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# Purification of pentoses from hemicellulosic hydrolysates without neutralization for sulfuric acid recovery

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## Abstract

The agro-industrial sector generates large amounts of coproducts such as lignocellulosic biomass which could be valorized into many chemicals and bio-based intermediates (sugars, paper pulp, surfactants, polymers or bioethanol). However, in the case of biomass hydrolysis by diluted sulfuric acid, current downstream processes involve a partial or complete neutralization which are not satisfactory for economic and environmental reasons.

This work presents a purification process of pentoses from hemicellulosic hydrolysates without neutralization for sulfuric acid recovery. Compared to conventional processes, less energy, water and chemicals are required. Very promising results were obtained at pilot scale with 100 L of wheat bran hydrolysates. The process is based on the combination of ultrafiltration, conventional electrodialysis and ion-exchange.

Ultrafiltration with a 10 kDa organic membrane totally removed harmful macromolecules which precipitate during electrodialysis operation because of pH rise. Till a volumetric concentration factor 3.6, the average flux kept good for industrial application ( $27 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ ). However suspended materials have to be filtered before ultrafiltration. Besides, a 2.5 diafiltration is required to recover most of sugars (99%).

Then conventional electrodialysis was performed to recover most of sulfuric acid (80%). The average faradic yield was quite good (80%) and the specific energy consumption of the electrodialysis stack was quite interesting (1.1 kWh per kg of  $\text{H}_2\text{SO}_4$  recovered and 8.4

25 kWh per m<sup>3</sup> of hydrolysate). Finally, the complete demineralization (conductivity < 10 μS.cm<sup>-1</sup>) and discoloration (420 nm absorbance < 0.01) of the sugars solution was performed by ion-exchange and an activated carbon polishing treatment. The sugars purity was close to 100% meanwhile the overall sugars recovery rate reach about 90%. Finally we checked that the reused sulfuric acid solution was as efficient as a fresh one in a second hydrolysis operation of wheat bran. Recovery rates could be increased by a scale-up operation or a continuous mode of the process.

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

### 33 **Highlights**

- 34 • Purification of pentoses from hemicellulosic hydrolysates without neutralization.
- 35 • Recycling of sulfuric acid for hydrolysis of lignocellulosic biomass.
- 36 • Decrease of water and chemicals required for hydrolysate demineralization.
- 37 • Combination of ultrafiltration, electrodialysis and ion-exchange.

38

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43

## 44 1. Introduction

45 Chemical industry has shown a rapid growth in the 20th century thanks to petroleum as  
46 carbon source. Oil has indeed become the base for almost every product made by industrial  
47 chemistry. However this field is now facing a new challenge because of global warming  
48 mostly due to the accumulation of carbon dioxide (greenhouse gas) into the atmosphere.  
49 Moreover oil is a fossil carbon resource whose world stocks are inevitably sinking while its  
50 price is strongly fluctuating. This is the reason why green chemistry is growing in many fields  
51 due to its advantages: carbon economy, more efficient syntheses, but also new renewable  
52 carbon sources.

53 Lignocellulosic biomass is considered as a very promising source of renewable carbon. A  
54 significant part is used by agro-industries, such as food- or forestry industries, generating  
55 large amounts of coproducts (wheat straw and bran, sugar beet pulp, wood waste ...), which  
56 are often poorly valorized [1]. Many chemical compounds and bio-based intermediates  
57 (sugars, paper pulp, surfactants, polymers or bioethanol) can however be produced from  
58 these lignocellulosic residues [2,3]. This valorization of every part of crop is the goal of the  
59 biorefinery concept.

60 Among those residues, bran is the major by-product of wheat milling [4]. Bran is produced  
61 in very large quantities but is mainly used as livestock feed. Wheat bran is mainly composed  
62 of hemicellulose (20-40%w), starch (10-20%w), protein (15-22%w), cellulose (9-15%w) and  
63 lignin (4-10%w) [5-7]. Arabinoxylans constitute the major part of wheat bran hemicellulose;  
64 therefore wheat bran is an attractive source of pentoses which have found growing  
65 applications, such as xylitol, surfactants and biopolymers productions [8].

66 Hydrolysis is necessary to extract monosaccharides from cellulose and hemicellulose.  
67 This chemical pretreatment is generally difficult and requires drastic conditions, such highly  
68 alkaline or acidic media or use of organic solvents, like ethanol [9]. A complex mixture of  
69 hexoses, pentoses, lignins and ashes is produced, needing further downstream separations.

70 This work studies the purification of pentoses obtained by hydrolysis of wheat bran  
71 with diluted sulfuric acid as a catalyst [9,10]. The classical separation methods involve ion-  
72 exchange [11–13], chromatography, adsorption or crystallization [14–16], but need a partial  
73 or complete pre-neutralization of the inorganic acid. Those processes are not sustainable as  
74 they consume a lot of chemicals and energy. Most notably large amounts of base are  
75 necessary to neutralize the acid catalyst, which is then lost for further hydrolysis. Besides,  
76 neutralization increases dramatically the amount of mineral salts which have to be removed  
77 in a further step.

78 Electrodialysis (ED) was studied here as an alternative to neutralization, allowing direct  
79 acid recovery and reducing chemicals consumption. This process is a separation technique  
80 using an electrical potential as driving force to move ions through selective exchange  
81 membranes to separate them from uncharged species [17]. It is widely used for whey  
82 demineralization, in order to produce an ingredient for infant formula [18]. ED is also  
83 implemented in bioprocesses for organic acids purification, for example lactic acid [19–  
84 22]. The major drawback of this technique is membrane clogging, leading to significant  
85 decreases in production. Indeed, during sulfuric acid extraction, pH rises and organic matters  
86 soluble at low pH (lignin, proteins...) precipitate [23]. This phenomenon strongly reduces both  
87 process efficiency and membrane durability. Macromolecules must then be removed before  
88 ED and membrane separation seems appropriate for this purpose [24,25].

89 A previous lab-scale study revealed the feasibility of sulfuric acid recovery from wheat  
90 bran hydrolysate using ultrafiltration followed by electrodialysis [26]. Operating conditions of  
91 both steps were optimized as well as the choice of ultrafiltration membranes. The retention of  
92 harmful macromolecules was effective only with organic membranes (10 to 50 kD), even with  
93 higher cut-off than ceramic membranes. Indeed, permeate flux and rejection rate are not only  
94 determined by pore size, but also by membrane nature, charge and hydrophobicity [27].

95 The present work aims at investigating the process feasibility at a larger scale. Indeed, it is  
96 necessary to estimate more accurately performances (recovery rates and productivities) that

97 could be obtained at the industrial scale. Moreover, the goal was to check the reliability and  
98 robustness of membranes for both processes. Furthermore, it was necessary to produce a  
99 significant amount of brine ( $15 \text{ g.L}^{-1} \text{ H}_2\text{SO}_4$ ) to carry on a new hydrolysis of wheat bran in  
100 order to verify the feasibility of acid recycling by our industrial partner.

101

## 102 2. Materials and methods

### 103 2.1. Wheat bran hydrolysate

104 The hydrolysate, which composition is given in table 1, was produced by an industrial  
105 partner by mixing destarched wheat bran with a sulfuric acid solution around  $12 \text{ g.L}^{-1}$ . The  
106 mixture has been heated at  $130 \text{ }^\circ\text{C}$  for 1 hour and roughly filtered after cooling. It was then  
107 splitted into three 23 L tanks. The hydrolysate contained suspended matter, which settled  
108 resulting in a roughly clear supernatant and a muddy tank bottom. When the withdrawn  
109 supernatant was not enough clear, a centrifugation was performed before further treatments  
110 to remove remaining suspended matter at  $4000 \text{ g}$ ,  $4 \text{ }^\circ\text{C}$  for 15 min.

111

**Table 1 -Composition of the wheat bran hydrolysate**

Total dry weight	%w	8.0
Solubles dry weight	%w	6.9
Dry suspended matter	$\text{g.kg}^{-1}$	11
pH	-	1.4
Conductivity	$\text{mS.cm}^{-1}$	34.0
420 nm absorbance	-	1.79
Glucose		11.4
Xylose	$\text{g.L}^{-1}$	25.5
Arabinose		14.6
Furfural		0.8
$\text{H}^+$ (total acidity)	$\text{mmol.L}^{-1}$	240
Na		6
$\text{NH}_4$	$\text{mg.L}^{-1}$	369
K		240
Total cations	$\text{meq.L}^{-1}$	27
$\text{SO}_4$	$\text{mg.L}^{-1}$	10375

	Cl	59
	PO <sub>4</sub>	913
Total anions		meq.L <sup>-1</sup> 256

## 112 2.2. Ultrafiltration

113 The filtration module was an Alfa Laval Test Unit M20, a crossflow membrane filtration unit  
114 equipped with a heat exchanger for temperature control, a recirculation pump and a 8 L  
115 stainless steel tank. A 2.5" spiral organic membrane UFX10 pHt was furnished by Alfa Laval  
116 for ultrafiltration at a molecular weight cut-off of 10 kDa. This membrane was chosen owing  
117 to its retention performances and its specific resistance to very acid conditions (till pH 1). The  
118 total membrane area was 0.6 m<sup>2</sup>. The dead volume in the system was estimated to 2 L.

119 Before filtration, the water flux was measured at 40 °C with a transmembrane pressure of  
120 5 bar, giving 340 L.h<sup>-1</sup>.m<sup>-2</sup>. This was the reference to evaluate membrane state after *in*  
121 *situ* cleaning with an alkaline solution (Ultrasil 110, Ecolab). The permeate and retentate have  
122 been recirculated to the feed tank for 1 h (time necessary to heat the feed) before  
123 withdrawing permeate and concentrating retentate. A volume higher than the tank volume  
124 was filtered in one run, so the run was conducted in fed-batch mode (1 L permeate out, 1 L  
125 feed in) at 40 °C and a transmembrane pressure of 5 bar. Temperature, tank pH and  
126 conductivity and permeate flowrate were monitored.

## 127 2.3. Electrodialysis

128 The conventional electrodialysis plant was supplied by Eurodia. It was composed of three  
129 2 L tanks containing the electrolyte, the product (ultrafiltered hydrolysate) and the brine  
130 (diluted sulfuric acid solution), three pumps for the circulation of each solution and a voltage  
131 generator. A conventional 10 unit cells stack, with an alternation of anion and cation  
132 exchange membranes was used. The unit cell area was 0.02 m<sup>2</sup>. It was operated at a  
133 constant voltage of 14 V and a free intensity, without temperature regulation. Pumps ensured

134 a 180 L.h<sup>-1</sup> flowrate in the brine and feed compartments and a 200 L.h<sup>-1</sup> flowrate in the  
135 electrolyte compartment (supplier recommended values).

136 The electrolyte was a 20 mS.cm<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> solution (11 g.L<sup>-1</sup>). The initial brine was a 5  
137 mS.cm<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution (0.7 g.L<sup>-1</sup>). The operation was run in batch mode until the  
138 conductivity drop rate was lower than 0.25 mS.cm<sup>-1</sup>.min<sup>-1</sup>. Temperature, pH and conductivity  
139 were monitored.

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

146 During this operation, sulfuric acid was transferred from the feed to the brine through the  
147 electric field. Two successive batch operations were performed; acid enriched brine of the  
148 first batch was reused in the second batch in order to reach the acid concentration required to  
149 recycle it for wheat bran hydrolysis (10-15 g.L<sup>-1</sup>).

#### 150 2.4. Polishing

151 The final product polishing was performed at lab-scale by ion-exchange and activated  
152 carbon because both techniques are commonly used and well understood at industrial  
153 scale. The goal was to check its final quality and to know in which extent the present process  
154 increased the capacity of ion-exchange resins compared to conventional method  
155 (neutralization with lime).

156 Firstly, the product (after ED) was further demineralized by ion-exchange to obtain a  
157 conductivity lower than 10 μS.cm<sup>-1</sup>. Two vertical glass columns operating in series were filled  
158 respectively with 100 mL of a strong cationic resin (Lanxess S2528 H<sup>+</sup> form) and 100 mL of a  
159 weak anionic resin (Lanxess S4368 OH<sup>-</sup> form). The product was injected by a peristaltic pump

160 at room temperature at 4.0 BV.h<sup>-1</sup> (400 mL.h<sup>-1</sup>) until the breakthrough point of salts was  
161 reached. Its brix, pH, 420 nm absorbance and conductivity were monitored at the output.

162 Finally the demineralized product was concentrated at 40 °C under vacuum with a rotating  
163 evaporator (Büchi), then percolated through 50 mL activated carbon (Chemviron Carbon) by  
164 a peristaltic pump at 1.5 BV.h<sup>-1</sup> (75 mL.h<sup>-1</sup>) at room temperature. Before use, carbon was  
165 dropped into boiling water and let for a night within the cooling water.

## 166 2.5. Analytic methods

167 Conductivity and pH were measured with a 340i conductimeter/pH-meter from WTW. Dry  
168 matter was estimated with a brixmeter (RFM732 Bellingham+Stanley). Sample color was  
169 evaluated by measuring absorbance at 420 nm with a spectrophotometer (UV-1800,  
170 Shimadzu). Total sample acidity was quantified by titration with 0.1 M NaOH solution.

171 Sugars and furfural were analysed with a HPLC system (Ultimate 3000, Dionex) equipped  
172 a RI-101 refractometer (Shodex). The analytical column was an Aminex HPX-87H (Biorad)  
173 and its temperature was maintained at 45 °C. The mobile phase was 2 mmol.L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>  
174 degassed by an on-line vacuum degasser. The flow rate was set to 0.5 mL.min<sup>-1</sup> and the  
175 injection volume to 10 µL.

176 Anions and cations were analysed with an HPIC system (ICS-5000<sup>+</sup>, Thermo Scientific  
177 Dionex) equipped with two eluent generators, a column oven controller set to 35 °C and two  
178 suppressors (table 2). Detection is performed by conductivity.

179 **Table 2 - Conditions of ionic chromatography**

	Column	Guard column	Eluent	Suppressor	Injection volume
Anion analysis	Ionpack AS11HC 2x250 mm (Dionex)	AG11HC 2x50 mm, Dionex	30 mM potassium hydroxide 0.3 mL.min <sup>-1</sup>	23 mA	2.5 µL

Cation analysis	Ionpack CS16 3x250 mm (Dionex)	CG16 3x50 mm, Dionex	30 mM methanesulfonic acid 0.36 mL.min <sup>-1</sup>	32 mA	10 µL
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180

### 181 3. Results and discussion

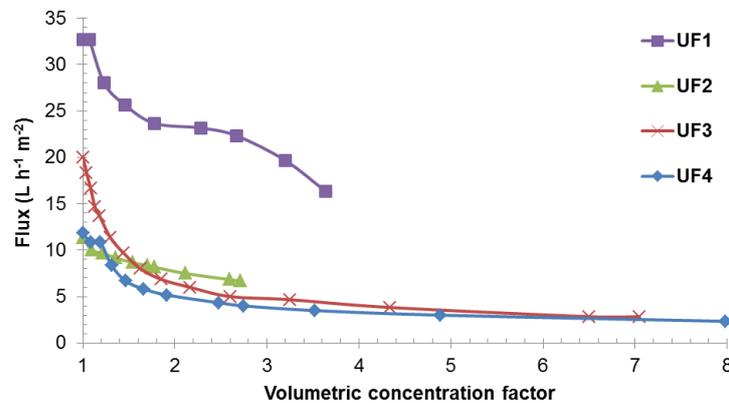
#### 182 3.1. Ultrafiltration

183 Ultrafiltration was carried out to remove the macromolecules present in the hydrolysate,  
 184 which could precipitate during electrodialysis, due to rising pH. Four batch operations were  
 185 performed with the same membrane, which was cleaned *in situ* between tests. This operation  
 186 was very efficient since no precipitate was detected in permeate samples after rising their pH  
 187 to ca. 7 with a 0.1 M NaOH solution.

188 For the first trial (UF1) 14 L of the first tank supernatant were introduced in the system  
 189 resulting in 16 L of initial retentate because of the 2 L dead volume (centrifugation not  
 190 required). It was concentrated till a volumetric concentration factor (VCF) 3.6. The initial flux  
 191 was about 33 L.h<sup>-1</sup>.m<sup>-2</sup> and decreased to 16 L.h<sup>-1</sup>.m<sup>-2</sup> during the operation, as seen on figure  
 192 1, resulting in an average flux of 27 L.h<sup>-1</sup>.m<sup>-2</sup>.

193 Then the 9 L remaining of the first tank supernatant had to be centrifuged because of the  
 194 suspended matter amount. The pellet contained the major part of the suspended matter as a  
 195 slurry. However, centrifugation splitted in two the liquid phase. The lighter phase also  
 196 contained suspended matter in the form of light flocs. Nevertheless, both phases were  
 197 filtered together and concentrated at VCF 2.7 during the second trial (UF2). A dramatic flux  
 198 reduction was observed during this operation. The initial flux was only 11 L.h<sup>-1</sup>.m<sup>-2</sup> and  
 199 dropped to 7 L.h<sup>-1</sup>.m<sup>-2</sup> (figure 1), resulting in an average flux of 8 L.h<sup>-1</sup>.m<sup>-2</sup>. It must be  
 200 explained by the increase of membrane fouling with suspended matters and the observed  
 201 flocs. Moreover, the liquid demixing could decrease the transfer velocity at the membrane  
 202 surface and consequently increase the concentration polarization. Indeed, in a recent work,  
 203 the improvement of suspended matter removal without using centrifugation lead to better and

204 sustainable permeate flux ( $> 20 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ ). *In situ* cleaning was performed until recovering a  
205 satisfactory water flux (ca.  $300 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ ). The slight decrease of water flux showed that the  
206 fouling was quite reversible, so suspended matters had to remain mainly at the membrane  
207 surface.



208

209 **Figure 1 - Evolution of permeate flux as a function of volumetric concentration factor (VCF) for each**  
210 **ultrafiltration trial**

211 The last two tests (3 and 4) were performed to concentrate a complete tank volume (ca.  
212 24 L) in one batch, achieving a higher VCF than the previous trials. The product was  
213 settled. The clear supernatant of each tank was recovered and the rest of the volume was  
214 centrifuged. Both liquid phases obtained after centrifugation were mixed to the clear  
215 supernatant to get a representative sample of a two phases industrial centrifugation. As seen  
216 on figure 1, the trends for both trials were rather similar, except for the initial flux values, and  
217 close to the UF2 curve. Indeed after UF3 and alkaline cleaning, it was not possible to reach  
218 the initial water flux of  $300 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ , but only  $200 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ . This highlights that membrane  
219 fouling was not totally reversible and some suspended matters was not removed by alkaline  
220 cleaning and progressively blocked membrane pores. However, the fouling by soluble  
221 macromolecules seems to be more reversible because the removal of suspended matter  
222 before ultrafiltration resulted in better and sustainable permeate flux.

223 The measured average fluxes were respectively of  $6.4 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$  and  $5.2 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$  for UF3  
224 and UF4. Those values are probably too low for an industrial application, whereas

225 fluxes obtained during UF1 are very interesting. So it is important to find a way to reach a  
 226 feed quality equivalent to the UF1 supernatant. Centrifugation does not seem to be the right  
 227 way as it segregates the liquid phase and produces light flocs. Consequently, before  
 228 ultrafiltration, the hydrolysate has to be better filtered with membranes which largely reduce,  
 229 even totally remove, suspended matters.

230 For the fourth ultrafiltration trial, analyses of the feed, the final retentate and the mean  
 231 permeate are given in table 3. Due to the system dead volume, the initial retentate was  
 232 slightly more diluted than the feed and its real volume was estimated to 25.2 L. So the final  
 233 volumetric concentration factor was around 9.5. Only 88% of sugars (glucose, xylose and  
 234 arabinose) were recovered in the permeate; such a sugars loss is not an option for the  
 235 process viability. So a continuous diafiltration has to be performed after ultrafiltration to  
 236 increase sugars recovery up to 99%. A 2.5 diafiltration volume should be enough to reach  
 237 this aim, namely a water volume which corresponds to 2.5 fold the final retentate volume.

238 **Table 3 -Experimental results of UF4 trial and recovery rates estimation after 2.5 diafiltration**

		Feed	UF4 Mean permeate	UF4 Final retentate	Recovery rate in UF4 permeate (%)	Total recovery rate after UF4+ 2.5 diafiltration (%)
Volume	L	23.2	22.5	2.7	90	-
Dry weight	%w	6.9	5.4	11.7	80	97
pH	-	1.4	1.4	1.3	-	-
Conductivity	mS.cm <sup>-1</sup>	34.0	32.7	29.1	-	-
Sugars		51.6	42.8	49.9	88	99
Furfural	g.L <sup>-1</sup>	0.8	0.8	1.0	87	99
Salts		12.0	9.6	23.7	78	98
Total anions		247	198	501	77	96
Total cations	meq.L <sup>-1</sup>	27	24	23	90	99
Acidity (A <sup>-</sup> -C <sup>+</sup> )		220	174	478	76	95

239

240 As a conclusion it is possible to remove efficiently precipitating macromolecules from  
 241 wheat bran hydrolysate by ultrafiltration with a 10 kDa organic membrane, without losing  
 242 sugars. Hydrolysate treatment prior to ultrafiltration, for removal of suspended matter, has to

243 be designed carefully as membrane clogging determines the permeate fluxes of  
244 ultrafiltration. The resulting permeate was afterwards demineralized by electro dialysis.

### 245 3.2. Electrodialysis

246 Electrodialysis was implemented to extract sulfuric acid from hydrolysate in order to  
247 recycle it to the hydrolysis step, provided the solution was concentrated enough in sulfuric  
248 acid (10-15 g/L). According to preliminary tests, when the acid enriched brine of the first  
249 batch was reused for a second batch, the second brine was suitable in terms of acid  
250 concentration.

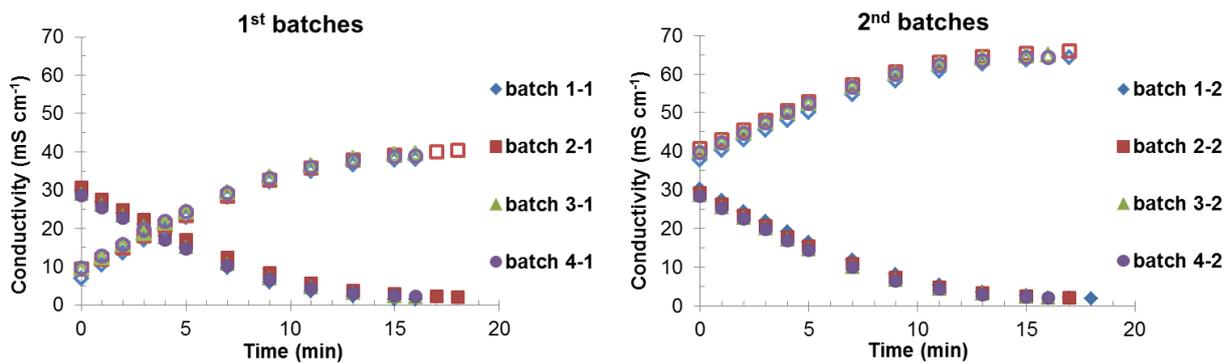
251 So 4 L of ultrafiltered permeate (feed) were demineralized by conventional ED using an  
252 initial 2 L brine of 5 mS.cm<sup>-1</sup> sulfuric acid. Around 22 L of permeate were treated in this way,  
253 producing 11 L of sulfuric acid solution. Results of four trial pairs are presented on figures 2  
254 and 3. The first batches correspond to trials made with fresh feeds and fresh brines. In the  
255 second batches fresh feeds and brines obtained after the first batches were used. The very  
256 good reproducibility proved that ion-exchange membrane performances remained quite  
257 constant. Consequently, biofouling is expected low and quite reversible. The ultrafiltration  
258 step must have removed the most part of macromolecules which can be responsible for  
259 biofouling, as well as macromolecules which can precipitate because of pH rise.

260 So as to keep productivity high enough, the product was always demineralized until only 2  
261 mS.cm<sup>-1</sup> (figure 2); its final pH was 2.7. From this moment, the conductivity drop velocity  
262 became lower than 0.25 mS.cm<sup>-1</sup>.min<sup>-1</sup>. No precipitation was observed. The brine was  
263 enriched in acid from 5 to 40 mS.cm<sup>-1</sup> (0.7 to 8.6 g.L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>) during the first batches and up  
264 to 65 mS.cm<sup>-1</sup> (14.7 g.L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>) during the second batches.

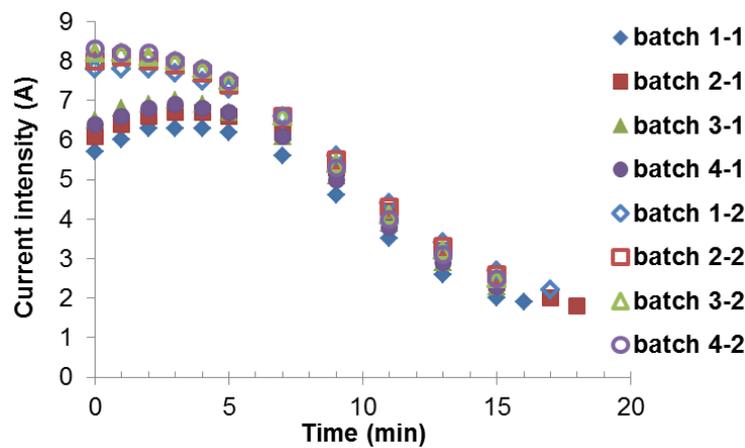
265 Moreover, ED was performed until the product conductivity reached only 2 mS.cm<sup>-1</sup> so as  
266 to recover most of acids and keep the faradic yield above 50%. In this case, the average  
267 faradic yield remained good (80%) and the specific energy consumption of the electro dialysis  
268 stack was quite interesting (ca. 1.1 kWh per kg of H<sub>2</sub>SO<sub>4</sub> recovered and ca. 8.4 kWh per m<sup>3</sup> of

269 hydrolysate). Better faradic yield was not expected because of high mobility of  $H^+$  that are  
 270 more difficult to keep in brine compartment than other cations.

271 It can be seen on figure 3 that the current intensity was also greatly reproducible. The  
 272 initial intensity of the second batches was higher than that of the first batches due to a  
 273 higher initial brine conductivity. After 7 min, both intensities were equivalent due to similar  
 274 product conductivities.



275 **Figure 2 - Evolution of brine (empty symbols) and product (full symbols) conductivities during the first**  
 276 **(fresh brine) and second (reused brine) batches**



277  
 278 **Figure 3 - Evolution of current during the first (full symbols) and second (empty symbols) batches**

279 Demineralized products of all the batches were gathered, as well as the final brines of the  
 280 second batches. The sugars recovery rate in the products was very good (99%) (table 4); no  
 281 sugar went through the ion exchange membranes into the brine. On the contrary 87% of the  
 282 acid was recovered into the brine, reaching about  $15 \text{ g.L}^{-1} \text{ H}_2\text{SO}_4$ . The resulting brine pH and  
 283 concentration were appropriate to perform a new hydrolysis.

**Table 4 -Electrodialysisresults of UF4 permeate**

		Feed	Fresh brine	Mean product	Mean brine	Recovery rate in product (%)
Volume	L	21.6	10.6	21.4	11.2	66
Dry weight	%w	5.4	0.1	5.0	2.4	80
pH	-	1.4	2.1	2.4	1.3	-
Conductivity	mS.cm <sup>-1</sup>	32.7	5.0	2.2	70.8	-
420 nm absorbance	-	1.79		1.07		-
Sugars		42.8	0.0	43.1	0.7	99
Furfural	g.L <sup>-1</sup>	0.8	0.0	0.7	0.0	97
Salts		9.6	0.7	1.1	18.0	11
Total anions		198	14	27	363	12
Total cations	meq.L <sup>-1</sup>	24	0	1	46	6
Acidity (A <sup>-</sup> -C <sup>+</sup> )		174	14	25	318	13

285

286 The produced brine was then used to carry on a new hydrolysis by our industrial partner.  
 287 It was mixed with the required destarched wheat bran quantity and heated at 130 °C during 1  
 288 hour. No sulfuric acid was added. In order to avoid the centrifugation step, which had a  
 289 dramatic impact on UF fluxes, the filtration method of suspended matter was improved. Its  
 290 concentration was clearly reduced (table 5). Similar results must be got with an industrial  
 291 operating press filter.

292 The composition of the hydrolysate obtained with this recycled brine was very close to the  
 293 reference (table 5). Only salts concentrations were significantly higher in the case of the  
 294 recycled brine. Indeed the salts were extracted by ED as well as H<sub>2</sub>SO<sub>4</sub>; but as they are in  
 295 minor concentrations, it must not be an inconvenient. However this accumulation has to be  
 296 watched and might require an occasional purge.

**Table 5 - Composition of both reference hydrolysate and hydrolysate obtained with recycled brine**

		Reference hydrolysate	Hydrolysate with recycled brine
Dry weight	%w	6.9	7.3
pH	-	1.4	1.4
Conductivity	mS.cm <sup>-1</sup>	34.0	38.2

Dry suspended matter	g.kg <sup>-1</sup>	11.0	0.2
Glucose		11.4	11.3
Xylose		25.5	26.8
Arabinose	g.L <sup>-1</sup>	14.6	15.4
Furfural		0.8	1.1
SO <sub>4</sub>		10375	12514
Cl	mg.L <sup>-1</sup>	59	196
PO <sub>4</sub>		913	1610
Total anions	meq.L <sup>-1</sup>	256	334
Na		6	358
NH <sub>4</sub>	mg.L <sup>-1</sup>	369	632
K		240	513
Total cations	meq.L <sup>-1</sup>	27	64

298

299 The feasibility of recycling sulfuric acid was then demonstrated. The whole process  
300 including suspended matter filtration, 10 kDa ultrafiltration with organic membrane, 2.5  
301 diafiltration and conventional electrodialysis, seems to be reliable with a very good  
302 reproducibility. The recycled brine was successfully used for hydrolysis of destarched wheat  
303 bran.

304 Overall recovery rates in the brine (sulfuric acid) and the product (sugars, furfural) were  
305 calculated and summed up in table 6. The sugars recovery rate was limited by the dead  
306 volume of the UF pilot device; a continuous operation and the scale-up could easily improve  
307 the recovery rates, by limiting losses due to the system dead volume. Sugars purity was of  
308 84%; further purification steps would be necessary to reach higher purities.

309

**Table 6 - Performance of the global process before polishing treatment**

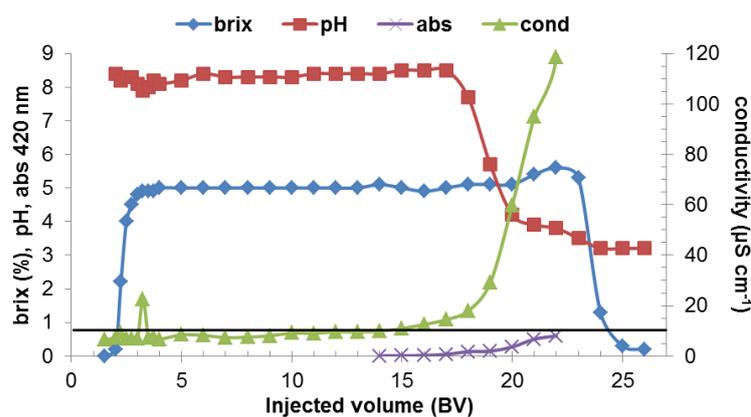
Sugars recovery in product	94%
Furfural recovery in product	92%
Acid recovery in brine	79%
Sugars purity	84%

310

### 3.3. Polishing

311 After electro dialysis, the major impurities in the sugar solution were salts, furfural and  
312 organic elements (color); the remaining acid concentration was about 0.3 g/L. A polishing by  
313 ion-exchange and adsorption is necessary to remove salts and organic molecules. Previous  
314 electro dialysis step allowed to divide conductivity by fifteen and salts concentration by nine.  
315 Thus ion-exchange capacity (expressed as treated volume per ion-exchange resin amount)  
316 was expected to be much higher than observed capacity with conventional purification  
317 methods including a first step of acid neutralization with soda or lime.

318 Figure 4 presents the evolution of the composition of demineralized fractions, at the output  
319 of the ion-exchange system, as a function of injected volume of electro dialyzed product (one  
320 bed volume (BV) corresponded to 100 mL). Up to 15 BV of electro dialyzed hydrolysate were  
321 demineralized with a resulting conductivity lower than  $10 \mu\text{S}\cdot\text{cm}^{-1}$  during one batch. The  
322 product was also completely decolorized (420 nm absorbance = 0.00). Moreover the furfural  
323 concentration was reduced by 58%. As a comparison the same treatment was realized on a  
324 hydrolysate only neutralized with lime, as it is done in the conventional process. Only 2 BV  
325 were demineralized before resin saturation. This clearly highlights the advantages of the  
326 present process, which greatly reduces chemicals and water consumption, in particular for  
327 resin regeneration.



328  
329 **Figure 4 - Evolution of brix, pH, 420 nm absorbance and conductivity during ion-exchange treatment**

330 In order to eliminate remaining furfural, the product was treated after concentration by  
331 activated carbon. The initial product dry weight (4.9%w) was increased by concentration up to

332 52.2%w, without losing sugars. A minor increase in coloration was also observed with 420  
 333 nm absorbance rising from 0.00 to 0.07. The product composition after concentration and  
 334 activated carbon treatment was summed up in table 7. Furfural and color were totally  
 335 removed. The sugars recovery rate for the global process, including rough filtration,  
 336 ultrafiltration, 2.5 diafiltration, conventional electrodialysis and polishing, reached 90% with  
 337 a purity close to 100%. Sugars can afterwards be separated classically by continuous  
 338 chromatography or crystallization [14-16].

339 **Table 7 - Composition of wheat bran hydrolysate after activated carbon treatment**

	Dry weight %w	pH -	Sugars g/L	Conductivity $\mu\text{S}\cdot\text{cm}^{-1}$	Abs 420 nm -	Furfural g/L
Purified product	33.7	4.9	385.0	38.5	0.00	0.0
Recovery rate	>99%	-	>99%	-	-	0%

340

#### 341 4. Conclusion

342 This work is a significant contribution for the valorization of agricultural by-products as  
 343 wheat bran. It presents a reliable process for the purification of hemicellulosic sugars,  
 344 reducing chemicals and water consumption. Ultrafiltration is carried out with an organic  
 345 membrane in a first time to remove precipitating macromolecules. Afterwards conventional  
 346 electrodialysis allows the sulfuric acid recovery from hydrolysate in order to recycle it for the  
 347 hydrolysis step. ED is a key step as it allows a double chemical saving: less fresh sulfuric acid  
 348 is needed for hydrolysis and no alkaline chemicals are consumed to neutralize acid and  
 349 precipitate macromolecules. Thus the salts content is considerably decreased, facilitating the  
 350 further demineralization by ion-exchange and also resulting in the reduction of chemicals  
 351 consumption. After activated carbon treatment, the product contains only sugars (glucose,  
 352 xylose and arabinose). They can be separated from each other by continuous  
 353 chromatography or crystallization.

354 The acid recovery rate in brine after electrodialysis is around 80%, whereas the overall  
 355 sugars recovery rate after polishing is close to 90%. Both recovery rates could be increased

356 by a scale-up operation or a continuous mode of the process, limiting losses due to the  
357 system dead volumes.

358 Attention has to be paid to the initial hydrolysate quality, as it influences greatly  
359 ultrafiltration fluxes; the improvement of suspended matter filtration method gave better and  
360 sustainable permeate flux ( $> 20 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ ) with the hydrolysate obtained with the reused brine.  
361 Moreover during electrodialysis, not only sulfuric acid but also mineral salts are extracted into  
362 the brine; their initial concentrations are very low but their accumulation during recycling  
363 cycles may require an occasional purge.

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#### 368 **References**

- 369 [1] T. Hasunuma, F. Okazaki, N. Okai, K.Y. Hara, J. Ishii, A. Kondo, A review of enzymes and  
370 microbes for lignocellulosic biorefinery and the possibility of their application to consolidated  
371 bioprocessing technology, *Bioresour. Technol.* 135 (2013) 513–522.  
372 doi:10.1016/j.biortech.2012.10.047.
- 373 [2] K.K. Cheng, B.Y. Cai, J.A. Zhang, H.Z. Ling, Y.J. Zhou, J.P. Ge, et al., Sugarcane bagasse  
374 hemicellulose hydrolysate for ethanol production by acid recovery process, *Biochem. Eng. J.* 38  
375 (2008) 105–109. doi:10.1016/j.bej.2007.07.012.
- 376 [3] H.J. Huang, S. Ramaswamy, U.W. Tschirner, B.V. Ramarao, A review of separation  
377 technologies in current and future biorefineries, *Sep. Purif. Technol.* 62 (2008) 1–21.  
378 doi:10.1016/j.seppur.2007.12.011.
- 379 [4] M. Prückler, S. Siebenhandl-Ehn, S. Apprich, S. Höltinger, C. Haas, E. Schmid, et al., Wheat  
380 bran-based biorefinery 1: Composition of wheat bran and strategies of functionalization, *LWT -*  
381 *Food Sci. Technol.* 56 (2014) 211–221. doi:10.1016/j.lwt.2013.12.004.
- 382 [5] C. Maes, J.A. Delcour, Alkaline Hydrogen Peroxide Extraction of Wheat Bran Non-starch  
383 Polysaccharides, *J. Cereal Sci.* 34 (2001) 29–35. doi:10.1006/jcres.2001.0377.

- 384 [6] R. Cripwell, L. Favaro, S.H. Rose, M. Basaglia, L. Cagnin, S. Casella, et al., Utilisation of wheat  
385 bran as a substrate for bioethanol production using recombinant cellulases and amylolytic yeast,  
386 Appl. Energy. 160 (2015) 610–617. doi:10.1016/j.apenergy.2015.09.062.
- 387 [7] R. Zeitoun, Procédés de fractionnement de la matière végétale: application à la production des  
388 polysaccharides du son et de la paille de blé, 2011. [http://ethesis.inp-](http://ethesis.inp-toulouse.fr/archive/00001508/)  
389 [toulouse.fr/archive/00001508/](http://ethesis.inp-toulouse.fr/archive/00001508/) (accessed September 11, 2013).
- 390 [8] C. Dumon, L. Song, S. Bozonnet, R. Fauré, M.J. O'Donohue, Progress and future prospects for  
391 pentose-specific biocatalysts in biorefining, Process Biochem. 47-3 (2012) 346-357.  
392 doi:10.1016/j.procbio.2011.06.017.
- 393 [9] M. FitzPatrick, P. Champagne, M.F. Cunningham, R.A. Whitney, A biorefinery processing  
394 perspective: treatment of lignocellulosic materials for the production of value-added products,  
395 Bioresour. Technol. 101 (2010) 8915–8922. doi:10.1016/j.biortech.2010.06.125.
- 396 [10] N. Sarkar, S.K. Ghosh, S. Bannerjee, K. Aikat, Bioethanol production from agricultural wastes:  
397 An overview, Renew. Energy. 37 (2012) 19–27. doi:10.1016/j.renene.2011.06.045.
- 398 [11] J.M. Asko, H. Lauri, Process for making xylose, US Patent 4075406, 1975.
- 399 [12] D. Ballerini, F. Nativel, Procédé et unité de production en continu d'un mélange de sucres  
400 contenant au moins 80% de xylose à partir d'un substrat lignocellulosique, FR Patent 2655661  
401 (B1), 1994.
- 402 [13] J.A. Ferreira, C.O. Teixeira, S.M. Soares, Process for the production of crystalline xylose from  
403 sugar cane bagasse, crystalline xylose obtained by said process, process for the production of  
404 xylitol from the said xylose and crystalline xylitol obtained thereby, WO Patent 108739 (A2),  
405 2004.
- 406 [14] H. Heikkilä, K. Hyoky, Method for recovering xylose, US Patent 5084104, 1992.
- 407 [15] H. Heikkilä, J. Kuisma, M. Lindroos, O. Puuppo, Method of producing xylose, US Patent  
408 6239274, 2001.
- 409 [16] H. Heikkilä, J. Lewandowski, M. Lindroos, P. Saari, Process of producing xylose and dissolving  
410 pulp, WO Patent 046532 (A1), 2010.
- 411 [17] P.V. Vyas, B.G. Shah, G.S. Trivedi, P.M. Gaur, P. Ray, S.K. Adhikary, Separation of inorganic  
412 and organic acids from glyoxal by electrodialysis, Desalination. 140 (2001) 47–54.  
413 doi:10.1016/S0011-9164(01)00353-8.
- 414 [18] B. Batchelder, N. Reading, Electrodialysis method for demineralization of liquid, whey-based  
415 material, US5223107, 1993.

- 416 [19] C. Huang, T. Xu, Y. Zhang, Y. Xue, G. Chen, Application of electrodialysis to the production of  
417 organic acids: State-of-the-art and recent developments, *J. Membr. Sci.* 288 (2007) 1–12.  
418 doi:10.1016/j.memsci.2006.11.026.
- 419 [20] E.G. Lee, S.H. Kang, H.H. Kim, Y.K. Chang, Recovery of lactic acid from fermentation broth by  
420 the two-stage process of nanofiltration and water-splitting electrodialysis, *Biotechnol. Bioprocess*  
421 *Eng.* 11 (2006) 313–318. doi:10.1007/BF03026246.
- 422 [21] E. Gyo Lee, S.H. Moon, Y. Keun Chang, I.K. Yoo, H. Nam Chang, Lactic acid recovery using  
423 two-stage electrodialysis and its modelling, *J. Membr. Sci.* 145 (1998) 53–66.  
424 doi:10.1016/S0376-7388(98)00065-9.
- 425 [22] H.J. Lee, S.J. Ahn, Y.J. Seo, J.W. Lee, A feasibility study on the multistage process for the oxalic  
426 acid pretreatment of a lignocellulosic biomass using electrodialysis, *Bioresour. Technol.* 130  
427 (2013) 211–217. doi:10.1016/j.biortech.2012.12.061.
- 428 [23] J.H. Lee, J. An, S. Park, T. Kim, S. Kim, Economic process for producing xylose from  
429 hydrolysate using electrodialysis and direct recovery method, US 2012211366 (A1), 2012.
- 430 [24] H. Lyu, K. Chen, X. Yang, R. Younas, X. Zhu, G. Luo, et al., Two-stage nanofiltration process for  
431 high-value chemical production from hydrolysates of lignocellulosic biomass through  
432 hydrothermal liquefaction, *Sep. Purif. Technol.* 147 (2015) 276–283.  
433 doi:10.1016/j.seppur.2015.04.032.
- 434 [25] Y. He, D.M. Bagley, K.T. Leung, S.N. Liss, B.Q. Liao, Recent advances in membrane  
435 technologies for biorefining and bioenergy production, *Biotechnol. Adv.* 30 (2012) 817–858.  
436 doi:10.1016/j.biotechadv.2012.01.015.
- 437 [26] J. Lemaire, C.L. Blanc, F. Duval, M.A. Theoleyre, D. Pareau, Purification of pentoses from  
438 hemicellulosic hydrolysates with sulfuric acid recovery by using electrodialysis, *Sep. Purif.*  
439 *Technol.*, 2016. In Press. doi: 10.1016/j.seppur.2016.04.030
- 440 [27] G. Liu, Y. Liu, H. Shi, Y. Qian, Application of inorganic membranes in the alkali recovery  
441 process, *Desalination* 169 (2004) 193–205. doi:10.1016/j.biotechadv.2012.01.015.

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