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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 ($27 \text{ L.h}^{-1}.\text{m}^{-2}$). 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 H_2SO_4 recovered and 8.4

kWh per m³ of hydrolysate). Finally, the complete demineralization (conductivity < 10 µS.cm⁻¹) 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.

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

Highlights

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

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1. Introduction

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

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

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

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

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

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

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

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

could be obtained at the industrial scale. Moreover, the goal was to check the reliability and robustness of membranes for both processes. Furthermore, it was necessary to produce a 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 order to verify the feasibility of acid recycling by our industrial partner.

2. Materials and methods

2.1. Wheat bran hydrolysate

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

Table 1 -Composition of the wheat bran hydrolysate

Total dry weight	%w	8.0
Solubles dry weight	%w	6.9
Dry suspended matter	g.kg^{-1}	11
pH	-	1.4
Conductivity	mS.cm^{-1}	34.0
420 nm absorbance	-	1.79
Glucose		11.4
Xylose	g.L^{-1}	25.5
Arabinose		14.6
Furfural		0.8
H^+ (total acidity)	mmol.L^{-1}	240
Na		6
NH_4	mg.L^{-1}	369
K		240
Total cations	meq.L^{-1}	27
SO_4	mg.L^{-1}	10375

Cl		59
PO ₄		913
Total anions	meq.L ⁻¹	256

2.2. Ultrafiltration

The filtration module was an Alfa Laval Test Unit M20, a crossflow membrane filtration unit equipped with a heat exchanger for temperature control, a recirculation pump and a 8 L stainless steel tank. A 2.5" spiral organic membrane UFX10 pHt was furnished by Alfa Laval for ultrafiltration at a molecular weight cut-off of 10 kDa. This membrane was chosen owing to its retention performances and its specific resistance to very acid conditions (till pH 1). The total membrane area was 0.6 m². The dead volume in the system was estimated to 2 L.

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

2.3. Electrodialysis

The conventional electrodialysis plant was supplied by Eurodia. It was composed of three 2 L tanks containing the electrolyte, the product (ultrafiltered hydrolysate) and the brine (diluted sulfuric acid solution), three pumps for the circulation of each solution and a voltage generator. A conventional 10 unit cells stack, with an alternation of anion and cation exchange membranes was used. The unit cell area was 0.02 m². It was operated at a constant voltage of 14 V and a free intensity, without temperature regulation. Pumps ensured

a 180 L.h⁻¹ flowrate in the brine and feed compartments and a 200 L.h⁻¹ flowrate in the electrolyte compartment (supplier recommended values).

The electrolyte was a 20 mS.cm⁻¹ Na₂SO₄ solution (11 g.L⁻¹). The initial brine was a 5 mS.cm⁻¹ H₂SO₄ solution (0.7 g.L⁻¹). The operation was run in batch mode until the conductivity drop rate was lower than 0.25 mS.cm⁻¹.min⁻¹. Temperature, pH and conductivity were monitored.

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 performed with a constant tension so the limiting current density is not a constant and decreases during demineralization. Tension was fixed to work always under the limiting current density so as to optimize energy consumption and faradic yield.

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

2.4. Polishing

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

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

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

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

2.5. Analytic methods

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

Sugars and furfural were analysed with a HPLC system (Ultimate 3000, Dionex) equipped a RI-101 refractometer (Shodex). The analytical column was an Aminex HPX-87H (Biorad) and its temperature was maintained at 45 °C. The mobile phase was 2 mmol.L⁻¹ H₂SO₄ degassed by an on-line vacuum degasser. The flowrate was set to 0.5 mL.min⁻¹ and the injection volume to 10 µL.

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

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 ⁻¹	23 mA	2.5 µL

Cation analysis	Ionpack CS16 3x250 mm (Dionex)	CG16 3x50 mm, Dionex	30 mM methanesulfonic acid 0.36 mL.min ⁻¹	32 mA	10 µL
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3. Results and discussion

3.1. Ultrafiltration

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

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

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

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

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

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

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

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

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

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 ⁻¹	34.0	32.7	29.1	-	-
Sugars		51.6	42.8	49.9	88	99
Furfural	g.L ⁻¹	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 ⁻¹	27	24	23	90	99
Acidity (A ⁻ -C ⁺)		220	174	478	76	95

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

be designed carefully as membrane clogging determines the permeate fluxes of ultrafiltration. The resulting permeate was afterwards demineralized by electrodialysis.

3.2. Electrodialysis

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

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

So as to keep productivity high enough, the product was always demineralized until only 2 mS.cm⁻¹ (figure 2); its final pH was 2.7. From this moment, the conductivity drop velocity became lower than 0.25 mS.cm⁻¹.min⁻¹. No precipitation was observed. The brine was enriched in acid from 5 to 40 mS.cm⁻¹ (0.7 to 8.6 g.L⁻¹ H₂SO₄) during the first batches and up to 65 mS.cm⁻¹ (14.7 g.L⁻¹ H₂SO₄) during the second batches.

Moreover, ED was performed until the product conductivity reached only 2 mS.cm⁻¹ so as to recover most of acids and keep the faradic yield above 50%. In this case, the average faradic yield remained good (80%) and the specific energy consumption of the electrodialysis stack was quite interesting (ca. 1.1 kWh per kg of H₂SO₄ recovered and ca. 8.4 kWh per m³ of

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

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

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

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

Demineralized products of all the batches were gathered, as well as the final brines of the second batches. The sugars recovery rate in the products was very good (99%) (table 4); no sugar went through the ion exchange membranes into the brine. On the contrary 87% of the acid was recovered into the brine, reaching about $15 \text{ g.L}^{-1} \text{ H}_2\text{SO}_4$. The resulting brine pH and 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 ⁻¹	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 ⁻¹	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 ⁻¹	24	0	1	46	6
Acidity (A ⁻ -C ⁺)		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 H₂SO₄; 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 ⁻¹	34.0	38.2

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

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

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

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

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

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

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%

4. Conclusion

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

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

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

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

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References

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