Treatment of Pulp Black Liquor with an Ionic Liquid: Modeling and Optimization by Using Response Surface Methodology and Central Composite Design

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Treatment of Pulp Black Liquor with an Ionic Liquid: Optimisation by Using Response Surface Methodology

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Abstract: In this study, selective extraction towards ionic liquid trihexyltetradecylphosphonium chloride ([P$_{66614}$]Cl) of lignin residues, polysaccharides and organic acids present in black liquor (BL), the main principal wastewater of pulping industry was studied. With the objective of finding optimized conditions allowing to extract lignin resideus while polysaccharides and organic acids remain in aqueous solution, a design of experiments approach based on a response surface methodology was used. Three continuous factors, namely initial pH varying from 9 to 13.5, dilution of BL varying from 5 to 20 and volumetric ratio of black liquor vs. ionic liquid R$_V$., varying from 1 to 19, were investigated. Concentration of ligni residues, polysaccharides and organic acids were measured using Folin-Ciocalteu method, the anthrone method and HPLC, respectively. Results showed that a multi-response optimization led to the extraction of 84.8 % of lignin residues, 66.0 % of polysaccharides, and no extraction of OA under optimised conditions.

Introduction

Ionic liquids (IL) are salts with melting temperatures below 100°C and their versatile physico-chemical properties render them interesting in different industrial and commercial applications such as biotechnology.[1–3] Recently, ionic liquids have been used as new solvents for pretreatment of lignocellulosic biomasses (switch-grass, wheat straw, corn stover, bagasse, ….)[4-9] but few studies have already appeared on the use of ILs for the selective extraction of compounds present in such complex systems as pulping factory black liquor, the most prominent aqueous waste issued from pulping factories.[10,11]
Several processes, such as well-known Kraft process are currently available for depolymerizing lignin from wood in order to obtain a paper pulp.[12,13] In all cases, a black liquor is formed along the process, with significant hazard and safety issues related to the volume and composition of waste produced. Black liquor represents up to 1200 Mt produced each year in the world.[14] It generally consists in an alkaline solution with pH close to 12 or 13, composed with polysaccharides (PS), organic acids (OA), and residues and fragments of lignin, a polyphenolic polymer that will be quantified here in polyphenols equivalents (PP). The presence of such polyphenolic polymer fragments givs its deep black color to so-called black liquor.[15,16] Polysaccharides and organic acids represent two classes of compounds with a high biodegradability, while lignin residues are not.[12,17] Consequently, the extraction of lignin residues from the black

liquor solution is a necessary step in order to increase the accessibility to polysaccharides and organic acids for further biological treatments, without losing the reuse potential of lignin, for instance under the form of polyphenols after depolymeriztion process, like adhesive,[18] composite materials,[19] or as active ingredients in cosmetics or food applications.[20,21] In a previous study, the efficiency of two phosphonium ionic liquids containing Cl⁻ or Br⁻ anions, namely [P$_{66614}$]Cl and [P$_{66614}$]Br, in order to extract polyphenolic lignin residues, polysaccharides, and organic acids from pulping factory black liquor was examined.[10] Extraction was found to be influenced by the dilution of black liquor (BLD), volume ratio of aqueous phase vs. ionic liquid (R$_v$) and initial pH.

Response Surface Methodology (RSM), introduced in the early 1950s, is an efficient and practical tool for designing experiments, fitting response surface models and determining optimum operating conditions.[22-24] Simple, interaction and quadratic effects of selected factors on the studied response can be studied simultaneously starting from an experimental matrix with limited number of runs.

Design of experiments (DOE) presents, in comparison to the classical OFAT methodology (One Factor At a Time), many advantages such as time and money saving, limited number of experiences, thereby making it possible to investigate factor interactions. It is widely used in different industrial fields such as food industry,[25,26] analytical chemistry,[27] food flavor and sensor analysis,[28] in energy application,[29] in biotechnological processes[30] and in extraction of plant materials.[31,32]

More specifically, RSM has been successfully used in several applications using ILs, such as chemical analysis,[33] in food industry,[34] catalyst applications,[35] biomass pre-treatment[36] or organic synthesis.[37]

In a previous article[10], phosphonium ionic liquids were proven to be promising solvents for extracting lignin residues from black liquor. OFAT (one factor at a time) methodology was previously used for studying influence of black liquor dilution and volume ratio on extraction. None combined effect between parameters were however studied. In addition, initial pH effect was examined for one unique combination of BL dilution and Rv, 0.1% and 10, respectively.

Therefore and in order to go beyond the proof of concept reported previously,[10] the aim of this study is first to model the individual extraction percentages and distribution coefficients for lignin residues, hereafter studied as polyphenol equivalent (PP), PS and OA towards [P$_{66614}$]Cl, using Response Surface Methodology.

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That way, all three parameters, BL dilution, initial pH and Rv are take extensively into account over expanded ranges, so that all possible interactions between these three parameters are described. In a second step, with the objective of further treating such waste, multiresponse optimization is established in order to maximize extraction of lignin residue while minimizing PS and OA extraction percentages. Finally, possibilities to extract selectively PP towards [P$_{66614}$]Cl, starting from different initial conditions is discussed.

Results and Discussion

DOE observations

According to the DOE methodology, 35 experiments were carried out with varying pH, BLD an R$_V$. Because black liquor exhibits a pH of 13.5 and because lignin residues are less soluble in acidic water,[15] pH was used as an extraction parameter. Black liquor dilution and aqueous vs. IL phase volumes are common parameters in extraction experiments, the former being related to the initial concentration of extractable species while the latter correspond to the amount of extracting phase used compared to that of black liquor. Reasons for the value ranges selected for each parameter, namely pH, BLD and Rv varying between 9 and 13.5, 0.2 and 0.05 or 1 and 19, accordingly, are detailed in the experimental section.

For clarity reasons, all results are collected in the support information file. Extensive details and results for the experimental CCD design and extraction percentage and distribution yields for lignin parts, discussed here as polyphenolic equivalents, polysaccharides and organic acids are collected in the supplementary information file (Table S1).

In agreement with previous results[6], black liquor solution studied here contains 30 g.L^{-1} of PP equivalents, 23 g.L^{-1} of PS and 19 g.L^{-1} of OA. In all extraction experiments, upon contacting the ionic liquid with a black liquor sample, a marked change in color is observed within 30 s. The initially black aqueous solution becomes yellow or translucent while the ionic liquid turns brown or black depending on the experimental conditions. For clarity reasons, only two snapshots of a typical extraction experiment are shown in Fig. 1. Snapshots for all extraction experiments are collected in Fig. S1 of the SI file.

Dark color of the black liquor is due to the presence of lignin residues. The transfer of this black liquor towards the ionic liquid implies that these lignin residues are significantly extracted out from the black liquor. Results reveal that generally, lignin residues are well extracted towards the ionic liquid, exhibiting distribution coefficients range from 5 to 500. PS are somehow less extracted, with distribution coefficient (DPs) raging from 0.3 to 72. Distribution coefficient below 1 are however scarce. 4 experiments yield D values below 1, and 4 additional lead to D values between 1 and 2. Organic acids are barely extracted. Values for D$_{OA}$ range between 0 and 13 but unlike polysaccharides, 22 experiments yield DOA values below 2, and under our experimental conditions, the highest extraction percentage for OA is 68 % (run 35).

Because the experiments presented in table S1 were done following recommendations of the experimental design software, discussing the data and find specific trends in the influence of parameters on the extraction of PP, PS and OA is not straightforward. Nevertheless, it first appears that worse extraction results for both PP and PS occur when initial pH is left at 13.5, while best results are obtained at pH 9. Second, for the same pH and BLD, an increase in R$_V$ yields an increase in distribution coefficients. The influence of BLD on distribution coefficients is less clear and not linearly correlating the extraction yields or distribution coefficients. Besides, the trend in extraction for PP and PS appear to be similar. That is, low and high values for D$_{PS}$ or D$_{PP}$ are obtained under the same experimental conditions, namely with an initial pH value of 11.25 or 9 and a high R$_V$ value.

Depending on the experimental conditions, a small dark precipitate appears both all along a few tube walls and in the bottom of the tubes after centrifugation, as showed in figure S1 of the supporting information file. It is known that lignin solubility depends on pH, the lower the pH, the lower the solubility of lignin.[15] However, only a few tubes, namely tubes 10 and 23 exhibit a low pH of approximately 6.6 and 6.3, respectively, and a precipitate. One possible explanation might be in some cases related to the solubility of lignin in acidic solutions. But it is also related to an interaction between acid groups of lignin and ionic liquid. Such an interaction can between, say, an acid group of lignin residues and an ionic liquid cation, might lead to a deprotonation of this acidic group, yielding formation of ion pair with an increased molecular weight. The solvation energy of these ions is thus expected to increase, as well as hinder the interaction between such acid group and water. This interaction, or ion association phenomenon, might yield to an extraction towards the ionic liquid phase as mentioned above, but also to some precipitation when the ionic liquid is saturated or the resulting pair is too large. Such result was previously obtained with a variety of ionic liquids and extracted compounds.[38–40]
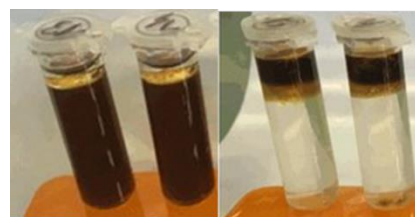

Figure 1. Selected snapshots for the extraction of diluted BL using ionic liquid [P$_{66614}$]Cl. Top phase is [P$_{66614}$]Cl. Left: vials prior extraction. Right: Vials after vortex and centrifugation, as detailed in the experimental section. BLD: 0.12, pH 9, R$_V$: 10.

A more thorough investigation of the pH is presented in Figure 2, plotting the pH measured after extraction of black liquor as a function of initial pH for various R$_V$ factors 2, 10 and 19. Final pH measured in black liquor after extraction ranged from 1 to 13, depending on initial pH. It appears that with initial pH values of 9, final pH is significantly lower than the initial value of 9. Variation between final and initial pH ($|\Delta pH|$) thus range from 0.7 to 7.75 with seven experiments out of ten yielding $|\Delta pH|$ above 2. Such a decrease is less pronounced starting from a pH value of 11.25: values range from 0.34 to 7.73, with four experiments out of fifteen yielding $|\Delta pH|$ values above 2. Starting from a value of 13.5 for

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the initial pH value, hardly any variation is observed. This reveals a certain formation of H⁺ ions upon extraction, a phenomenon that can be related to the above-mentioned explanation, no linear nor evident correlation was found between $|\Delta pH|$ and R_V or BLD. Therefore, influence of both factors on both responses was studied using the RSM methodology.
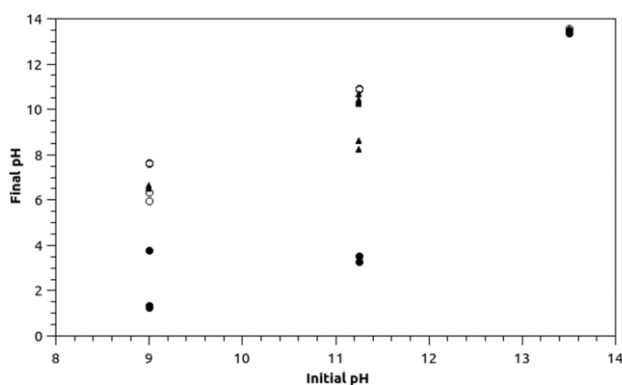

Figure 1. A: Evolution of final pH as a function of initial pH and R_V. ●: R_V=1.

■ : R_V = 10. ○: R_V=19.

Modeling of ΔpH, extraction percentage and distribution coefficient

Experimental results of CCD were analyzed with the help of Design Expert software according to the polynomial quadratic response function given in eq. (1):

$$Y(BLD, pH, R_v) = a - b(BLD) + c(pH) + d(R_v) + e(BLD).(pH) + f(BLD).(R_v) + g(pH).(R_v) + h(pH)^2 + i(R_v)^2 + j(BLD)^2 \quad (1)$$

with Y a linear, logarithmic or square root function of each experimental result obtained in this work, that is either ΔpH, the extraction percentages or distribution coefficients of PP, PS or OA, accordingly. BLD, R_V and pH are the black liquor dilution, volume ratio and the final pH, respectively. a to j values are the adjustable parameters of the model. Their values are collected in Table S2 of the supplementary information file.

Each individual response model, namely, a response to be compared to experimental data, is analyzed in a first step by Analysis of Variance (ANOVA). During this step, response function Y from eq. (3) is fitted to experimental results as presented in Table S2 and the software selects various models for describing experimental results. Response function was allowed to describe experimental responses, namely $|\Delta pH|$, D_{PP}, D_{PS}, D_{OA}, P_{PP}, P_{PS} and P_{OA} respectively, under the form of either $Y=X$, $Y = ln(X + \varepsilon)$ or $Y = \sqrt{X + \varepsilon}$, X being an experimental response as detailed above and ε a numerical value. The latter value was necessary in case some experimental data exhibited null values. From that analysis, detailed in the supplementary information file, the best suited models for the extraction percentage and distribution coefficients of PP, PS and OA, as well as the pH variation are collected in Table S2.

It is worth noticing that run 14 shows unusual data points that deviate significantly from other observations. Because this is most probably due to incorrect experimental run, according to ref. [32], the run is withdrawn from the analysis of externally studentized

residuals after model refining and eventual response transformation. Therefore, run 14 is an outlier point located outside standard deviation limits (data not shown) and was consequently eliminated for future analysis.

Fitting of response functions was carried out individually by analyzing distributions of residual plots according to the residual normal probability plots for each response, residual values versus predicted plot, and predicted values versus actual values (not shown). In all cases, a linear distribution of residuals along a straight line was observed, and a disordered organization of residuals and predicted values against predicted response values and values of runs is obtained. Along with the results obtained by the ANOVA analysis detailed in the supplementary information file, all diagnostic tests are thus satisfactory, implying that the models can be used in a wide spectrum of design.

Modeling of pH variation

According to the fitting procedure described in the preceding sub-section, $|\Delta pH|$ response was successfully described as a function $ln(|\Delta pH|+0.00775)$ and was found to depend on all three factors, R_V, BLD, and pH (Table 1). In this work, because three factors are investigated, response, such as $|\Delta pH|$, extraction percentages or distribution coefficients, as detailed later in the manuscript, will be discussed following two representations. One is a classical, so-called 3D representation, corresponding to the evolution of response as a function of two mains parameters out of the three parameters studied here, namely pH, R_V and BLD. The two main parameters are selected according to the perturbation graph available in the complementary material. The third parameter is fixed at its central value, for example, value of 11.25 for pH. In such a representation of the surface response, the bottom of the 3D-plot (shown in yellow in the plots) is representing the corresponding 2D iso-response curves. The second representation is a so-called cubic representation, with each axis of the cube corresponding to a parameter ranging from -1 to 1. The main objective of the 3D and cubic graphs is to evaluate the behavior of the response related to two or three factors and thus to better know about the space of study.

In the case of pH variation response, perturbation graph reveals that BLD is the factor influencing most $ln(\Delta pH+0.00775)$, while influence of R_V and initial pH on $ln(\Delta pH+0.00775)$ are similar.
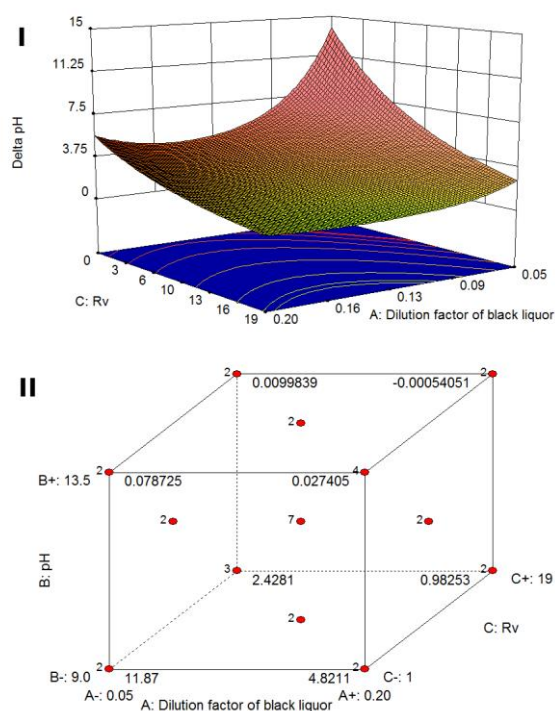
Figure 3. I: 3D representation for $|\Delta pH|$ as a function of R_V and BLD at the central point value of pH, corresponding to a pH value of 11.25. Blue, green, and red areas represent lower, intermediary and high values of responses, with 25, 50, 75 % of the maximal value, respectively. Delta pH stands for $|\Delta pH|$. Dilution factor of black liquor stands for BLD. II: Cubic representation for $|\Delta pH|$ as a function pH, R_V and BLD. Values for $|\Delta pH|$ given at the cube corners.

3D representation of ΔpH response (shown in 3.I), at the central point value (pH 11.25), indicates that variation of pH is only significant when R_V and BLD exhibit low values. Maximal value of 5.5 for $|\Delta pH|$ is obtained when R_V and BLD exhibit values of 1 and 0.05.

Cubic representation reveals that, whatever R_V and BLD, higher initial pH values led to low values in $|\Delta pH|$, typically ranging between 0 and 0.079. Maximal ΔpH value is estimated to be obtained with values for R_V, BLD and initial pH of 1, 0.05 and 9, respectively. Because $|\Delta pH|$ is an accessory response compared to the extraction percentage and distribution coefficient of PP, PS and OA, further optimization step of $|\Delta pH|$ response was not carried out here.

Optimization of extraction percentage and distribution coefficient

Because optimization step depends on both selected responses and factors, response optimization was carried out either individually or by coupling responses in the case of multi-response analysis. In order to obtain the optimum value for a given response, such as extraction percentage or distribution coefficient, each factor, namely R_V, BLD and pH, was individually optimized in its value range. Different extraction goals can be established in the case of a solution containing multiple

compounds to extract or remove, such as those found in a black liquor solution. Because lignin residues within black liquor present a certain toxicity and are hardly biodegradable at the concentration they are in, and because they can yield valuable compounds, the main goal of this work was thus to remove polyphenols while keeping polysaccharides and organic in solution in the diluted black liquor. In this study, both goals were studied either individually or in multi-response analysis. Optimized experimental conditions are summarized in Table 1.

Table 1. Optimized experimental factors for each individual response, leading to individual maximized responses in the studied experimental area.

Factors	BLD	pH	R_V	Calc. results	Response range[a]	Exp. results
P_{PP}	0.07	9.11	5.46	99.6	98.3-100.8	99.2
D_{PP}	0.05	9.04	13.5	762	608-1029	955
P_{PS}	0.05	9.01	12.75	79.1	74.9-83.3	78.2
D_{PS}	0.05	9.00	17.26	62.3	53.5-84.3	75.6
P_{OA}	0.15	13.5	1.00	63.4	45-85	62.4
D_{OA}	0.17	9.05	12.00	20.7	9.9-43	25.2

[a] Low and high values of the 95% confidence interval in which one could expect to find the average response of a group of runs.

Validation of each optimized model, as detailed in Table 1, was carried out by comparing maximal responses to experimental results carried out under optimized conditions, as shown in Table 1. It appears that experimental values are close to mathematical values, that straightforwardly validates each model. Extraction percentage or distribution coefficient can thus be predicted by each model in the experimental field studied by the DOE.

Highest values for polyphenol or polysaccharide extraction percentages as well as distribution coefficients are obtained when black liquor is highly diluted, that is when a BLD value close to 0.05 – 0.066 is used. An opposite result is found for organic acid extraction. In the latter case, a higher BLD value close to 0.15-0.17 yielded highest distribution coefficients.

3D and cubic model representation of extraction

The previous validation for models collected in Table 1 allowed to describe the evolution of each response, namely extraction percentage and distribution coefficient for all three families of compounds over the whole experimental range of values for R_V, BLD and pH.

Representation of lignin residue extraction model

Figure 4 summarizes 3D and cubic representations for the extraction percentage (P_{PP}) and distribution coefficient (D_{PP}) of lignin residues, calculated as polyphenolic equivalents.

Extraction of lignin residues (PP) was plotted as a function of pH and R_V (Fig. 4.I and 4-III) because perturbation graph revealed that P_{PP} and D_{PS} depended mostly on these two parameters. Both maximal responses, P_{PP} and D_{PP}, are situated at the limit of the experimental studied field as indicated in Fig. 4-I and 4-III. As shown in Fig. 4-I and 4-II, whatever the factors, lignin residues are significantly extracted, as shown by P_{PP} values. Extraction efficiency ranges from 82.1 to 99.6 %, respectively (Fig. 4.II).

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Highest value for P_{PP} (99.6 %) is obtained at 9, 0.07 and 6 for pH, BLD and R_V values, respectively. Furthermore, P_{PP} generally decreases with pH, BLD, or R_V, accordingly. The highest value of 99.7 is very close to that of 99.4 obtained at the lowest pH, BLD and R_V values.

Distribution coefficient for lignin residues described as polyphenol-equivalent (D_{PP}) varies from 4.8 to 658 and greatly depends on all three parameter value, as observed in the 3D graph and cubic representation. The maximal value of 658 is obtained at values of 9, 0.05 and 14 for pH, BLD and R_V, respectively. According to Fig. 4-II, D_{PS} generally decreases with pH and BLD.

indicating approximately half of polysaccharides are extracted towards the ionic liquid.

According to Fig.5-II, it appears that pH and BLD exhibit antagonistic influence on P_{PS}. At low pH, P_{PS} decreases with BLD, a trend that is inversed at high pH. Similar observations can be done at low and high BLD values. On the opposite, P_{PS} increases with R_V, whatever the evolution of pH or BLD, accordingly. Optimum set of parameters was located at values of 9, 0.05 and 11 for pH, BLD and R_V, yielding a value of 79 % for P_{PS}, as shown in Fig. 5-II. On the contrary, lowest value for P_{PS} obtained according to the model is 25%, for values of 13.5, 0.05 and 1 for pH, BLD and R_V, respectively.

Values for the distribution coefficient of polysaccharides (D_{PS}) range between 0.3 and 62, with most values being above 1, an
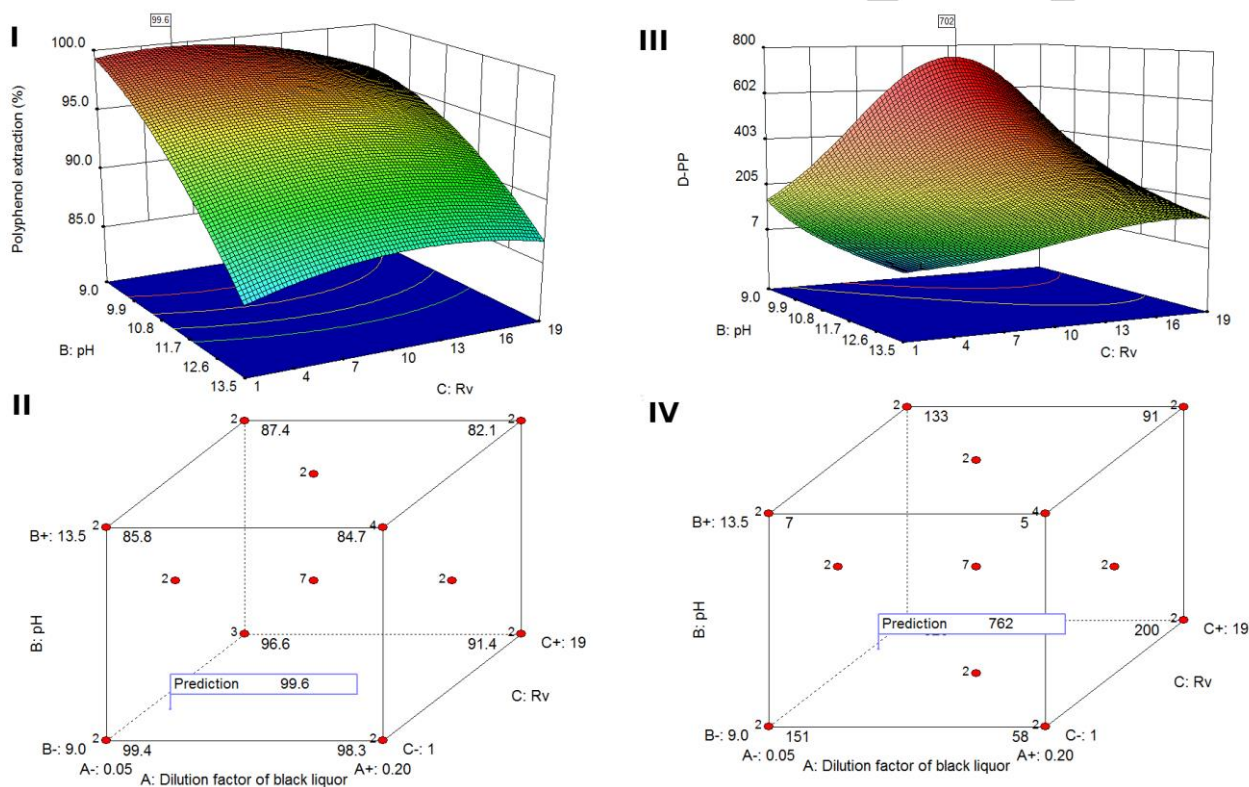

Figure 4. 3D (left side) and cubic (right side) representation for extraction percentage of polyphenol (I-II) and corresponding distribution coefficient (III-IV). Parameter values are indicated in Table 1. Blue, green, and red areas represent lower, intermediary and high values of responses, with 25-50-75 % of the maximal value, respectively.

Representation of extraction model for polysaccharide

Extraction percentage of polysaccharides by ionic liquid [P_{66614}]Cl is lower than that of PP, exhibiting values varying from 24.9 to 79% according to our experimental conditions (Fig. 5).

Starting from the perturbation graph shown in the complementary material, R_V appears to have a somewhat smaller influence on the extraction percentage of polysaccharides (P_{PS}) than BLD and pH. Plot of P_{PS} as a function of pH and BLD at a fixed value of 10 for R_V, as shown in Fig. 5-I, reveals that P_{PS} exhibits a narrow region of low values around 30 % extraction at values of 13.5 and 0.2 for pH and BLD, respectively. High values for P_{PS} are observed at either low or high pH or BLD ends, accordingly. Most of the surface exhibits P_{PS} values of approximately 50 %,

indication of a preferential partition of polysaccharides towards the ionic liquid phase. D_{PS} appears to depend mainly on the phase volume ratio and pH as shown in Fig. 5.III and the perturbation graph. A somehow narrow domain of high values for the distribution coefficient, typically above 30, is found in the region of low pH and high R_V values. When moving away from that region, distribution coefficient decreases rapidly, reaching a plateau of low values ranging between 0.2 and 10 over half of the response surface shown in Fig. 5.III. Values below 1 are all located around pH 13.5 and R_V equal to 1. As shown in Fig. 5.IV, the same observations as those for P_{PS} can be done, that is, pH and BLD behave antagonistically, whereas distribution coefficient increases with R_V, whatever pH or BLD evolution.
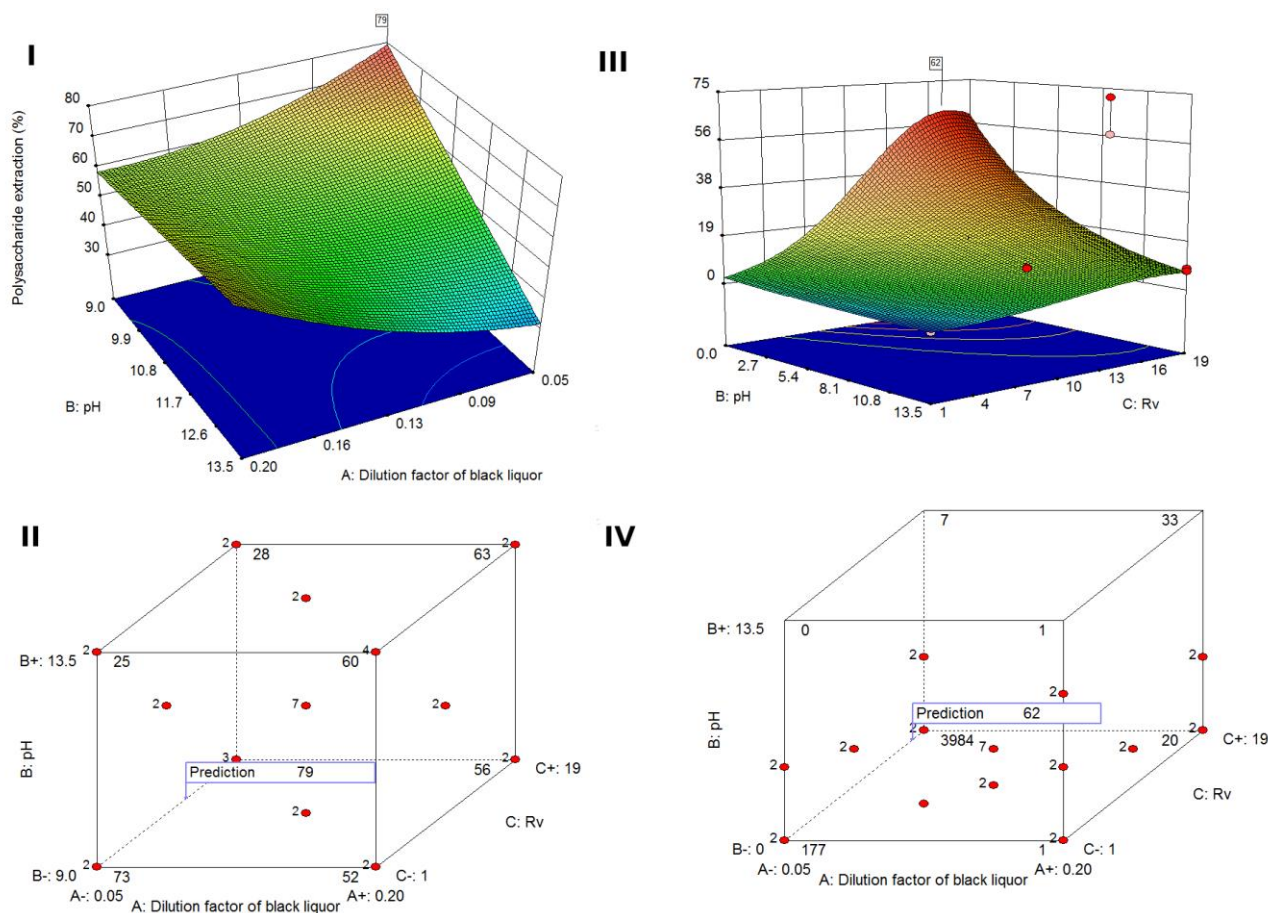
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Figure 5. 3D (left side) and cubic (right side) representation for extraction of polysaccharides (I-II) and its distribution coefficient (III-IV). Parameter values are indicated in Table 1. Blue, green, and red areas represent lower, intermediary and high values of responses, with 25, 50 and 75 % of the maximal value, respectively.

Representation of extraction model for organic acids

Black liquor principally contains lactic acid as an organic acid. Results indicate that extraction percentage of organic acid varies from 0 to 63 %. According to perturbation graphs, extraction of lactate depends mainly on R_V and BLD (Fig. 6-I). Highest values for the extraction of organic acids are located at the borders of the studied experimental field, namely at low and high values for R_V and BLD, respectively. Value of 63 % for the extraction yield of organic acids (P_{OA}), the highest value obtained here, is found with values for pH, BLD and R_V of 13.5, 0.13 and 1, respectively. Furthermore, at a given R_V value, extraction yield of organic acids decreases monotonously with BLD. The higher the R_V value, the lower the influence of BLD on P_{OA} is, the latter becoming nearly negligible when R_V is equal to 19. No extraction of organic acid is observed with a low BLD value, either at pH 9 whatever R_V, and at high R_V whatever pH. This absence of organic acid extraction is represented by the blue area in Fig. 6.I.

Plotting the distribution coefficient of organic acids (D_{OA}) as a function of BLD and R_V, as shown in Figure 6.III yields a steep and well defined peak centered around the optimal value calculated here, namely 20.7 obtained at values of 9, 0.17 and 11 for pH, BLD, pH and R_V, respectively. The peak covers over half

of the response surface of Fig. 6.III. D_{OA} is close to 0 as long as BLD is lower than approximately 0.11.

Cubic representation shown in Fig. 6-IV is characterized by presence of null or very low response values in four out of eight corners: at low pH and BLD whatever R_V, and at high pH and R_V whatever the BLD value. In agreement with Fig. 6-III, higher values for the distribution coefficient are located within the cube. It appears that at high pH values, no extraction is found to occur. This can be explained by the fact organic acids are under their basic form at high pH, the latter being well solvated in water, hence poorly extracted towards an ionic liquid phase.
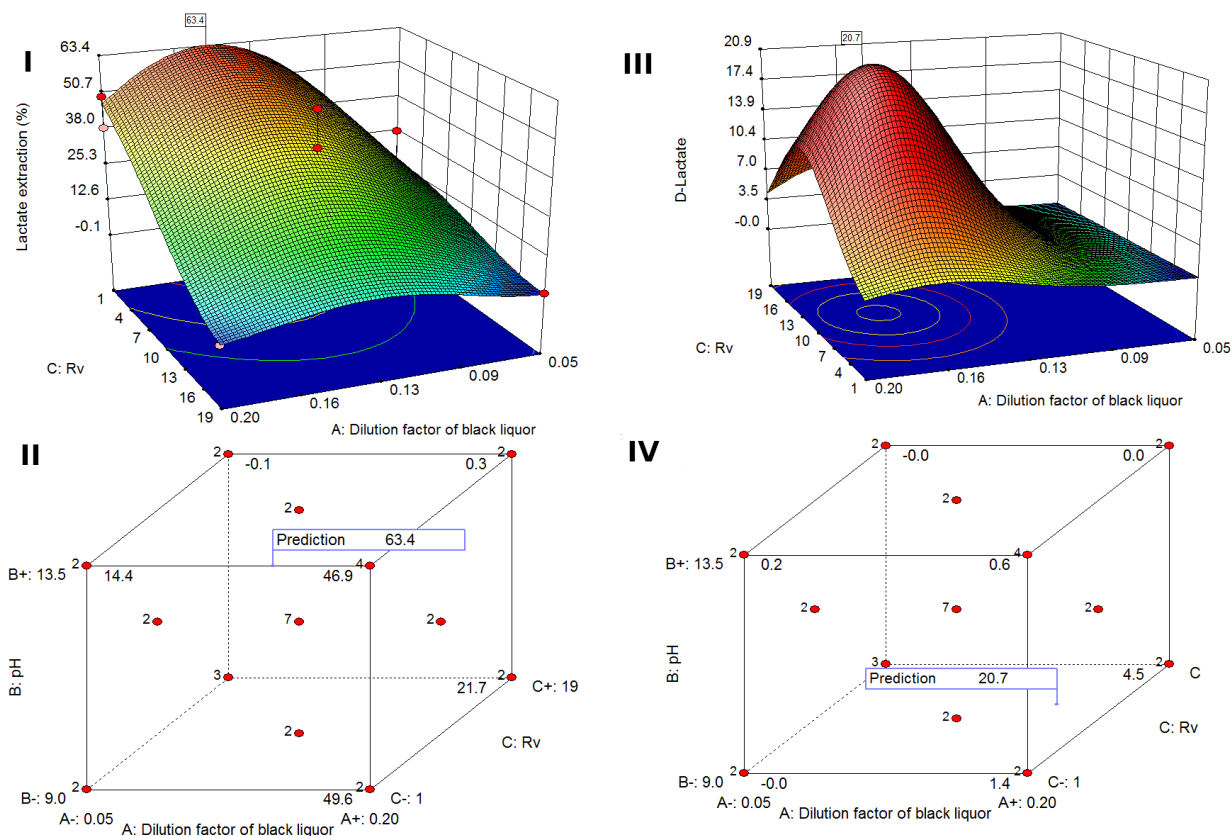
Figure 6. 3D (left side) and cubic (right side) representation for extraction of lactate (I-II) and its distribution coefficient (III-IV). Parameter values are indicated in Table 1. Blue, green, and red areas represents lower, intermediary and high values of responses, with 25-50-25 % of the maximal value, respectively.

Optimization of multi responses

Because lignin residues might be broken down to smaller polyphenolic units, valuable compounds with known biological activity, currently the most widely used antioxidant compounds in cosmetics for instance,[41] and because a black liquor only containing polysaccharides and organic acids would exhibit a much higher biodegradability and be much less of a hazardous solution, extracting lignin residues from black liquor towards an ionic liquid, while polysaccharides and organic acids remain in the black liquor, was investigated. Furthermore, in order to use black liquor in further biological processes, for example to degrade biologically such liquor, lignin fragments need be removed from BL, while organic acids, and polysaccharides remain in the liquor, as it provides a necessary feed material for living organisms.

The objective of this study is thus to obtain an extraction of polyphenolic part of the black liquor as high as possible as opposed to extraction of polysaccharides and organic acids. To that end, optimization of all responses was carried out simultaneously in a so-called multi-response optimization procedure. In such a procedure, values for factors R_V, pH and BLD were adjusted in order to yield optimized values for the two sets of responses, namely extraction percentage and distribution coefficients for all extracted compounds.

Under our experimental conditions, two constraints on pH and BLD were initially set. First, for convenience reasons, treating this aqueous phase without acidifying it was preferred. Furthermore, because black liquor exhibits very high concentrations of lignin residues, it is usually diluted several times with water. However, in order to avoid the production of too large volumes of effluent, a low dilution, that is, diluting black liquor 5 times, corresponding to a BLD value of 0.2 was chosen for the optimization process. Under those conditions and keeping in mind that the objective of the procedure is to obtain an extraction of PP as high as possible, unlike for PS and OA, multi-response optimization procedure was carried out in order to adjust R_V factor with set values of 13.5 and 0.2 for pH and BLD, respectively. Simultaneous optimization of all three extraction percentages, namely P_{PP}, P_{PS} and P_{OA} was first carried out, followed by a maximization of D_{PP} and minimization of D_{PS} and D_{OA} under the same conditions. Table 2 summarizes the results obtained. Optimum values for extraction percentages and distribution coefficients were obtained at values of 11.6 and 15.6 for R_V, respectively. These values for R_V indicate that one volume of IL was able to treat efficiently more than 10 times its volume in black liquor.

On the one hand, in agreement with our objective, PP was found to be extracted significantly, exhibiting a value of 84.8 % for the extraction percentage, while only a small fraction of organic acids was extracted towards the ionic liquid. On the other hand, lowest extraction value for polysaccharides obtained in this multi-response optimization procedure, was 66 % for P_{PS} and 31 for D_{PS}, implying a significant extraction of these compounds towards the ionic liquid. Please note that a value of 31 for D_{PS} implies that for an equal volume of black liquor and ionic liquid, the concentration of polysaccharides in ionic liquid will be 31 times higher than in black liquor, corresponding to an extraction of approximately 97 % of PS extracted. This important co-extraction between PP and PS

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could be explained by the fact that a fraction of PS is linked to PP as hemicellulose fraction, existing in original black liquor. Furthermore, because PP and PS are compounds with high molecular weight, with large hydrophobic domain in the case of PP, they are more easily transferred towards a hydrophobic ionic liquid. Satisfyingly, extraction experiments carried out under the conditions mentioned above, namely, with BLD and pH of 0.2, 13.5, respectively, and an R_V value of 11.6 or 15.6, accordingly, gave results very close to the ones calculated here, and in all case within the optimized value range calculated by the software.

In order to optimize further the extraction conditions, for instance in order to obtain a lower valued for P_{PS}, multiple-response optimization procedure was carried out by setting pH and BLD to values of 13.5 and 0.05, respectively. The value of 0.05 for BLD was selected because in agreement with the results detailed in section 3.6.2, values for PPS significantly below 66% are obtained with low BLD values. Results shown in Table 2 confirm that selecting a lower BLD value yields a much lower extraction of polysaccharides, namely 31 %, a result in better agreement with our objectives.

Finally, when letting the optimization procedure adjust all three factors, the multiple-response optimization procedure yields values of 94, 47 and 4 % for the extraction yields of PP, PS and OA, respectively, with values of 11.5, 0.05 and 1 for pH, BLD and R_V, respectively. This implies that despite a higher extraction of PP, nearly half of polysaccharides are also extracted towards the ionic liquid phase. In addition, R_V was adjusted to a value of 1, implying that an equal value of ionic liquid and BL is needed in such a case. This cannot be considered as a favorable condition compared to those presented in Table 2, where R_V values are always above 10.

These results show that lignin residues can be efficiently removed from a black liquor using an ionic liquid such as $[P_{66614}]Cl$. Polysaccharides are also extracted, though to a lesser extent. The amount of polysaccharides extracted can be significantly reduced by a factor of 2, by diluting four times the aqueous, that is, by changing BLD from 0.2 to 0.05. Organic acids, unlike lignin residues and polysaccharides, remain mostly quantitatively in the aqueous phase.

Table 2. Optimization of multi-responses for extraction percentage and distribution factor with fixed values for both BLD and initial pH

Responses		Optimized value	Optimized value range	Exp. value
pH = 13.5; BLD = 0.2	R_V = 11.6			
P_{PP}	Maximize	84.8	82.1 – 99.5	88.2
P_{PS}	Minimize	66.0	22.0 – 79.1	72.3
P_{OA}	Minimize	16.7	0 – 68.0	0
pH = 13.5; BLD = 0.2	R_V = 15.6			
D_{PP}	Maximize	104	34 – 317	125
D_{PS}	Minimize	31.5	13.3 – 74.7	22.5
D_{OA}	Minimize	0.14	0 – 7.34	0
pH = 13.5; BLD = 0.05	R_V = 15.6			
P_{PP}	Maximize	88.0	34 – 317	-
P_{PS}	Minimize	31.0	13.3 – 74.7	-
P_{OA}	Minimize	1.58	0 – 7.34	-

Conclusion

In order to propose new ways of recycling wastewater from pulping factory, so-called black liquor, extraction of lignin residues, polysaccharides and organic acids from black liquor, towards an phosphonium-based ionic liquid, $[P_{66614}]Cl$, was studied. The influence of the initial pH of the black liquor, the dilution in water of black liquor and the volume ratio of black liquor vs. ionic liquid on the extraction of three family of compounds, namely polyphenolic polymers, polysaccharides and organic acids, was considered. It appears that polyphenols are generally extracted along with polysaccharides, unlike organic acids that remain preferably in the aqueous phase.

Results were then modeled according to a design of experiment approach. Response Surface Methodology was used to describe extraction percentage and distribution coefficient of all three compounds. Single responses were successfully optimized, describing accurately experimental data gathered in this work.

In order to provide a black liquor mostly depleted from lignin residues, hence further treatable by simple recycling processes, multi-response optimization procedure was carried out with varying initial conditions. When setting pH, R_V and BLD to 13.5, 15.2 and 0.2, respectively, values simplifying the pretreatment of black liquor prior to extraction, 85, 66 and 0 % of lignin residues, polysaccharides and organic acids, respectively, were found to be extracted from the aqueous phase. When black liquor was diluted 20 times, (BLD 0.05), 88, 31 and 1.6 % of PP, PS and OA were extracted, respectively. Finally, highest extraction of lignin residues was possible by reducing the initial pH of black liquor down to 11.25. Good agreement was found between the expected values optimized using a design of experiment and experimental ones.

The work presented here therefore proposes three different ways of pretreatment of black liquor, by removing efficiently polyphenols. Further recycling of resulting black liquor, depending in these different optimized conditions proposed here will be carried out shortly. So far, ionic liquid was successfully reused as an extracting phase four times by contacting it with fresh black liquor, without any treatment for removing PP or PS, without any observable los of extraction efficiency. Finally, ways to recover the lignin fragments within the ionic liquid, for example using contacting the ionic liquid with an acidic aqueous solution, as well as ways to break down lignin part to exploitable polyphenolic units is currently under investigation and should be reported shortly.

Experimental Section

Chemicals

Ionic liquid trihexyl(tetradecyl)phosphonium chloride ($[P_{66614}]Cl$) was purchased from Solvionic, and used as received. Stock solution of black liquor resulted from a heat-pressure-basic treatment of pine wood (30% NaOH g/g dry wood, 1% anthraquinone, 175°C, 60 min). It was stored in

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a fridge at low temperature (4-6°C). Regarding extraction experiments, diluted samples were prepared from this stock solution using distilled water, with three dilution factors: 0.050, 0.125, and 0.200. Dilution factor will hereafter be named as black liquor dilution (BLD) and is defined as the volume of initial black liquor used and completed to 1 ml of distilled water. A dilution factor of 0.05 of black liquor, therefore, corresponds to 0.05 mL of BL diluted in 1 mL of distilled water. pH was adjusted with diluted sulfuric acid before final dilution.

Analytical methods

Analyses are exclusively carried out on the aqueous phase. pH is estimated with an Electrode Inlab Semi Micro, connected to a pH-meter (Crison GLP21, sensitivity of 0.01 pH). Measurement is performed in a small working volume (200μl). Variation of pH is calculated as the difference between initial pH and final pH measured after extraction by ionic liquid.

Because of an impossibility to quantify separately all residues resulting from the lignin degradation within the Kraft process, concentration of these water soluble lignin residues is measured in accordance to the Lowry-Ciocalteu method,[42] classically used in order to quantify polyphenolic compounds. Therefore, in the following manuscript, these residues will be discussed in terms of polyphenolic equivalent (PP).

Concentration of polysaccharides (PS) is measured using the anthrone method.[43] Optical density is monitored using a double-beam molecular adsorption spectrophotometer (Shimadzu UV-2501PC, Jasco V-530 software).

Concentration of organic acids (OA) is represented by its major compound, namely lactic acid, as analyzed according to the following HPLC methodology. Lactate concentration is quantified by HPLC (Agilent Technologies, 1260 Infinity, Refractive Index detector) using a Hi-Plex H column (Agilent). Eluent is a sulfuric acid solution (0.05 M). Aqueous samples are firstly filtered (nitrocellulose filter, 0.45μm) in order to remove all solid particles. The analyses are carried out at 65°C on the filtered aqueous solutions, prior and after ionic liquid extraction. They are diluted 10 times with distilled water before HPLC analysis. No effect of matrices, due to the chemical complexity of BL, is observed during quantitative determination of each compound.

From these concentrations, distribution coefficients (D) and global extraction percentages, P, all three types of compounds studied here are calculated according to eqs. (2) and (3):

$$D = \frac{(c_i - c_f) * R_v}{c_f} \quad (2)$$

$$P = \frac{(c_i - c_f) * 100}{c_i} \quad (3)$$

with C_i, the initial compound concentration (PP, PS or OA) in initial BL phase, C_f the final compound concentration in BL phase after extraction run, and R_V, the volume ratio of aqueous phase vs. ionic liquid. In the following, D_{PP}, D_{PS} and D_{OA} correspond to the distribution coefficients for PP, PS and OA respectively. P_{PP}, P_{PS}, and P_{OA} refer to the global extraction percentages for PP, PS and OA respectively.

General extraction protocol

All extraction experiments are carried out in sterile polypropylene tubes (2 ml) at room temperature (26±2°C). Black liquor is manipulated using normal micropipettes and the ionic liquid is manipulated with a positive-displacement micropipette (Microman R). Typically, a sample of 100-1000 μL of aqueous solution is added to a microtube, followed by the ionic liquid.

The microtube is mechanically shaken during 30 s with a Vortex mixer. Emulsion is formed after stirring. It is broken by centrifugation as previously described in the case of L-lactic extraction by phosphonium ionic liquid[44] (i.e. centrifugation at 13,000 rpm during 5 minutes). In all extraction experiments, the bottom phase is the aqueous phase because the density of diluted black liquor is 1.096 g.mL-1, a value higher than that of 0.882 g.mL-1 obtained at 25 °C for undiluted [P$_{66614}$]Cl.[45]

An aliquot of the aqueous phase at the bottom of the tube is taken by making a hole in the microtube with a sterile needle and transferred in a new sterile microtube for further analysis.

Experimental Design

Table 3 summarizes the experimental ranges for the three studied continuous factors: dilution factor of black liquor, hereafter named BLD, pH, and volume ratio of liquor vs. ionic liquid, so-called R_V. Ranges for the parameter values studied here were selected according to the following general objectives: i) to modify as little as possible the initial black liquor prior to its extraction using an ionic liquids and ii) to reduce the amount of chemical and liquid phases needed for extracting lignin residues, polysaccharides and organic acids. The amount of ionic liquid was thus always considered smaller than that of BL. R_V values ranging between 1 and 19 were thus studied. The initial pH value for black liquor is known to be around 13. In order to study the influence of pH without introducing too large quantities of acids, values for the initial pH ranging between 9 to 13.5 were thus studied. Finally, because black liquor is extremely concentrated and is always diluted, BLD range was fixed between 0.2 and 0.05, corresponding to BL diluted 5 and 20 times, respectively.

A Central composite design (CCD) of experiments is applied using the statistical software Design Expert 8.0 (Stat Ease, Minneapolis, USA). A 35-experiment containing matrix is obtained with 7 repeated experiments to determine experimental error (runs 16/22/24/25/27/30/32 of Table S1 of the SI file). Repeated experiments are situated at the center of the studied area. This central location on the design of experiment corresponds to experimental values of 0.125, 11.25 and 10 for BLD, pH and R_V, respectively and coded values of 0 within the design of experiment.

For each compound under study, two different final objectives were pursued. First, one may look for a high extraction percentage, no matter the volume of ionic liquid which would be required for this or one may look for a high distribution ratio, a parameter which depends on R_V. In order to match these two different goals, six different responses were individually examined: three global extraction percentages (P_{PP}, P_{PS}, and P_{OA}) and three distribution coefficients (D_{PP}, D_{PS}, and D_{OA}). Additionally, variation of pH of the aqueous solution after IL extraction was analyzed.

Table 3. Chemical and physical factor ranges studied in the Central Composite Design (CCD).

Factor	Name	Min.	Max.	Coded values	Coded values	Coded values
A	BLD	0.050	0.200	-1 =0.050	0 =0.125	1 =0.200
B	pH	9.00	13.50	-1 =9.00	0 =11.25	1 =13.50
C	R_V	1	19	-1 =1	0 =10	1 =19

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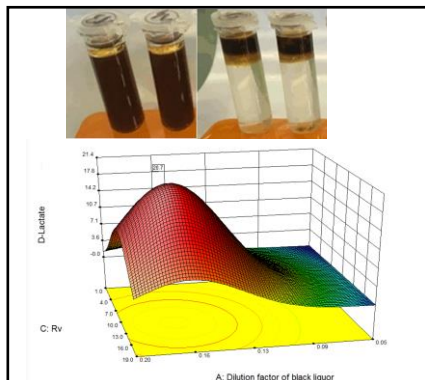
Selective removal of polyphenolic polymers, polysaccharides and organic acids present in pulping factory wastewater, so-called black liquor, was studied using an ioniliquid tetrahexylphosphonium chloride. Optimised conditions were obtained using a design of experiment methodology with three variables, namely black liquor pH, dilution factor and water to ionic liquid ratio.

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