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Julien Lemaire, Claire-Line Blanc, Fanny Duval, Marc-André Théoleyre, Dominique Pareau. Purification of pentoses from hemicellulosic hydrolysates with sulfuric acid recovery by using electrodialysis. Separation and Purification Technology, 2016, 166, pp.181-186. 10.1016/j.seppur.2016.04.030 . hal-01310364

HAL Id: hal-01310364 https://hal.science/hal-01310364

Submitted on 9 Nov 2016

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

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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 wheat bran hydrolysates are very promising. The process is based on the combination of 16 17 ultrafiltration, conventional electrodialysis and ion-exchange. A special organic UF membrane (Alpha Laval - UFX10pHt), resistant to acidic conditions, removed 18 totallymacromolecules which can damage the electrodialysis unit by precipitation, with good 19 mean permeate flow rate (24 L.h⁻¹.m⁻² till VCF = 4.4). Then, conventional electrodialysis was 20 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 was interesting (0.6 kWh per kgof H_2SO_4 recovered and 4.2 kWh per m³ of hydrolysate). 23 Finally, the complete demineralization (conductivity $< 10 \ \mu S.cm^{-1}$) and discoloration (420 nm 24

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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41 **1. Introduction**

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

49 Lignocellulosic biomass is mainly composed of cellulose (40 to 50%), lignins (10 to 50 35%, and hemicellulose (20 to 45%, 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 industry, "Organo-solv" processes using organic solvents such as acetone, ethanol or acetic 55 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 environmental reasons. Indeed, large amount of base is required, resulting in greatly 66 increased amount of salts, needing more water and chemical reagents to separate them. 67

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 precipitate during ED. Indeed, ED membranes are quite expensive and are dramatically 80 81 damaged by clogging.

82 The objective of this study was to investigate the feasibility of sulfuric acid recovery from lignocellulosic hydrolysates in the frame of pentoses valorization. The present process 83 84 combines ultrafiltration (UF), conventional electrodialysis and ion-exchange (IE) and does not need neutralization step, that is a significant advantage in terms of economy and 85 environment. First, the influence of the nature (mineral or organic) and the cut-off of UF 86 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 sugars with very low conductivity (< 10 μ S.cm⁻¹) and totally discolored. This work proposes 90 91 an eco-efficient process to purify pentoses from hemicellulosic hydrolysates.

92 2. Materials and methods

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2.1. Hemicellulosic hydrolysate

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

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

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

99 2.2. <u>Ultrafiltration device</u>

Our pilot device can perform cross-flow filtration through different kinds of membrane with various cut-offs for microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) or reverse osmosis (RO). Two ceramic tubular membranes in series (TAMI) and up to 40 organic flat sheet membranes (Alpha-Laval), composed of polysulfone and polypropylene, in a plateand-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 ²)	50	180
Length (cm)	25	-
Diameter (mm)	6	100
рН	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)

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

110 2.3. <u>Conventional electrodialysis unit</u>

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

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

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Table 3 – Operating conditions of the conventional electrodialysis unit

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

124 2.4. lon-exchange system

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

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

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

140 2.5. <u>Analytical methods</u>

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_2SO_4 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.

Sugars were analysed with an HPLC system (Ultimate 3000, Dionex) equipped with a pump, an auto sampler and a RI-101 refractometer at 35 °C (Shodex). The analytical column was an Aminex HPX-87H (Biorad) along with a matching guard column (Micro-Guard cartridge, Biorad). The column temperature was maintained at 45 °C with a column oven controller. The mobile phase was 2 mM H_2SO_4 in milli-Q water (Direct 8, Millipore), degassed by an on-line vacuum degasser. The flowrate was set to 0.5 mL.min⁻¹ and the injection volume to 10 µL.

153 Anions and cations were analysed with an HPIC system (ICS-5000⁺, 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 lonpack 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⁻¹, the suppressor to 23 mA and the 159 injection volume to 2.5 µL. For cation analysis, the column was an lonpack 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⁻ 162 ¹, the suppressor to 32 mA and the injection volume to 10 μ L.

163 3. Results and discussion

164 3.1. <u>Removal of macromolecules by ultrafiltration</u>

Macromolecules like lignins or proteins must be removed from the hydrolysate before performing ED because they will damage the electrodialysis stack by precipitation due to pH increase during the treatment. UF with ceramic membranes and organic membranes (2 flat sheets, total surface = 0.036 m2) was investigated to remove macromolecules, without pH adjustment so without reagents consumption in contrast with existing processes. Temperature was set to 40°C and transmembrane pressure to 6 bar. So as to evaluate their performance, the amount of precipitates in hydrolysate samples before and after UF was measured at different pH, which was adjusted with soda (table 4). Precipitates were filtered on 0.22 µm PTFE filter then their dry weight was measured by a moisture analyzer (Sartorius MA150).



Table 4 – Amount of precipitates (g _{dry} perkg of hydrolysate sample) before and after different UF
treatments as a function of pH

рН	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 which precipitate with increasing pH, although some of them had a higher cut-off than the 178 179 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 by membrane charge and hydrophobicity. The influence of membrane nature for the 182 183 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⁻¹.m⁻² 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.

	Feed	Retentate	Permeate
Volume (L)	8.0	1.8	6.2
Dry weight (% _w)	7.3	11.6	7.0
рН	1.3	1.3	1.3
Conductivity (mS.cm ⁻¹)	31.5	30.2	34.5
Absorbance at 420 nm	2.1	6.5	0.5

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

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

198 3.2. <u>Acid recovery and demineralization by conventional electrodialysis</u>

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 H₂SO₄ 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.

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



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211 212

Figure 1 – Monitoring of conductivity and pH of brine and product and variation of current intensity and faradic yield during the 1st ED with fresh brine

213 The product was almost totally demineralized (conductivity < 1 mS.cm⁻¹) 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⁺ 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 in the product (> 99%). H₂SO₄ concentration of the brine reached 5.9 g.L⁻¹, which was not 218 219 enough to be used for hydrolysis step. This is the reason why this brine was reused for the 2nd ED. 220

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

Table 6 – Analysis of brine and product after the 1st ED with fresh brine and the 2nd ED with brine reuse

The 2^{nd} ED was performed with 2.2 L of hydrolysate and 1.2 L of the brine recovered after the 1^{st} ED so as to get a H₂SO₄ concentration up to 15 g.L⁻¹. As previously, the product was almost totally demineralized after 20 min and the same pH, conductivity and current intensity profiles were observed over time. About 80% of sulfuric acid was recovered in the reused brine, meanwhile most of sugars (> 99%) remained in the product (table 6). The H_2SO_4 concentration of the brine reached 14.2 g.L⁻¹ and its pH was equal to 1. So, this time, the 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 order to study the transfer rate of acids and different salts during the treatment. Indeed, if 230 231 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 acidsand keep the faradic yield above 50%. In 238 this case, the faradic yield remained acceptable (70%) and the specific energy consumption of the electrodialysis stack was quite interesting (0.6 kWh per kg of H_2SO_4 recovered and 4.2 239 240 kWh per m³ of hydrolysate). The recovery rates of major cations and anions are detailed.





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

We observed that acids are transferred slightly faster than other salts but not enough to recover most of them without most of other salts. Consequently the implementation of ED in two steps did not appear advantageous for this kind of hydrolysates, containing mainly 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 accumulation in brine will be relatively slow. Thus, if a periodic purge is sometimes 252 253 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 produced with reused sulfuric acid had exactly the same content except for salts. The brine 255 256 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.

Finally an additional polishing treatment by IE was required to remove salts completely and economically. Indeed, the faradic yield of ED dropped below 30% after 20 min when the product conductivity was around 1 mS.cm⁻¹.

262 3.3. Polishing treatment by ion-exchange

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





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⁻¹, salts ca. 20 meg.L⁻¹) were completely demineralized (conductivity < 10 μ S.cm⁻¹) before saturation of one of the 272 273 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

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

This new process is based on the combination of ultrafiltration, conventional electrodialysis and ion-exchange. First, the ultrafiltration step with organic membranes can efficiently remove macromolecules which can damage irreversibly the electrodialysis unit by precipitation. Then, most of the sulfuric acid can be recovered effectively by conventional electrodialysis. Most of other salts (mainly ammonium, potassium and calcium salts) are coextracted and their accumulation in the recycled brine has to be watched and might require anoccasional purge. Nevertheless, the recycling of sulfuric acid keeps very interesting economically. Finally, the polishing treatment by IE can fully demineralize and discolor the solution of pentoses whose purification can be achieved classically by continuous chromatography or crystallization.

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

304 Acknowledgements

The authors would like to thank Fondation Paris-Reims, Région Champagne-Ardenne, Département de la Marne and Reims Métropole for their financial support and ARD for the hydrolysate supply.

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