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Title	Polyphenol, polysaccharide and lactate extraction from pulping factory black liquor by ionic liquids.
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Abstract

Extraction of polyphenols, polysaccharides and organic acids present in a liquor issued from a pulping factory, so-called black liquor, was studied using two ionic liquids trihexyltetradecylphosphonium chloride ([P66614]Cl) and trihexyltetradecylphosphonium bromide ([P66614]Br). The extraction of each of the three compounds mentioned above was reported as a function of the dilution of the initial black liquor, the volume ratio of liquor vs. ionic liquid, and the initial pH of the black liquor. Polyphenols and polysaccharides were quantitatively extracted at room temperature with both ionic liquids. Extraction of lactate anions was found to be low, exhibiting distribution coefficients below 8 in all cases.

Keywords black liquor; ionic liquid; polyphenol; lactate; polysaccharides; extraction

Manuscript category Extraction & purification of natural materials

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April 17, 2017

Editorial Board

Separation and Purification Technology

Dear Sir/Madam,

On behalf of all co-authors, I have the pleasure of submitting the manuscript entitled "Polyphenol, polysaccharide and lactate extraction from pulping factory black liquor by ionic liquids" to Separation and Purification Technology journal.

This original work described has not been published before and it is not under consideration for publication anywhere else. Its publication has been approved by all co-authors.

This paper presents the first report providing information on the application of ionic liquids as extracting phase for complex chemical compounds, namely polyphenols, polysaccharides, and organic acids, that are present together in a real aqueous effluent from a pulping factory, so-called black liquor. Trihexyltetradecylphosphonium chloride ($[P_{66614}]Cl$) and trihexyltetradecylphosphonium bromide ($[P_{66614}]Br$) ionic liquids were used as extracting phases. The influence of the dilution of the initial black liquor and the volume ratio of liquor vs. ionic liquid on the extraction of each of the three compounds mentioned above was studied. Polyphenols and polysaccharides were found to be quantitatively extracted at room temperature with both ionic liquids. On the opposite, extraction of lactate anions was found to be low.

Because the article deals with the extraction of chemical species from an aqueous effluent and because to the best of our knowledge; no similar work dealing with the use of ionic liquids to extract organic compounds from such complex solutions, we believe this manuscript falls within the scope of your journal and that it will interest its readers.

Yours Sincerely,

Nicolas Papaiconomou

Highlights

Soda pulping factory black liquor contained high concentrations of polyphenols.

Phosphonium based ionic liquids extracted polyphenols from black liquor.

[P66614]Cl and [P66614]Br were both studied for extraction characterization.

Lactate and polysaccharides were also co-extracted but with a lower efficiency.

[P66614]Cl showed better polyphenol extraction capacities than [P66614]Br.

Polyphenol, polysaccharide and lactate extraction from pulping factory black liquor by ionic liquids.

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Abstract

Extraction of polyphenols, polysaccharides and organic acids present in a liquor issued from a pulping factory, so-called black liquor, was studied using two ionic liquids trihexyltetradecylphosphonium chloride ([P66614]Cl) and trihexyltetradecylphosphonium bromide ([P66614]Br). The extraction of each of the three compounds mentioned above was reported as a function of the dilution of the initial black liquor, the volume ratio of liquor vs. ionic liquid, and the initial pH of the black liquor. Polyphenols and polysaccharides were quantitatively extracted at room temperature with both ionic liquids. Extraction of lactate anions was found to be low, exhibiting distribution coefficients below 8 in all cases.

Keywords: black liquor, [P66614]Cl, polyphenol, lactate, polysaccharides, extraction, distribution coefficient

1. Introduction

The pulping industry is the main actor in terms of biomass consumption tonnage and also in final product amounts [1-4]. The principal product, represented by the paper, is coupled with the production of a large amount of black liquor. The black liquor consists of a basic solution (pH close to 12-13) containing polysaccharides, organic acids, and polyphenols, these latter giving the black color to the solution. Polysaccharides came from cellulose and hemicellulose component. Organic acids are produced during NaOH-based treatment at high temperature according to the peeling reaction. Polyphenols and other cyclic components are issued from the degradation of the lignin part. The chemical composition of black liquor depends on the nature of the pretreatment and the nature of treated wood. For example, Kraft pretreatment leads to the presence of sulfur compounds in the black liquor. Currently, the black liquor solution is incinerated or gaseified, after a preliminary dehydration step, to assure energetic autonomy of pulping factories.

Polysaccharides, polyphenols and organic acids present in black liquor can have a better end. In particular, polyphenolic compounds are valuable starting materials in the pharmaceutical industry, while organic acids and polysaccharides might be used as feeding mixtures for various bacteria. However, the presence of polyphenols, molecules having a strong antioxidant activity, leads to a weak biodegradability. Only few fungi and bacteria are able to degrade them. Consequently, the extraction of polyphenols –instead of their degradation– from the black liquor solution is a necessary step in order to increase the accessibility to polysaccharides and organic acids to further biological treatments, without losing the potential of reuse of polyphenols.

Ionic liquids (ILs) are molten salts with melting temperatures below 100°C. Their versatile physico-chemical properties render them interesting liquid media in several domains, such as catalysis, liquid/liquid extraction of ions, organic synthesis etc. Recently, ionic liquids have been used as new solvents for pretreatment of lignocellulosic biomasses (switch-grass, wheat straw, corn stover, bagasse, ...) [5-10] but very few studies have already appeared on the use of ILs for the selective extraction of compounds present in such complex systems as black liquor [11]

Therefore, the aim of this study was to compare and characterize the efficiency of two ILs, based on phosphonium cation associated with either Br⁻ or Cl⁻ anions, to extract polyphenolic compounds from pulping black liquor. The contingent co-extraction of polysaccharides and organic acids was also examined, in order to assess the ability of the ILs under study to provide an post-treatment aqueous solution of interest for other bio or chemical usages.

2. Materials and methods

2.1 Chemicals

Ionic liquid trihexyl(tetradecyl) phosphonium chloride ([P₆₆₆₁₄]Cl) was purchased from Solvionic and trihexyl(tetradecyl) phosphonium bromide [P₆₆₆₁₄]Br was purchased from Cytec Solvay Group. Both ionic liquids were used as received. Concentrated chloridric acid was furnished by Aldrich.

The stock solution of black liquor resulted on a heat-pressure-basic treatment of pine wood (30% NaOH (g/g dry wood, 1% anthraquinone, 175°C, 60 min). It was stored at low temperature (4-6°C). For the extraction experiments, diluted samples were prepared from this stock solution using distilled water, with dilution factors ranging from 0.67 to 10. In the following, they are indicated as BL_x, where x corresponds to the dilution factor. In the text, these BL_x samples will also be referred to as aqueous solutions.

2.2 Analytical methods

Analyses were exclusively carried out on the aqueous phase.

pH was measured with a pH-meter (Crison GLP21, sensitivity of 0.01 pH) associated with an Electrode Inlab Semi Micro allowing to measure pH in a small working volume (200 µl).

Polyphenol (PP) and polysaccharide (PS) concentrations were determined according to the Lowry-Ciocalteu method [12] and anthrone based method [13], respectively. Non filtered samples were analysed after previous dilution in order to obtain

Optical density was measured with the help of a double-beam molecular adsorption spectrophotometer (Shimadzu UV-2501PC, software Jasco V-530).

Lactate concentration was quantified by HPLC (Agilent Technologies, 1260 Infinity, Refractive Index detector) using a Hi-Plex H column (Agilent). Eluant was constituted by a sulfuric acid solution (0.05 M). The analyses were carried out at 65°C on the filtered aqueous solution, prior and after ionic liquid extraction. Aqueous sample were firstly filtered (nitrocellulose filter, 0.45µm), in order to remove all nefaste particules for the HPLC column. They were 10-time diluted with distillated water before HPLC analysis.

The concentration of polyphenolic compounds, characteristics of lignin, was reported in this study as equivalent of concentration of ferulic acid, due to the impossibility to experimentally quantify separately all polyphenolic compounds. Similarly, the charge of organic acids was represented by the major compound, lactic acid, as analyzed according to the previously described HPLC methodology. On the contrary, the measured concentration of saccharides was directly issued from polysaccharides after a basic hydrolysis of them, according to the described methodology. The data given in this study might therefore not be representative of the exact and accurate concentration of all polyphenols or organic acids in the black liquor. In the following, the terms polyphenols (PP), polysaccharides (PS) and organic acids (OA), will be used to refer to these quantities.

None effect of matrice, due to the chemical complexity of BL, was observed during quantitative determination of each compounds.

From these concentrations, distribution coefficients (D) for polyphenols, polysaccharides, and organic acids were calculated according to:

$$D = \frac{(C_i - C_f) * R_v}{C_f} \quad (1)$$

with C_i , the initial compound concentration, C_f the final compound concentrations, and R_v , the volume ratio of ionic liquid vs. aqueous solution. In the following, D_{PP} , D_{PS} et D_{OA} correspond to the distribution coefficients for PP, PS and OA respectively.

2.3 General extraction protocol

All extraction experiments were carried out in sterile polypropylene tubes (1.5 or 2 ml) at room temperature. Black liquor was manipulated using normal micropipettes and ionic liquids were manipulated with a positive-displacement micropipette (Microman R). Typically, a sample of 100-1000 µL of aqueous solution was added to a microtube, followed by the ionic liquid.

The microtube was mechanically shaken during 30 sec with a Vortex mixer. Emulsions were formed for both ionic liquids after stirring. They were broken by centrifugation as previously described in the case of L-lactic extraction by phosphonium ionic liquid [14]. (i.e. centrifugation at 13,000 rpm during 5 minutes). In all extraction experiments, the bottom phase was the aqueous phase because the density of diluted black liquor is 1.096 g.mL⁻¹, a value higher than that of [P₆₆₆₁₄]Cl or [P₆₆₆₁₄]Br, that exhibit densities of 0.882 and 0.955 g.mL⁻¹, respectively.[15]

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

On this general basis, several experimental parameters were varied, one at a time, as detailed below.

2.4 Influence of dilution factor

The influence of the dilution of the black liquor with distillated water on the extraction of PP, PS and OA with both ILs was studied using a constant value (10%) for the volume ratio between the aqueous phase and the IL, denoted as R_v ($R_v = V_{BL}/V_{IL}$). Please note that high concentrations of compounds (PP, PS or OA) correspond to a low dilution factor of the black liquor.

2.5 Influence of volume ratio, R_v

The influence of R_v ($R_v = V_{BL}/V_{IL}$), on the extraction of PP, PS and OA with both ILs was studied using a constant dilution factor equal to 10 (BL_{10}). R_v ranged between 0.67 and 10.

2.6 Influence of initial pH

The influence of the initial pH was tested by adding a mineral acid HX. In order to limit the number of ions in the samples, the H^+ counter-anion X should be identical to the anion of the IL under study. The use of concentrated hydrochloric acid being more easy than that of hydrobromic acid, this experimental series is only performed for $[P66614]Cl$. Experiments were carried out on BL_{10} and with R_v ratio of 10. Low variation in BL volume, inferior to 2.5%, was due to the addition of concentrated HCl.

2.7 Two consecutive extraction steps

Successive extractions were carried out by re-using either the same ionic liquid or the same black liquor solution.

For reuse of BL_{10} , a first extraction was carried out with a R_v value of 10. Then, the BL_{10} phase was picked up as previously described and a known volume was re-injected in a new sterile microtube. A 10% volume of fresh ionic liquid was added. Similar extraction protocol as previously described was realized (stirring, centrifugation, and pick-up). After centrifugation, aqueous phase was picked-up and analyzed.

For reuse of ionic liquid, a first extraction was carried out with $R_v = 10$ and BL_{10} . The upper organic phase was picked-up with the displacement positive micropipette, and re-introduced in a new microtube and contacted with fresh BL_{10} , maintaining $R_v = 10$. Previously described protocol concerning stirring, centrifugation, pick-up, and analysis was applied.

These two protocols were applied for the two ionic liquids.

The global extraction, $P_{extract}$, of a compound by ionic liquid was defined as

$$P_{extract} = (C_i - C_f) * \frac{100}{C_i}$$

where C_i is the initial compound concentration (PP, PS or OA) in initial BL_{10} phase, C_f the final concentration in BL phase after the second run.

3. Results

According to the analysis protocols detailed in the previous section, the initial black liquor solution studied here and issued from a laboratory paper milling process was found to contain 30 g L⁻¹ of PP, 23 g L⁻¹ of PS and 19 g L⁻¹ of OA. The deep black color of the liquor is related to the large amount of polyphenols present in the solution.

In all extraction experiments, upon contacting an ionic liquid with a black liquor sample, a marked change in color was observed within 30 s. The aqueous solution became yellow or translucent while the ionic liquid turned brown or black depending on the experimental conditions. This change in color was observed for both $[P_{66614}]Cl$ and $[P_{66614}]Br$.

3.1 Influence of initial dilution of the black liquor

Extraction experiments were carried out starting from black liquor diluted from 2 to 20 times. In all experiments, the proportion of polyphenols, polysaccharides and organic acids contained in the black liquor remained identical. Results are given in Figures 1 to 3.

A first observation is that the extraction of polyphenols (PP) appears to be high whatever the conditions (Fig. 1). $[P_{66614}]Cl$ is more efficient for polyphenol extraction than $[P_{66614}]Br$. The distribution coefficient for polyphenols (D_{PP}) range from 100 to 180 for $[P_{66614}]Cl$ and from 24 to 35 for $[P_{66614}]Br$. Extraction appears to be mostly constant for $[P_{66614}]Cl$ at concentration of PP

ranging from 2000 to 16000 mg L⁻¹. Only at 1600 mg L⁻¹, the value for D_{PP} is higher than those observed at higher concentrations. For [P₆₆₆₁₄]Br, D_{PP} values are fairly constant at 31.6 ± 6.6. The extraction of polysaccharides towards [P₆₆₆₁₄]Cl is also efficient (Fig. 2). D_{PS} values range from 30 to 95. In the case of [P₆₆₆₁₄]Br, D_{PS} values are lower, ranging from 6 to 20. No clear trend in the distribution coefficient for polysaccharides with respect to their concentration can be observed. Unlike PP or PS, organic acids were extracted much less efficiently. D_{OA} values ranged from nearly 1 to 8 whatever the ionic liquid. The extraction appeared to increase with the initial concentration of organic acids.

As a general trend, polyphenols are extracted similarly to or better than polysaccharides, while organic acids are the least extracted species of the three compounds under study.

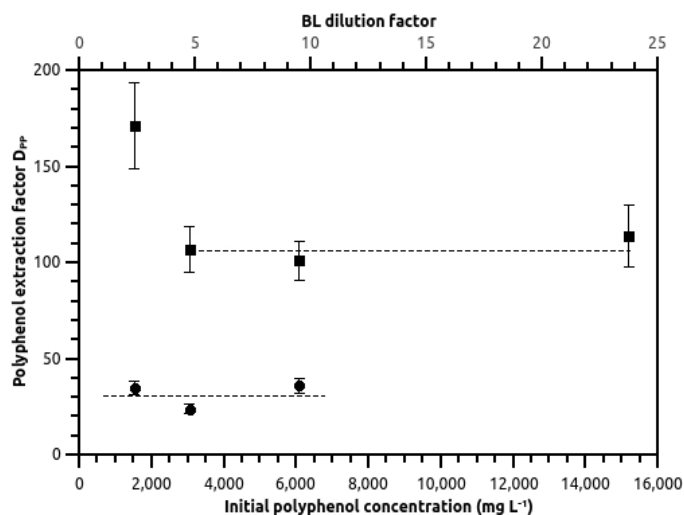


Figure 1: Distribution coefficients for polyphenols extracted towards an ionic liquid plotted against the initial concentration of polyphenols. Squares: [P₆₆₆₁₄]Cl. Circles: [P₆₆₆₁₄]Br. R_v = 10 and initial pH was equal to 12.71.

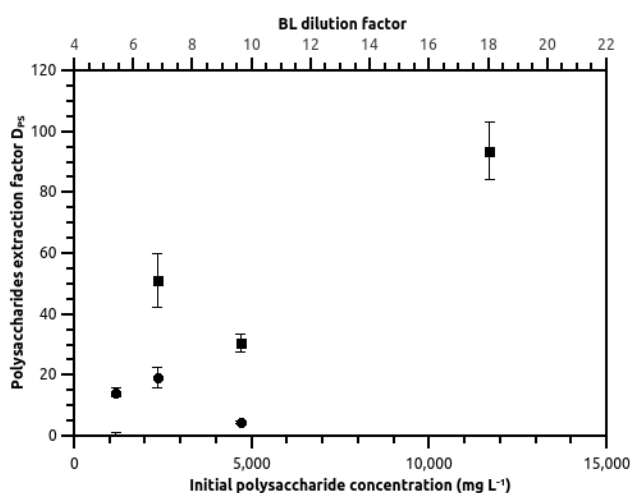


Figure 2: Distribution coefficients for polysaccharides extracted towards an ionic liquid plotted against the initial concentration of polysaccharides. Squares: [P₆₆₆₁₄]Cl. Circles: [P₆₆₆₁₄]Br.

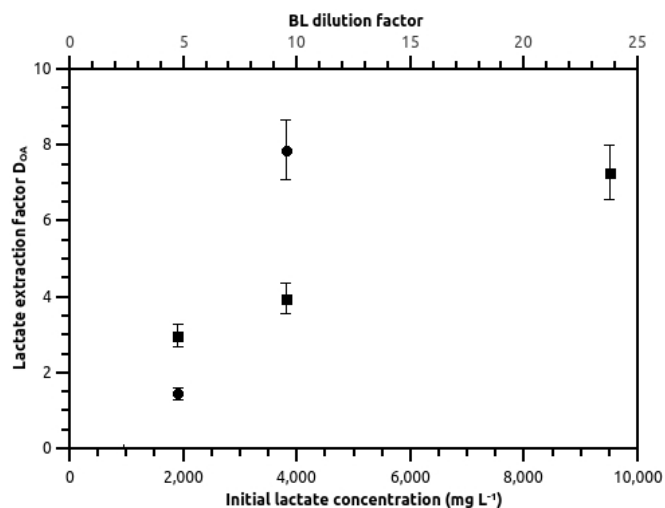


Figure 3: Distribution coefficients for organic acid extracted towards an ionic liquid plotted against the initial concentration of organic acid. Squares: [P₆₆₆₁₄]Cl. Circles: [P₆₆₆₁₄]Br.

3.2 Influence of R_v

Extraction was carried out using ratio of black liquor vs. ionic liquid ranging from 2 to 10. The black liquor solution used for this set of extraction experiments was diluted 10 times prior to extraction and will be denoted as BL₁₀. Results for the D values for PP, PS and OA with respect to R_v are collected in figures 5 to 7.

Snapshots of extraction experiments carried out using different R_v values and using BL₁₀ and the two ILs are presented in Figure 4.

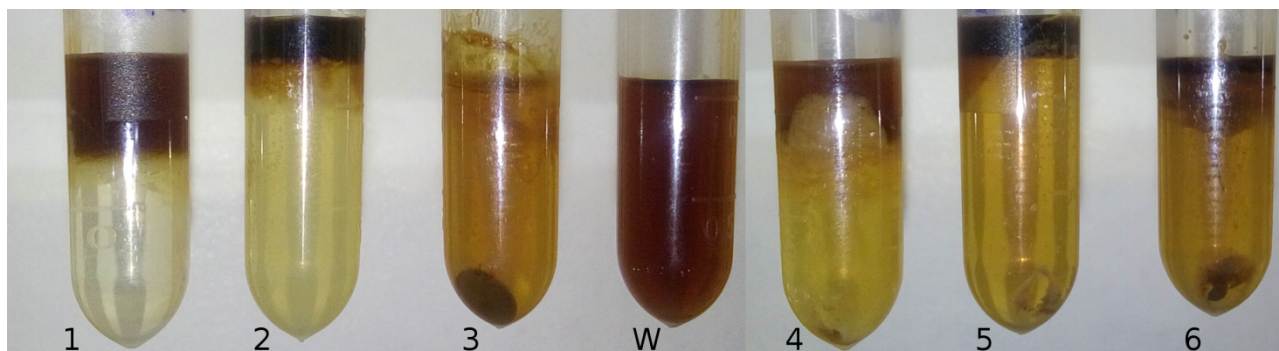


Figure 4: snapshots for the extraction of BL₁₀ using ionic liquids [P₆₆₆₁₄]Cl and [P₆₆₆₁₄]Br. Position W: BL₁₀ alone. Positions 1 to 3: After BL₁₀ extraction using [P₆₆₆₁₄]Cl with a R_v value of 2, 6.66, 10, respectively. Positions 4 to 6: After BL₁₀ extraction using [P₆₆₆₁₄]Br with a R_v value of 2, 6.66, 10, respectively.

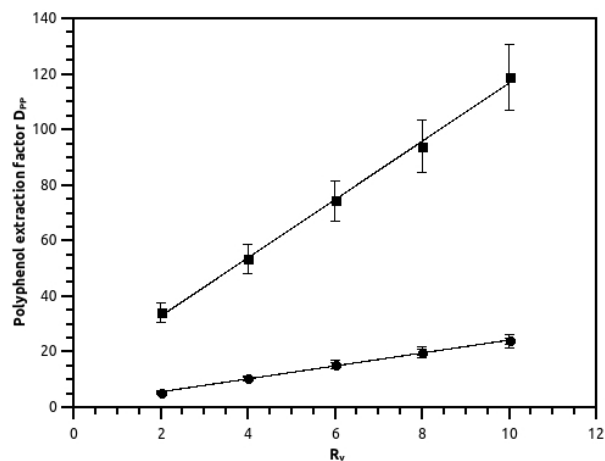


Figure 5: Distribution coefficients for polyphenols extracted towards an ionic liquid plotted against R_v . Squares: [P₆₆₆₁₄]Cl. Circles: [P₆₆₆₁₄]Br. Lines are guides to the eye.

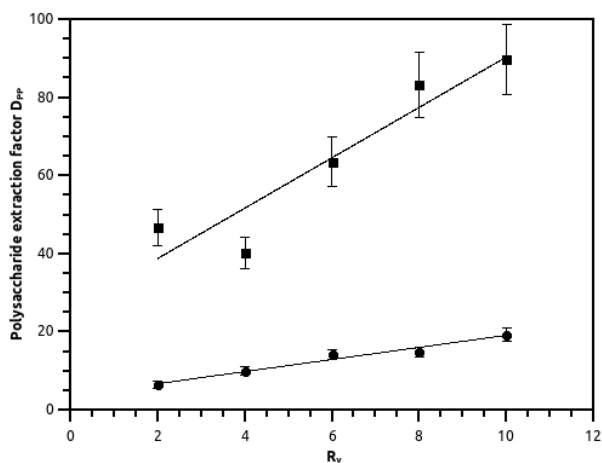


Figure 6: Distribution coefficients for polysaccharides extracted towards an ionic liquid plotted against R_v . Squares: [P₆₆₆₁₄]Cl. Circles: [P₆₆₆₁₄]Br. Lines are guides to the eye.

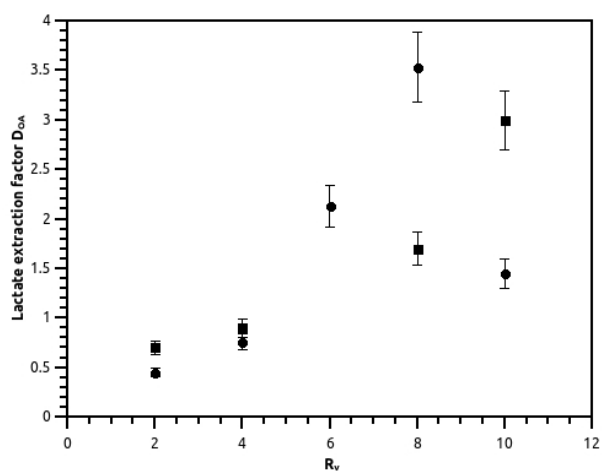


Figure 7: Distribution coefficients for organic acids extracted towards an ionic liquid plotted against R_v . Squares: [P₆₆₆₁₄]Cl. Circles: [P₆₆₆₁₄]Br.

As mentioned above, [P₆₆₆₁₄]Cl appears to be better at extracting polyphenols than its bromide homologue. Values for the distribution coefficients of the polyphenols are found to range from 32 to 120 and from 5 to 20 for [P₆₆₆₁₄]Cl and [P₆₆₆₁₄]Br, respectively. Moreover, the extraction increases almost linearly with the volume ratio. That is, the larger the volume of black liquor, the higher the extraction of polyphenols.

Similarly, polysaccharides are best extracted using [P₆₆₆₁₄]Cl. Values ranging from 40 to 90 and from 6 to 20 are obtained using [P₆₆₆₁₄]Cl and [P₆₆₆₁₄]Br, respectively. Once again, D increases with R_v in an almost linear way.

The distribution coefficient for organic acids, on the contrary, never reaches the value of 4, whatever R_v. In addition, an increase in D with R_v is observed for [P₆₆₆₁₄]Cl, while in the case of [P₆₆₆₁₄]Br, D increases up to 3.5 for R_v = 8 and then drastically decreases to reach a value of 1.4 for R_v = 10. Again, organic acids appear to be the least extracted among all three compounds studied in this work.

Overall, two different trends in extraction are observed depending on the ionic liquid used. The distribution coefficients of the three organic compounds (D_{PP}, D_{PS} and D_{OA}) under investigation followed the order:

$$\begin{array}{ll} D_{PP} \approx D_{PS} > D_{OA} & \text{for [P}_{66614}\text{]Cl} \\ D_{PS} > D_{PP} > D_{OA} & \text{for [P}_{66614}\text{]Br} \end{array}$$

3.3 Successive extraction steps

This set of experiments was carried out in order to see whether the same sample of ionic liquid could be used several consecutive times as an extracting phase or whether extracting consecutively a sample of black liquor with two different samples of ionic liquid would increase the increase the extraction.

Two successive extraction experiments using two black liquor samples and the same aliquot of ionic liquid was first carried out, as detailed in the experimental section. The distribution coefficients for PP, PS and OA at the end of each step are shown in Figure 10. Under these conditions, D_{PP} and D_{PS} decrease when using [P₆₆₆₁₄]Cl. D_{PS} decreases in a more pronounced way, changing from 82 to 17 after the 1st and 2nd extraction step respectively. For [P₆₆₆₁₄]Br, D_{PP} values are similar in step 1 and 2, while D_{PS} values decrease from 35 down to 9.

By contrast, for both ionic liquids, D_{OA} values start from approximately 2 and increase to 10 or 15 using [P₆₆₆₁₄]Cl or [P₆₆₆₁₄]Br, accordingly. When the same BL₁₀ sample is extracted twice using two different aliquots of the same ionic liquid (fig. 11), results are mostly the same as those discussed above.

When extraction of the same black liquor sample using two different ionic liquid samples is carried out, results are different, as shown in Figure 11. D_{PP} and D_{PS} decrease drastically during the second extraction step using [P₆₆₆₁₄]Cl. Using [P₆₆₆₁₄]Br, D_{PP} decreases also very sharply while D_{PS} varies from approximately 35 to 24 between the two extraction steps. On the opposite, and as observed above, the value for DOA obtained in the first extraction step is lower than that obtained in the second extraction step. Final concentrations of polyphenol, polysaccharide, and organic acid in the aqueous phase and their respective global extraction yield, P_{extract}, calculated as detailed in the experimental section for the experiments involving the same black liquor sample are summarized in Table 1.

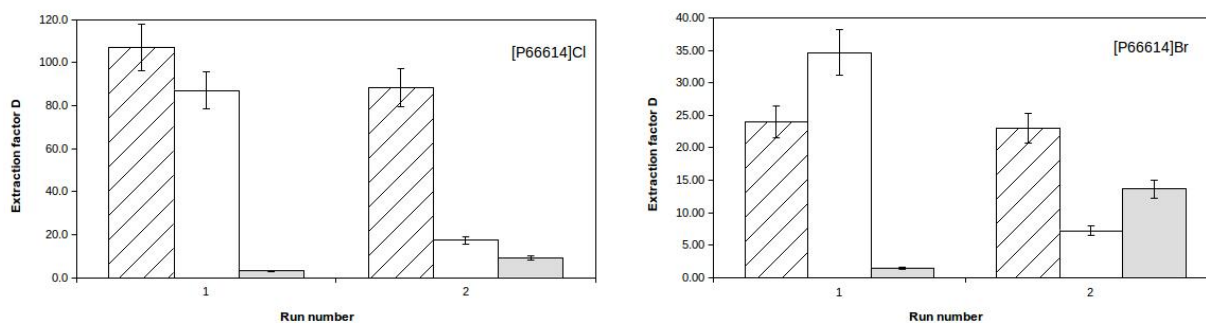


Figure 10: Evolution of extraction capacity of two ionic liquids ([P₆₆₆₁₄]Cl (left graph), [P₆₆₆₁₄]Br (right graph), during two successive extraction steps using two black liquor samples (BL₁₀) and one ionic liquid sample: polyphenols (hashed gradient), polysaccharides (white), and lactate (grey).

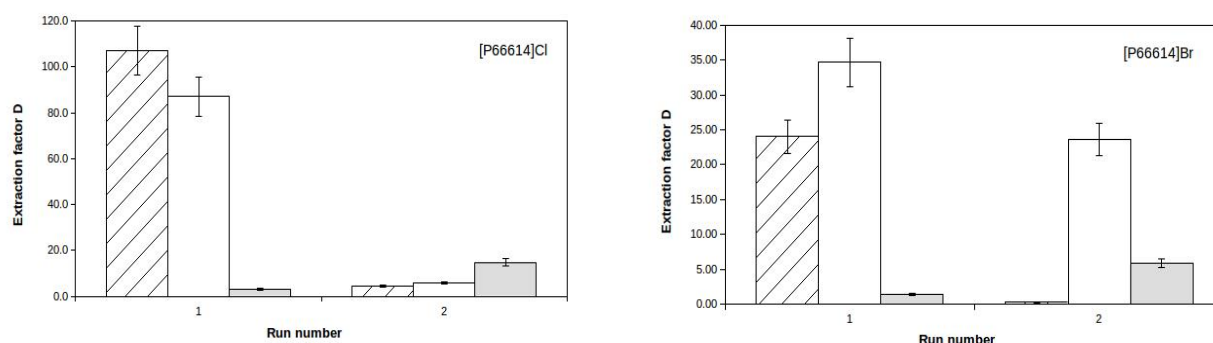


Figure 11: Evolution of extraction capacity of two ionic liquids ([P₆₆₆₁₄]Cl (left graph), [P₆₆₆₁₄]Br (right graph), during two successive extraction steps using the same diluted black liquor (BL₁₀) sample and two fresh ionic liquids: polyphenols (hashed gradient), polysaccharides (white), and lactate (grey).

Ionic liquid	Compounds	Extraction using twice the same black liquor sample	
		Final concentration (mg L ⁻¹)	Global extraction yield P _{extract} (%)
[P ₆₆₆₁₄]Cl	PP	181	94.1
	PS	152	93.5
	OA	589	69.0
[P ₆₆₆₁₄]Br	PP	868	71.5
	PS	156	93.3
	OA	1045	45.0

Table 1: Final concentrations of polyphenols (PP), polysaccharides (PS), and lactate (OA) and total percent of extraction after two extraction runs according to the reuse of ionic liquid phase or BL phase. Initial concentrations of PP, PS, and OA were 3038, 2337, and 1900 mg L⁻¹, respectively.

4. Discussion

A first striking result of this study lies in the fact that for the same cation of a phosphonium-based ionic liquid, a slight change in the nature of the anion, from Cl⁻ to Br⁻ for instance, has a significant influence on the extraction of PP, PS and OA. PP and PS, for instance, are significantly better extracted using [P₆₆₆₁₄]Cl than [P₆₆₆₁₄]Br. This is in opposition with previous results dealing with the extraction of metal ions such as Pd(IV) or Rh(III) towards the same ionic liquids. In these cases, these results were explained by the fact that metal ions were extracted under the form of different anionic complexes. [P₆₆₆₁₄]Cl, for instance, led to the extraction of PdCl₄²⁻, where [P₆₆₆₁₄]Br led to the formation of PdBr₄²⁻, the latter being more keen on partitioning towards the ionic liquid. Such phenomena are not expected to occur in our study.

Generally, PP and PS are extracted significantly better than OA. Because PP exhibit pK_a values around 9, and because all the black liquor samples (diluted or not) used here exhibited pH values above 9.5, PP are expected to be mainly under the form of polyphenolate anions. That, combined to the fact that PP are bulky moieties, might form hydrophobic ion pair with the cation of the ionic liquid, an extraction mechanism often suggested in liquid-liquid extraction of metallic ions towards ILs.

Polysaccharides, on the opposite, are cellulose-like compounds. Cellulose is known to be soluble in chloride-based ionic liquids, due to hydrogen-bonding interactions. Despite the fact that PS differs in structure and physical chemical properties with cellulose, one can expect such hydrogen-bonding interactions to occur with [P₆₆₆₁₄]Cl, and, to a lesser extent, with [P₆₆₆₁₄]Br. This, combined with a large molecular weight of PS, might lead to the extraction of this type of compounds towards an ionic liquid.

OA such as lactic acid, on the opposite, are small molecules exhibiting a high solvation energy in water. Even though the pK_a of such species is also around 9, implying they are under a basic form, they are not expected to be significantly extracted towards the ionic liquids studied here.

Extraction of lactate from pure [P₆₆₆₁₄]Cl has been previously studied.[14,16] Extraction mechanism was suggested to be based on ion exchange especially at basic pH (pH 11). Under such conditions, 40.4% of extraction was observed with an initial lactate concentration of 0.5 M. In our case, the maximal initial concentration of lactate was 9.5 g.L⁻¹ corresponding to 0.084 M, and lactate extraction was close to 42-44 %, whatever the tested ionic liquid.

Most surprising results come from the fact that D_{PP} and D_{PS} values increase almost linearly with the volume ratio R_v. The fact that the extraction appears to be more efficient when a large volume of BL₁₀ is used is unexpected. Classical behavior in extraction systems usually yields either a constant extraction whatever the volume ratio, or an extraction that is enhanced when large volumes of extracting phases are employed. Similarly, the successive extraction experiments using either the same sample of black liquor contacted with two fresh samples of IL, or contacting the same IL with two different samples of black liquors lead to unexpected results. For instance, extraction of PP and PS is generally lower during the second extraction step compared to that observed during the first extraction step. OA, on the opposite, are extracted more efficiently during the second extraction experiment compared to the first one.

Extraction experiments carried out using the same ionic liquid contacted with two different BL₁₀ samples allows to gain better insight into the possibilities of reusing the ionic liquid without the need of washing the ionic liquid. The fact that in such a case, the ionic liquids studied here are equally efficient at extracting PP in the two extraction experiments implies that [P₆₆₆₁₄]Cl or [P₆₆₆₁₄]Br are not saturated in PP after the first extraction step and that the presence of PP and PS in the ionic liquid has no significant influence on the extraction of PP. On the opposite, extraction of PS decrease drastically in the second extraction step, implying that the ionic liquid is not able to extract anymore PS than already present. The IL is therefore close to its saturation. The fact that OA increases between the two extraction steps is less easily explained. It is worth acknowledging here that black liquor is an excessively complex solution containing a large range of compounds, one can

expect that cross interactions between these compounds and coupled extraction phenomena to occur. In the current state of this study, it is therefore tedious to explain in further details our results.

Finally, in order to investigate on the possibilities of extracting as much compounds as possible from a BL10 sample, two successive extractions of the same BL10 sample with two different samples of the same IL give surprising results. Extraction of PP and PS appears to be drastically reduced when the same black liquor is treated consecutively with two different samples of ionic liquid. This is in apparent opposition with results obtained using classical extracting systems based on an organic solvent and an extracting agent.[17] Similar results were however very recently reported in a report dealing with the extraction of metal ions using the same ionic liquids as those studied here.[18] The drastic decrease in the extraction of the metal ions observed in this case was then explained by the fact that the aqueous phase was saturated with the ionic liquid after the first extraction step. This hindered further extraction of metallic ions with fresh samples of ionic liquids because the extraction mechanism involving the formation of an ion pair, and a subsequent transfer of some ions of the ionic liquid towards the aqueous phase was not possible anymore.

5. Conclusion

In this work, it is shown that phosphonium-based ionic liquids can be used as efficient extractants from a chemically complex aqueous solution named black liquor. The latter, produced during pulping factory, contains high concentrations of polyphenols, polysaccharides and organic acids like lactate.

Trihexyltetradecylphosphonium chloride, $[P_{66614}]Cl$ appears to be a better extractant of polyphenols, polysaccharides and organic acids from aqueous dilute black liquor than trihexyltetradecylphosphonium bromide $[P_{66614}]Br$.

90% of polyphenols and polysaccharides were extracted by $[P_{66614}]Cl$ during the first extraction run under basic pH conditions. Organic acids were co-extracted at lower efficiency (23%).

It also appears that an ionic liquid loaded with polyphenols, polysaccharides and organic acids can be reused at least once as an extracting phase for polyphenols and organic acids. Improving the extraction of polyphenols and polysaccharides from an aqueous phase by contacting it with several IL samples is not efficient.

Further studies are necessary to find an efficient solvent in order to reuse ionic liquid and to efficiently back-extract organic compounds. In the same way, future studies will be carried out to test the bio-availability of organic acids and polysaccharides present in the final aqueous phase.

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