cross-flow rates were generally  
107 comprised between 5 and 100 L.h<sup>-1</sup>.m<sup>-2</sup> with operating conditions recommended by suppliers.  
108 The temperature was controlled between 20 to 80°C by using a heat exchanger combined  
109 with a thermostat. The volume of the UF tank containing the retentate was about 8 L.

### 110 2.3. Conventional electro dialysis unit

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

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

123 **Table 3 – Operating conditions of the conventional electro dialysis unit**

Stack	10 unit cells
-------	---------------

Total active surface	0,2m <sup>2</sup>
Initial brine	5 mS.cm <sup>-1</sup> H <sub>2</sub> SO <sub>4</sub>
Electrolyte	20 mS.cm <sup>-1</sup> NaCl
Voltage	12 V
Product flowrate	180 L.h <sup>-1</sup>
Brine flowrate	180 L.h <sup>-1</sup>
Electrolyte flowrate	200 L.h <sup>-1</sup>
Current density max	45 mA.cm <sup>-2</sup>

#### 124 2.4. Ion-exchange system

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

132 The flow rate was controlled by a peristaltic pump and the mobile phase flew from the top  
133 to the bottom of glass columns. An automatic sampling system was used at the output in  
134 order to monitor pH, conductivity, acid concentration, sugar concentration and ion  
135 concentration of the product.

136 The regeneration procedure for the anionic and cationic resins begins with the elution of 2  
137 BV at 2 BV.h<sup>-1</sup> of respectively 1M NaOH solution and 1M HCl solution in separated columns.  
138 Then, columns are connected and resins are rinsed with reverse osmosis water till the  
139 conductivity of output solution remains constant (close to input conductivity).

#### 140 2.5. Analytical methods

141 Conductivity and pH were measured with a 340i conductimeter/pH-meter from WTW. Dry  
142 matter was estimated by refractometry using a brixmeter (RFM732 Bellingham+Stanley).  
143 Sample color was estimated by measuring absorbance at 420 nm with a spectrophotometer



144 (UV-1800, Shimadzu). H<sub>2</sub>SO<sub>4</sub> concentration was evaluated by titration with 0.1 M NaOH from  
145 the volume required to reach pH 4.0, so as to consider only strong acidity.

146 Sugars were analysed with an HPLC system (Ultimate 3000, Dionex) equipped with a  
147 pump, an auto sampler and a RI-101 refractometer at 35 °C (Shodex). The analytical column  
148 was an Aminex HPX-87H (Biorad) along with a matching guard column (Micro-Guard  
149 cartridge, Biorad). The column temperature was maintained at 45 °C with a column oven  
150 controller. The mobile phase was 2 mM H<sub>2</sub>SO<sub>4</sub> in milli-Q water (Direct 8, Millipore), degassed  
151 by an on-line vacuum degasser. The flowrate was set to 0.5 mL.min<sup>-1</sup> and the injection  
152 volume to 10 µL.

153 Anions and cations were analysed with an HPIC system (ICS-5000<sup>+</sup>, Thermo Scientific  
154 Dionex) equipped with two pumps, an auto sampler, two eluent generators, a column oven  
155 controller set to 35 °C and two suppressors. Detection is performed by conductivity. For  
156 anion analysis, the column was an Ionpack AS11HC 2x250 mm along with a matching guard  
157 column (AG11HC 2x50 mm). The eluent generator produced a 30 mM KOH solution for the  
158 mobile phase. The flowrate was set to 0.3 mL.min<sup>-1</sup>, the suppressor to 23 mA and the  
159 injection volume to 2.5 µL. For cation analysis, the column was an Ionpack CS16 3x250 mm  
160 along with a matching guard column (CG16 3x50 mm). The eluent generator produced a 30  
161 mM methanesulfonic acid solution for the mobile phase. The flowrate was set to 0.36 mL.min<sup>-1</sup>  
162 <sup>1</sup>, the suppressor to 32 mA and the injection volume to 10 µL.

### 163 **3. Results and discussion**

#### 164 **3.1. Removal of macromolecules by ultrafiltration**

165 Macromolecules like lignins or proteins must be removed from the hydrolysate before  
166 performing ED because they will damage the electrodialysis stack by precipitation due to pH  
167 increase during the treatment. UF with ceramic membranes and organic membranes (2 flat  
168 sheets, total surface = 0.036 m<sup>2</sup>) was investigated to remove macromolecules, without pH  
169 adjustment so without reagents consumption in contrast with existing processes.

170 Temperature was set to 40°C and transmembrane pressure to 6 bar. So as to evaluate their  
 171 performance, the amount of precipitates in hydrolysate samples before and after UF was  
 172 measured at different pH, which was adjusted with soda (table 4). Precipitates were filtered  
 173 on 0.22 µm PTFE filter then their dry weight was measured by a moisture analyzer (Sartorius  
 174 MA150).

175 **Table 4 – Amount of precipitates (g<sub>dry</sub>perkg of hydrolysate sample) before and after different UF**  
 176 **treatments as a function of pH**

pH	Before UF	Ceramic 15 kD	Ceramic 8 kD	Organic 10/20/50 kD
1.1	0	0	0	0
2	0.22	0.19	0.19	0
2.5	0.42	0.42	0.38	0
3	0.62	0.60	0.53	0
6	0.80	0.81	0.71	0

177 Only the organic membranes (10 to 50 kD) were efficient to retain totally macromolecules  
 178 which precipitate with increasing pH, although some of them had a higher cut-off than the  
 179 ceramic membranes. These results highlighted the great influence of the membrane nature  
 180 on macromolecules retention. Liu et al. [23] also found that permeate flux and rejection rate  
 181 (for lignin removal) were not only determined by pore size of inorganic membrane, but also  
 182 by membrane charge and hydrophobicity. The influence of membrane nature for the  
 183 treatment of hemicellulosic hydrolysates is not well detailed in literature. Besides, the  
 184 membrane geometry (tubular or flat sheets in a plate-and-frame module) can play also a  
 185 significant role. Indeed, it affects the membrane fouling, concentration polarization or cake  
 186 formation which impact the permeate flux and retention rates.

187 Initial permeate fluxes were respectively equal to 25, 28 and 94 L.h<sup>-1</sup>.m<sup>-2</sup> with 10, 20 and  
 188 50 kD organic membranes. A more detailed experiment was performed with the 10 kD  
 189 organic membrane to evaluate UF performances till a volumetric concentration factor (VCF)  
 190 equal to 4.4 (table 5). Indeed, generally the permeate flux decrease progressively owing to

191 membrane fouling. The dead volume of the UF device was about 1 L, so the feed was initially  
192 slightly diluted with the rinsing water retained inside.

193 **Table 5 – Properties of feed, retentate and permeate at VCF = 4.4 with the 10 kD organic membrane**

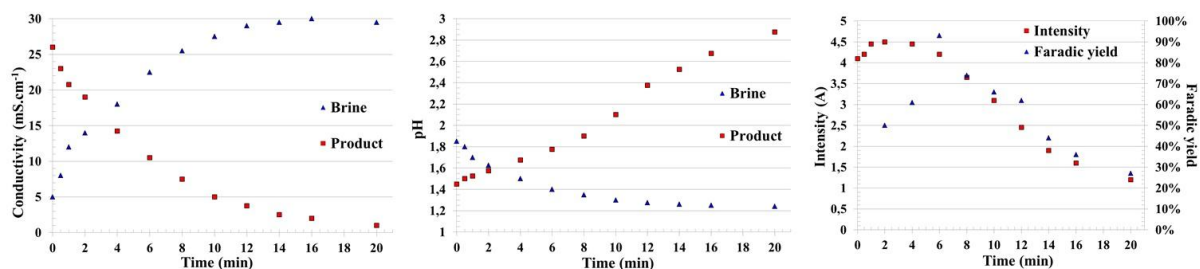
	<b>Feed</b>	<b>Retentate</b>	<b>Permeate</b>
Volume (L)	8.0	1.8	6.2
Dry weight (% <sub>w</sub> )	7.3	11.6	7.0
pH	1.3	1.3	1.3
Conductivity (mS.cm <sup>-1</sup> )	31.5	30.2	34.5
Absorbance at 420 nm	2.1	6.5	0.5

194 Till VCF = 4.4, the mean flow rate of permeate remained quite good (24 L.h<sup>-1</sup>.m<sup>-2</sup>), so the  
195 implementation at industrial scale is conceivable. Besides, the retention of macromolecules  
196 was highlighted by the drop of the absorbance at 420 nm below 0.5. Indeed, some of them  
197 are the main coloring agents.

### 198 3.2. Acid recovery and demineralization by conventional electrodialysis

199 Conventional ED was used to extract most of the sulfuric acid present in the  
200 lignocellulosic hydrolysate which is partially demineralized in the same time. Two hydrolysate  
201 samples, previously ultrafiltered with 10 kD organic membranes, were treated successively  
202 with the same brine. The brine was reused for the second treatment in order to increase its  
203 H<sub>2</sub>SO<sub>4</sub> concentration and made it reusable in hydrolysis step of lignocellulosic biomass.  
204 These experiments aimed at proving the feasibility of acid recovery in the frame of pentoses  
205 purification in lignocellulosic hydrolysates.

206 The 1<sup>st</sup> ED was performed with 2 L of hydrolysate and 2 L of fresh brine. The dead  
207 volume of the ED unit is about 0.5 L. So the feed was again slightly diluted with the rinsing  
208 water retained inside. Figure 1 presents the variation of conductivity, pH, current intensity  
209 and faradic yield over time.



210

211 **Figure 1 – Monitoring of conductivity and pH of brine and product and variation of current intensity and**  
 212 **faradic yield during the 1<sup>st</sup> ED with fresh brine**

213 The product was almost totally demineralized (conductivity < 1 mS.cm<sup>-1</sup>) after 20 min of  
 214 treatment, meanwhile its pH reached 2.9. The faradic yield decreased below 50% after 14  
 215 min and was equal to 62% on average. This low faradic yield was expected because of high  
 216 mobility of H<sup>+</sup> that are difficult to keep in brine compartment. According to table 6, about 90%  
 217 of sulfuric acid was transferred into the brine, meanwhile sugars remained almost completely  
 218 in the product (> 99%). H<sub>2</sub>SO<sub>4</sub> concentration of the brine reached 5.9 g.L<sup>-1</sup>, which was not  
 219 enough to be used for hydrolysis step. This is the reason why this brine was reused for the  
 220 2<sup>nd</sup> ED.

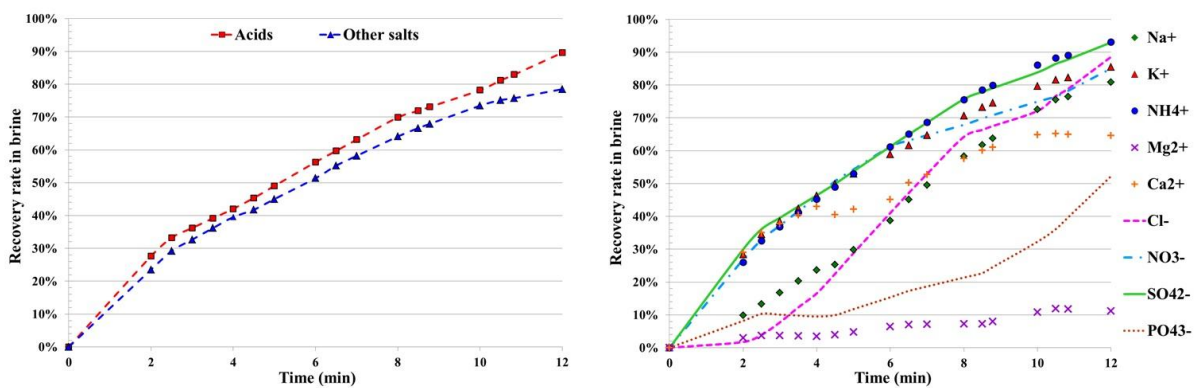
221 **Table 6 – Analysis of brine and product after the 1<sup>st</sup> ED with fresh brine and the 2<sup>nd</sup> ED with brine reuse**

		Volume (L)	pH	Conductivity (mS.cm <sup>-1</sup> )	H <sub>2</sub> SO <sub>4</sub> (g.L <sup>-1</sup> )	Glucose (g.L <sup>-1</sup> )	Xylose (g.L <sup>-1</sup> )	Arabinose (g.L <sup>-1</sup> )
Before ED	Product	-	1.4	27.2	6.0	7.5	15.5	7.3
	Brine	-	1.9	5.1	0.9	0	0	0
1 <sup>st</sup> ED with fresh brine	Product	2	3.1	0.5	0.8	7.5	15.4	7.3
	Brine	2	1.3	27.1	5.9	<0.2	<0.2	<0.2
2 <sup>nd</sup> ED with brine reuse	Product	2.2	2.8	0.9	1.5	7.4	15.4	7.3
	Brine	1.2	1.0	60.0	14.2	<0.2	0.4	<0.2

222 The 2<sup>nd</sup> ED was performed with 2.2 L of hydrolysate and 1.2 L of the brine recovered after  
 223 the 1<sup>st</sup> ED so as to get a H<sub>2</sub>SO<sub>4</sub> concentration up to 15 g.L<sup>-1</sup>. As previously, the product was  
 224 almost totally demineralized after 20 min and the same pH, conductivity and current intensity  
 225 profiles were observed over time. About 80% of sulfuric acid was recovered in the reused

226 brine, meanwhile most of sugars (> 99%) remained in the product (table 6). The H<sub>2</sub>SO<sub>4</sub>  
227 concentration of the brine reached 14.2 g.L<sup>-1</sup> and its pH was equal to 1. So, this time, the  
228 brine could be recycled to the hydrolysis step.

229 A last ED experiment was performed with 2 L of hydrolysate and 2 L of fresh brine in  
230 order to study the transfer rate of acids and different salts during the treatment. Indeed, if  
231 acids are extracted faster than other salts (mainly sodium, potassium, ammonium,  
232 magnesium and calcium salts), ED could be performed advantageously in two steps: a first  
233 one with a reduced operation time to recover most of acids in a first brine, a second one to  
234 extract most of other salts in a second brine. This method could be used to limit the  
235 accumulation of other salts in the brine intended to be recycled for hydrolysis step. Figure 2  
236 presents the recovery rates of acids and other salts in the brine over time. ED was performed  
237 during only 12 min so as to recover most of acids and keep the faradic yield above 50%. In  
238 this case, the faradic yield remained acceptable (70%) and the specific energy consumption  
239 of the electro dialysis stack was quite interesting (0.6 kWh per kg of H<sub>2</sub>SO<sub>4</sub> recovered and 4.2  
240 kWh per m<sup>3</sup> of hydrolysate). The recovery rates of major cations and anions are detailed.



241

242

**Figure 2 – Recovery rate of acids and other salts over time during ED with fresh brine**

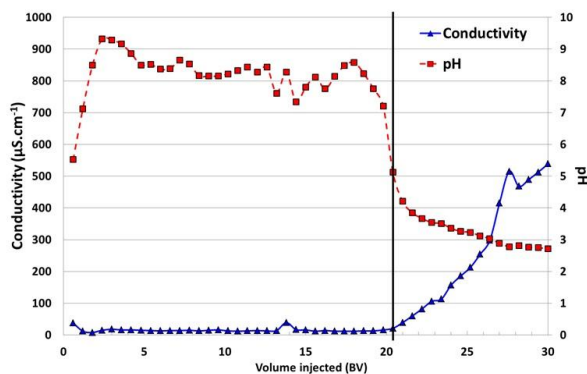
243 We observed that acids are transferred slightly faster than other salts but not enough to  
244 recover most of them without most of other salts. Consequently the implementation of ED in  
245 two steps did not appear advantageous for this kind of hydrolysates, containing mainly  
246 ammonium, potassium and calcium salts (table 1). Indeed, these cations were extracted as

247 fast as acids (mainly sulfuric acid). Nevertheless, it could be advantageous for hydrolysates  
248 containing almost sodium or magnesium salts since these cations were recovered quite  
249 slower than acids (figure 2). The accumulation of ammonium, potassium and calcium salts in  
250 the brine recycled for hydrolysis step has to be watched and might require a periodic purge.  
251 As the concentration of cations is quite low compared to acid, we expect that their  
252 accumulation in brine will be relatively slow. Thus, if a periodic purge is sometimes  
253 necessary, it must be only occasional. Currently, in a pilot scale study, the brine reused for  
254 hydrolysis was as efficient as fresh sulfuric acid to treat wheat bran. Indeed, hydrolysates  
255 produced with reused sulfuric acid had exactly the same content except for salts. The brine  
256 which has to be purged could be considered as a waste or might be valorized if it is relevant  
257 economically. For example, it could be treated by chromatography with ion-exchange resins  
258 to separate acids from salts.

259 Finally an additional polishing treatment by IE was required to remove salts completely  
260 and economically. Indeed, the faradic yield of ED dropped below 30% after 20 min when the  
261 product conductivity was around  $1 \text{ mS}\cdot\text{cm}^{-1}$ .

### 262 3.3. Polishing treatment by ion-exchange

263 The product of ED was treated by IE to remove totally the salts and organic impurities  
264 which could be retained in the polymer matrix of resins. The strong anionic and cationic  
265 resins have respectively a total capacity of 1.0 and  $1.75 \text{ eq}\cdot\text{L}_{\text{bed}}^{-1}$ . Figure 3 presents the  
266 product pH and conductivity as a function of the volume injected. The same treatment was  
267 applied to a sample of hydrolysate neutralized with lime as in conventional processes, in  
268 order to highlight the advantages of the present process.



269

270 **Figure 3 – Monitoring of the product pH and conductivity during demineralization by ion-exchange**

271 20 BV of hydrolysate treated by ED (conductivity = 1.5 mS.cm<sup>-1</sup>, salts ca. 20 meq.L<sup>-1</sup>)  
 272 were completely demineralized (conductivity < 10 µS.cm<sup>-1</sup>) before saturation of one of the  
 273 resins, while only 2 BV of hydrolysate neutralized with lime were treated before saturation.  
 274 Consequently, the present process greatly reduces water and chemical reagents needs,  
 275 particularly in the resin regeneration and rinsing steps. Besides, the product was totally  
 276 discolored (absorbance at 420 nm < 0.01). Finally, the separation of sugars (glucose, xylose  
 277 and arabinose) can be achieved classically by continuous chromatography (SMB, SSMB or  
 278 ISMB methods) or crystallization [9–11].

279 **4. Conclusion**

280 The developed process is a promising pathway to reduce energy, water and chemicals  
 281 consumptions, the cost of pentoses purification and the impacts on environment. Currently,  
 282 the improvement of downstream processing is a key factor to make biorefinery productions  
 283 more cost-competitive. The results at the laboratory scale proved that pentoses can be  
 284 purified eco-efficiently from dilute sulfuric acid hydrolysates of wheat bran, with acid  
 285 recovery.

286 This new process is based on the combination of ultrafiltration, conventional  
 287 electro dialysis and ion-exchange. First, the ultrafiltration step with organic membranes can  
 288 efficiently remove macromolecules which can damage irreversibly the electro dialysis unit by  
 289 precipitation. Then, most of the sulfuric acid can be recovered effectively by conventional

290 electro dialysis. Most of other salts (mainly ammonium, potassium and calcium salts) are co-  
291 extracted and their accumulation in the recycled brine has to be watched and might require  
292 an occasional purge. Nevertheless, the recycling of sulfuric acid keeps very interesting  
293 economically. Finally, the polishing treatment by IE can fully demineralize and discolor the  
294 solution of pentoses whose purification can be achieved classically by continuous  
295 chromatography or crystallization.

296 In comparison with traditional processes that involve hydrolysate neutralization with lime  
297 or caustic soda, the present method gets several economic and environmental advantages:  
298 a) recovery of most of sulfuric acid that can be reused for hydrolysis step, b) saving of lime or  
299 caustic soda that would be required for neutralization, c) consecutive decrease of salts to be  
300 removed, resulting in energy, water and chemicals savings for demineralization, d) reduction  
301 of effluents and other wastes.

302 Further investigations will be done at a larger scale in order to study the process  
303 feasibility and reliability, meanwhile to optimize its performances.

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