




Article

Recovery and Elimination of Phenolic Pollutants from Water Using [NTf₂] and [Nf₂]-Based Ionic Liquids

Olalla G. Sas , Ángeles Domínguez  and Begoña González * 

Chemical Engineering Department, University of Vigo, Campus Lagoas-Marcosende, 36310 Vigo, Spain; olallags83@uvigo.es (O.G.S.); admiguez@uvigo.es (Á.D.)

* Correspondence: bgp@uvigo.es

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Abstract: At present, pollution is one of the most important problems worldwide. Industrial growth makes it necessary to develop techniques to remove pollutant substances from water, since water is an important natural source for life. One of these techniques is liquid–liquid extraction, which is used to remove phenolic compounds from wastewaters. Volatile organic compounds are used as common extraction solvents in liquid–liquid extractions; nevertheless, some of their properties, such as toxicity and volatility, make it necessary to replace them with other less toxic solvents. In this work, the capability of four ionic liquids, based on bis(trifluoromethylsulfonyl)imide [NTf₂] and bis(fluorosulfonyl)imide [Nf₂] anions and different cations to remove phenolic compounds from water was studied. The phenolic compounds used in this study were phenol, o-cresol, and 2-chlorophenol, and the effects of the extraction solvent and phenol structures were analyzed. For that, a liquid–liquid extraction was carried out, and the extraction yield was determined. In general, high extraction efficiencies were obtained for all studied systems, obtaining the highest extraction efficiencies using the pyrrolidinium cation-based ionic liquids.

Keywords: pollution; ionic liquids; phenolic compounds; recover; liquid–liquid extraction

1. Introduction

The growth of industrial activities, as well as the increase in population, has boosted the consumption of natural resources and the concentration of pollutant substances both in the air and in water. Over the last years, the concern about the pollution problem has increased, and many countries and organizations, including the European Union, have established new laws to protect the environment, decreasing the limit concentration of different kind of pollutant substances. In this context, the European Commission directive 2001/81/EC established emission thresholds for acidifying, eutrophying, and other pollutant substances, with the aim of protecting the environment and the human health from the harmful effects of the poor quality of air that we breathe and water that we drink [1].

Water is a natural resource that is essential for life, and due to the industrial growth previously mentioned, many pollutant substances can be found in water, and they have to be eliminated in order to get water that can be used in farming and domestic activities. In addition to the pollution problem, the scarcity that part of the planet suffers as a result of the climate change makes it necessary to develop techniques that allow removing toxic substances from water [2].

In the 2008/105/CE directive, the European Parliament set the normativity to the quality of waters, establishing that the “chemical contamination of surface waters is a threat for aquatic life which effects are the acute and chronic toxicity, as well as, the danger to human health”, and they created a list of priority pollutants where some phenolic compounds are included as very harmful and toxic substances [3].

Phenolic compounds are substances that are presented in the wastewaters of industries such as pharmaceutical, coal, or petrochemical, and the threshold quantities for these compounds are fixed by the Environmental Protection Agency (EPA) in $5 \text{ mg}\cdot\text{L}^{-1}$ if these waters are to be discharged into the public sewage system, and $1 \text{ mg}\cdot\text{L}^{-1}$ if they are to be discharged into inland waters. Due to this legal limitation, it is necessary to remove phenolic compounds from water before it was discharged [4,5].

Distillation, chemical oxidation, adsorption, or biodegradation techniques have been used to remove phenols from water. Nevertheless, these techniques have some drawbacks, such as high-energy consumption, inefficient treatment at low concentration of phenols, or the difficulty to control the process. Another and common separation technique is the liquid–liquid extraction (LLE), which is a simple and effective technique to remove or recover phenolic compounds from aqueous systems [6]. In spite of the high extraction efficiencies obtained with conventional solvents, the consumption of harmful substances, volatile organic compounds (VOCs), is the most important drawback, so it is necessary to replace them with other safer and more environmental friendly substances [7–9].

Ionic liquids (ILs) are considered as good replacement substances for traditional organic compounds due to their negligible vapor pressure, high thermal and chemical stability, and their capability to dissolve a huge variety of materials [7,10]. They are defined as salts that have a melting point lower than 373 K, most of them are liquids at room temperature, and they keep in this state in a wide range of temperatures [11]. Over the last few decades, the interest in the ILs has grown due to their versatility, and in recent works, it is possible to find studies with functionalized ionic liquids, incorporating hydroxyl, alkyl, and benzyl groups into the structures, improving phenolic extraction efficiencies [12]. On the other hand, Deng et al. [13] investigated hydrophobic magnetic ILs and their applicability to remove phenolic compounds from water. Another advantage of the ILs is the possibility to recover and reuse them without loss of their properties. Vidal et al. [14] obtained high extraction efficiencies in the elimination of phenolic compounds from water using [OMim][BF₄], even after six cycles. It is also possible to apply these solvents to remove phenols from other matrices; for instance, Hou et al. [15] used imidazolium-based ILs with different anions (Cl[−], Br[−], BF₄[−] and PF₆[−]) to remove phenol from a model oil. The results showed that phenol can be removed with high extraction efficiency, obtaining the best result with [BMim]Cl, and ILs can be recovered by evaporation and reused four times without loss of efficiency.

In this work, the capability of four ILs, 1-propyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)imide [¹P¹Mpip][NTf₂], 1-propyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide [¹P³Mpy][NTf₂], 1-propyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide [¹P¹Mpyr][NTf₂], and 1-propyl-1-methylpyrrolidinium bis(fluorosulfonyl)imide [¹P¹Mpyr][Nf₂] to remove phenol, o-cresol, 2-chlorophenol, and a mixture of these three phenolic compounds from water was studied. The structures of these compounds are presented in Table S1. The final concentration of phenolic compounds in the aqueous phase was measured using the 4-amineantipyrene method by UV-Vis spectrophotometric technique, and the extraction efficiencies were calculated [16].

The effect of the structure of the ILs and the structure and initial concentration of the phenolic compounds in the extraction efficiencies will be discussed in the work. As a result of the high extraction capacity of these solvents to remove phenolic compounds from water, a real wastewater was simulated, preparing an aqueous mixture of these three phenols, in order to analyze their capability to remove these pollutant substances when they are present together, as it happens in a real procedure.

2. Materials and Methods

1-propyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)imide [¹P¹Mpip][NTf₂] (purity ≥99%), 1-propyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide [¹P³Mpy][NTf₂] (purity ≥99%), and 1-propyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide [¹P¹Mpyr][NTf₂] (purity ≥99%) were supplied by Iolitec (Germany), and 1-propyl-1-methylpyrrolidinium bis(fluorosulfonyl)imide [¹P¹Mpyr][Nf₂] (purity ≥99.9%) were purchased from Solvionic (France). Ionic liquids were dried in vacuum conditions (*p* = 0.2 Pa) at moderate temperature, and then they were stored under argon gas.

Phenol (purity $\geq 99.5\%$) and o-cresol (purity $\geq 99\%$) were supplied by Sigma-Aldrich (Germany), and 2-chlorophenol (purity $\geq 99\%$) was purchased from Merck Scudart (Germany). 4-amineantipyrine method reagents: Potassium hexacyanoferrate (III) (purity $\geq 99\%$), potassium sodium L(+)tartrate tetrahydrate (purity $\geq 99\%$), ammonium chloride (purity $\geq 99\%$), and 4-amineantipyrine (purity $\geq 97\%$) were purchased from VWR Prolabo Chemicals (Belgium), and ammonium hydroxide solution (25% wt NH_3) was supplied by Sigma-Aldrich (Germany). All the aqueous solutions were prepared using Milli-Q water.

In order to evaluate the extraction efficiency of these four solvents, the ternary systems {water + phenolic compound + IL} were studied. The samples were prepared by weighing, using a Mettler Toledo Excellent plus XP205 analytical balance (USA) with an uncertainty of $\pm 3 \cdot 10^{-4}$ g. The used ratio of IL: aqueous phase selected for all these experiments was 1:3 (*v/v*). The mixtures were introduced in flasks and sealed with silicone rubber covers and stirred for 2 hours at 298.15 K in a Polyscience thermostatic bath (USA) (± 0.1 K), and then temperature controlled with a digital thermometer ASL model F200 with an uncertainty of ± 0.01 K, coupled to a Phoenix Instrument RSM-03-10 K magnetic stirrer (Germany). Then, they were left to settle down for 2 hours to ensure the correct separation of both phases. Finally, a sample of aqueous phase was collected, and the phenol concentration was determined with a Jasco V-630 UV-Vis spectrophotometer (Japan), with an uncertainty of ± 0.002 Abs (from 0 to 0.5 Abs) and ± 0.003 (from 0.5 to 1 Abs), respectively. The method used to quantify the phenolic concentration is the 4-amineantipyrine method [16], which is based on the formation of a colored dye between a phenolic compound and 4-amineantipyrine, in the presence of potassium ferricyanide at basic pH. The absorbance of the formed dye was measured at 510 nm by UV-Vis spectrophotometry, and the extraction efficiency was calculated following the equation:

$$E\% = ((C_i - C_f) / C_i) \times 100 \quad (1)$$

where C_i and C_f denote the initial and the final concentration in $\text{mg} \cdot \text{L}^{-1}$ of phenols in the aqueous phase, respectively.

3. Results and Discussion

The capability of the four ILs to remove phenolic compounds from water, using the liquid–liquid extraction technique, was studied. $[^1\text{P}^1\text{Mpip}][\text{NTf}_2]$, $[^1\text{P}^3\text{Mpy}][\text{NTf}_2]$, $[^1\text{P}^1\text{Mpyr}][\text{NTf}_2]$, and $[^1\text{P}^1\text{Mpyr}][\text{Nf}_2]$ were used to remove phenol, o-cresol, and 2-chlorophenol from water at 293.15 K and atmospheric pressure. The final concentrations of phenolic compounds in water (Table S2), as well as the extraction efficiencies, were calculated (Table S3). High extraction efficiencies were obtained for all the studied systems. According to the results, the legal limit ($5 \text{ mg} \cdot \text{L}^{-1}$ if wastewaters are to be discharged into public sewage system) is reached in only one extraction cycle for initial concentrations below $50 \text{ mg} \cdot \text{L}^{-1}$ in all the studied systems, except in the case of $[^1\text{P}^1\text{Mpip}][\text{NTf}_2]$ ionic liquid with o-cresol, for which the legal limit in only one step is reached for initial concentrations below $5 \text{ mg} \cdot \text{L}^{-1}$. For initial concentrations ranging between 50 and $2000 \text{ mg} \cdot \text{L}^{-1}$, two extraction cycles would be necessary for all systems, and three extraction cycles would be required for initial concentrations between 5000 and $15,000 \text{ mg} \cdot \text{L}^{-1}$.

ILs are considered green solvents because they have negligible vapor pressures; nevertheless, it is important to know their solubility and toxicity in water when they are used as extraction agents from aqueous solutions. It is also important to know the solubility of water in the ILs, since their physical properties, such as density or viscosity, are affected by the amount of water in the IL phase. The toxicity of these extraction solvents was not analyzed by this group; however, Freire et al. [17] published a work about the hydrophobicity study for nine ILs with different cations and anions with the aim of knowing the mutual solubility of ILs–water systems. The experimental results showed that the hydrophobicity trend for anions is as follows: $[\text{C}(\text{CN})_3] < [\text{PF}_6] < [\text{NTf}_2]$, while the influence of the cation in the hydrophobicity of the studied ILs is $[\text{C}_n\text{mim}] < [\text{C}_n\text{mpy}] \leq [\text{C}_n\text{mpyr}] < [\text{C}_n\text{mpip}]$. Their

studies also established that the solubility of water in the IL-rich phase is higher than the solubility of ILs in water, being the mole fraction in range from 10^{-3} to 10^{-4} .

3.1. Study of the ILs Structure

Ionic liquid anion and cation play an essential role in extraction processes; due to this fact, a study about the influence of ILs structure is performed.

The results of the extraction efficiencies for the two studied anions (NTf_2 and Nf_2) are shown in Table S3 and Figure 1. As it is possible to observe in this figure, the extraction efficiencies are higher than 90% for all the initial concentrations of phenolic compounds. Therefore, in this work, the experimental results showed that there are not significant differences between $[\text{P}^1\text{Mpyr}][\text{NTf}_2]$ and $[\text{P}^1\text{Mpyr}][\text{Nf}_2]$.

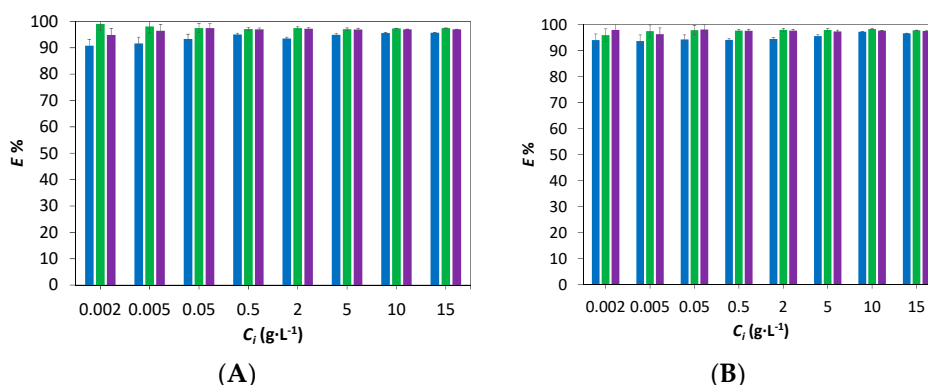


Figure 1. Extraction efficiency ($E\%$) versus initial concentration of phenolic compounds (C_i) for $[\text{P}^1\text{Mpyr}][\text{NTf}_2]$ (A) and $[\text{P}^1\text{Mpyr}][\text{Nf}_2]$ (B) to remove phenol (—), o-cresol (—), and 2-chlorophenol (—).

However, there are other works where the anion structure of the ILs' effect in the extraction process is important. For instance, Katsuta et al. studied ILs based on three different anions ($[\text{NTf}_2]$, $[\text{BF}_4]$, and $[\text{PF}_6]$) for the extraction of 14 phenolic compounds, and it was observed that the best results were obtained with the $[\text{BF}_4]$ anion, and no significant differences were found between the other two anions [8].

With the aim of comparing the effect of the cation structure into extraction efficiencies, the results obtained with $[\text{P}^1\text{Mpip}][\text{NTf}_2]$, $[\text{P}^3\text{Mpy}][\text{NTf}_2]$, and $[\text{P}^1\text{Mpyr}][\text{NTf}_2]$ were analyzed. These two ILs have the same number of carbon atoms in the cation ring, but only one of them presents aromatic character ($[\text{P}^3\text{Mpy}][\text{NTf}_2]$). The experimental results show that the aromaticity of the cation does not increase the extraction efficiencies (Table S3, Figure 2A). Similar results were observed by González et al. [18], who studied the capability of imidazolium and pyrrolidinium based ILs to remove phenol, o-cresol, and resorcinol from water, obtaining better results with the non-aromatic one (pyrrolidinium).

Regarding the non-aromatic cation, the best results were obtained when the $[\text{P}^1\text{Mpyr}][\text{NTf}_2]$ ionic liquid is used in all studied cases, increasing these differences when the results for o-cresol extraction were compared (Figure 2B).

In previous work carried out for this research group, where the influence of the alkyl chain of the cation structure in the extraction process was studied, it was observed that an increase in the alkyl chain promotes an increase in the extraction efficiency. $[\text{PMim}]$, $[\text{BMim}]$, and $[\text{HMim}]$ cations with the same anion $[\text{NTf}_2]$ were used to extract the same phenolic compounds studied in this work, and best results were obtained using $[\text{PMim}][\text{NTf}_2]$ IL [4]. In other work [7], 1-ethyl-3-methylimidazolium bis(fluorosulfonyl)imide ($[\text{C}_2\text{mim}]\text{FSI}$) ionic liquid was studied as the extraction agent for phenolic compounds. The results obtained in these two articles are compared with those obtained with the

studied ILs in this work (Figure S1). As it is possible to observe in this figure, the results obtained with the eight ILs are comparable, obtaining extraction efficiencies above 95% for all systems.

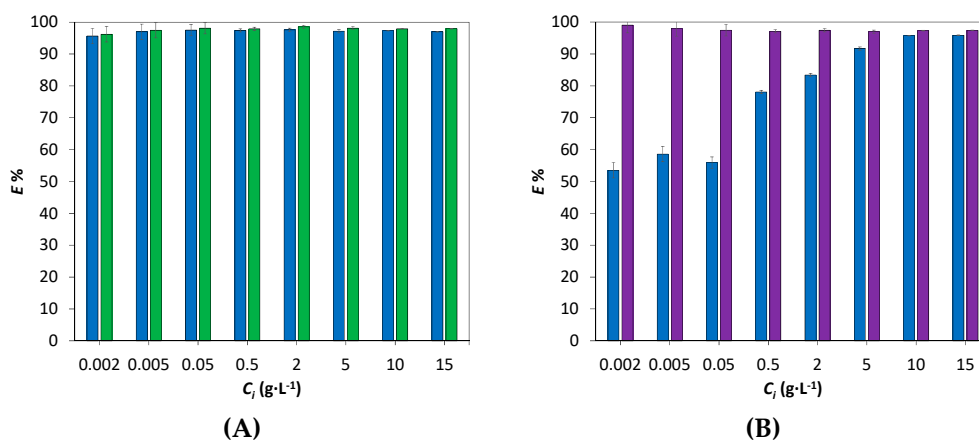
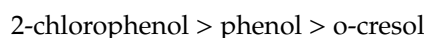


Figure 2. Extraction efficiency (E%) versus initial concentration of phenolic compounds (C_i), (A) for the extraction of 2-chlorophenol using $[1P^1Mpip][NTf_2]$ (—) and $[1P^3Mpy][NTf_2]$ (—); (B) for the extraction of o-cresol using $[1P^1Mpip][NTf_2]$ (—) and $[1P^1Mpyr][NTf_2]$ (—).

3.2. Study of the Phenolic Compound Structure

The three phenolic compounds used in this work were phenol, o-cresol, and 2-chlorophenol. When the $[1P^1Mpip][NTf_2]$ and $[1P^3Mpy][NTf_2]$ ILs were used, the extraction efficiency (Table S3) for a low concentration of phenolic compounds follows the next trend:



In the case of $[1P^1Mpyr][NTf_2]$ and $[1P^1Mpyr][Nf_2]$, the results of extraction efficiency were high and very similar for all the studied phenolic compounds and initial concentrations.

3.3. Study of the Phenolic Compound Initial Concentrations

In this work, different initial concentrations of extracted compounds were studied in order to evaluate if the initial concentration of the pollutant substances has some effect on the extraction efficiency. As it is possible to observe in Table S3, the extraction efficiency increases when the initial concentration of the phenolic compound increases, this being the behavior that is observed in all the studied systems. For the $[1P^1Mpip][NTf_2]$ + o-cresol system, at the lower initial concentration, the extraction efficiency is higher than 50%, increasing this result above 90% when the initial concentration is higher than $5 \text{ g}\cdot\text{L}^{-1}$. For all the other studied systems, the extraction efficiencies are higher than 90% even at low initial concentrations, increasing the efficiencies when the initial concentration increases. These results could be explained due to a more efficient solvation of the phenolic compounds in aqueous solution at low concentration. The same conclusions were obtained in our previous works [4,7].

3.4. Study of the Multicomponent Extraction Capability

Regarding the study of the extraction capability of these solvents to remove a mixture of phenols, an aqueous solution of these three phenolic compounds—phenol, o-cresol, and 2-chlorophenol (using equal amount of each one)—was prepared, and the extraction yield was determined following the same experimental procedure. The results plotted in Figure 3 show that high extraction efficiencies were obtained with all studied solvents, except when $[1P^1Mpyr][Nf_2]$ is used to extract phenolic compounds at low concentration.

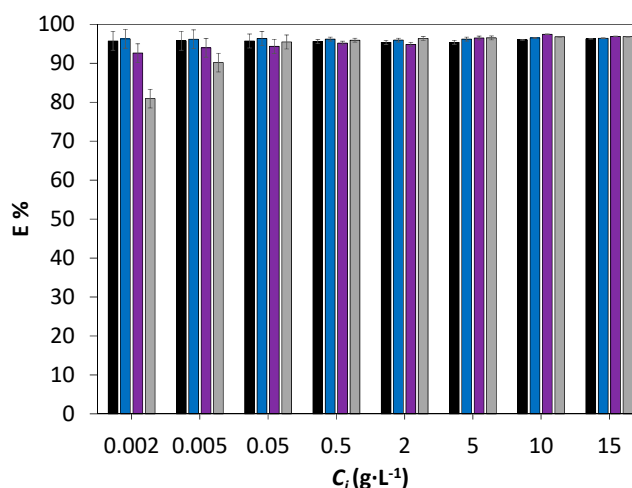


Figure 3. Extraction efficiency ($E\%$) versus initial concentration (C_i) of phenolic compound mixture (PCM) for $[1P1Mpip][NTf_2]$ (—), $[1P3Mpy][NTf_2]$ (—), $[1P1Mpyr][NTf_2]$ (—), and $[1P1Mpyr][Nf_2]$ (—).

The extraction efficiency remains practically constant when the initial concentration of phenol mixture is higher than $0.05 \text{ g}\cdot\text{L}^{-1}$, being above 90% (Table S4).

In spite of the presence of more than one phenolic compound, the extraction capability of these solvents was not affected, presenting high extraction efficiency values comparable with the results obtained to remove only one phenolic compound. Attending to the final concentration of the phenolic compound mixtures (Table S5), the legal limit was reached in only one cycle for initial concentrations below $50 \text{ mg}\cdot\text{L}^{-1}$ for all studied ILs, following the same behavior as when only one phenolic compound was studied. Consequently, it is possible to conclude that all these studied solvents are also good extraction agents for removing phenolic compounds from water when a mixture of them is present.

In industrial wastewaters, not only different phenolic compounds are present, but also other kind of substances, such as salts or other pollutant agents, can be found. Different studies about the influence of the presence of salts in aqueous solution on the extraction of phenolic compounds have been published. The effect of the NaCl in the extraction of resorcinol, phenol, guaiacol, o-cresol, and p-nitrophenol with $[C_4C_{11}OHim][BF_4]$ as extraction agents was carried out by Fan et al. [14]. Experimentally, it was observed that the presence of this salt increases significantly the extraction efficiency, being more remarkable when the concentration of salt increases. This behavior was explained through the salt ions attracting water molecules (salting-out effect), and thus decreasing the water free molecules concentration [14].

In general, good extraction efficiencies were obtained for all studied systems. The $[1P1Mpyr][Nf_2]$ ionic liquid presents good results even at low initial concentrations for individual phenolic compounds. These observations are in agreement with the results obtained in previous studies of this group, where the capability of 1-ethyl-3-methylimidazolium bis(fluorosulfonyl)imide (C_2mim)FSI to remove phenols from water were studied. High extraction efficiencies, greater than 90%, were also obtained for all initial concentrations of phenol, o-cresol, and 2-chlorophenol [7].

3.5. Reagent Recovery

Solvent recovery is essential in order to apply these solvents in industrial processes. For that, a recovery process of the ILs based on the use of NaOH aqueous solution was carried out. Both phases obtained after the extraction process were separated, and the IL-rich phase was treated with a 0.5 M NaOH solution. Two clean cycles were enough to recover the ILs. Due to the acid character of the OH group of the phenolic compounds, it was possible to remove phenols from ILs changing the pH of the solution. After that, ILs were analyzed by ^1H NMR spectroscopy in order to evaluate the presence of

phenols. The analyses confirmed the correct recovery of these solvents, and then they were reused in the extraction processes without loss of their properties (Figures S2–S3).

With this procedure, the recovery of the phenolic compounds is also possible. After the ILs' clean cycles, an aqueous phenolate solution was obtained, and these compounds can be easily converted in phenols, changing the pH of the solution, and they could be reused both as phenols or phenolates in industrial processes.

4. Conclusions

The main objective of this work was the study of the capability of ILs, based on different anions and cations, to remove and recover phenolic compounds from water.

Taking into account the experimental results, it is possible to conclude that the extraction efficiency was not affected significantly for the aromaticity of the cation ring, obtaining similar efficiencies for pyridinium and pyrrolidinium cations, with extraction yields above 90%. Furthermore, there were no significant differences between the results obtained with $[\text{NTf}_2]$ and $[\text{Nf}_2]$ anions.

Besides, the capability to remove a mixture of phenols from water was studied, obtaining also high extraction efficiencies, above 80%. All the studied ionic liquids present high and similar results, except in the case of low initial phenolic compounds concentration, where $[\text{P}^1\text{Mpyr}][\text{Nf}_2]$ presents the worst results.

After this study, it is possible to conclude that a method of elimination and recovery phenolic pollutant from wastewater was achieved. The $[\text{P}^1\text{Mpyr}][\text{NTf}_2]$ ionic liquid is a good candidate as an elimination agent of phenolic compounds, obtaining treated wastewater, complying the legal limits for their discharge or reuse, and attaining the recovery of both extraction solvents and phenolic compounds.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2076-3417/9/20/4321/s1>, Table S1: Cation and anion structure of the studied ionic liquids and their corresponding names, Table S2: Initial concentration C_i ($\text{mg}\cdot\text{L}^{-1}$) vs. final concentration C_f ($\text{mg}\cdot\text{L}^{-1}$) of phenol o-cresol and 2-chlorophenol after extraction process using $[\text{P}^1\text{Mpip}][\text{NTf}_2]$, $[\text{P}^3\text{Mpy}][\text{NTf}_2]$, $[\text{P}^1\text{Mpyr}][\text{NTf}_2]$ and $[\text{P}^1\text{Mpyr}][\text{Nf}_2]$ at $T = 298.15\text{ K}$ and $P = 101.3\text{ kPa}$, Table S3: Initial concentration C_i ($\text{mg}\cdot\text{L}^{-1}$) vs. extraction efficiency ($E\%$) of phenol o-cresol and 2-chlorophenol after extraction process using $[\text{P}^1\text{Mpip}][\text{NTf}_2]$, $[\text{P}^3\text{Mpy}][\text{NTf}_2]$, $[\text{P}^1\text{Mpyr}][\text{NTf}_2]$, and $[\text{P}^1\text{Mpyr}][\text{Nf}_2]$ at $T = 298.15\text{ K}$ and $P = 101.3\text{ kPa}$, Table S4: Initial concentration C_i ($\text{mg}\cdot\text{L}^{-1}$) vs. extraction efficiency ($E\%$) of a mixture of phenolic compounds (PCM) after extraction process using $[\text{P}^1\text{Mpip}][\text{NTf}_2]$, $[\text{P}^3\text{Mpy}][\text{NTf}_2]$, $[\text{P}^1\text{Mpyr}][\text{NTf}_2]$, and $[\text{P}^1\text{Mpyr}][\text{Nf}_2]$ at $T = 298.15\text{ K}$ and $P = 101.3\text{ kPa}$, Table S5: Initial concentration C_i ($\text{mg}\cdot\text{L}^{-1}$) vs. final concentration C_f ($\text{mg}\cdot\text{L}^{-1}$) of a mixture of phenolic compounds (PCM) after extraction process using $[\text{P}^1\text{Mpip}][\text{NTf}_2]$, $[\text{P}^3\text{Mpy}][\text{NTf}_2]$, $[\text{P}^1\text{Mpyr}][\text{NTf}_2]$, and $[\text{P}^1\text{Mpyr}][\text{Nf}_2]$ at $T = 298.15\text{ K}$ and $P = 101.3\text{ kPa}$. Figure S1. Extraction efficiencies ($E\%$) of 2-chlorophenol using $[\text{PMim}][\text{NTf}_2]$, $[\text{BMim}][\text{NTf}_2]$, $[\text{HMim}][\text{NTf}_2]$, $[\text{C}_2\text{mim}]\text{FSI}$, $[\text{PMpip}][\text{NTf}_2]$, $[\text{PMpy}][\text{NTf}_2]$, $[\text{PMpyr}][\text{NTf}_2]$, and $[\text{PMpyr}][\text{Nf}_2]$. Initial concentrations (—) $5\text{ mg}\cdot\text{L}^{-1}$ and (—) $50\text{ mg}\cdot\text{L}^{-1}$. Figure S2. ^1H NMR spectrum for the pure IL 1-methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide. Figure S3. ^1H NMR spectrum for the IL 1-methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide after the recovery process using 0.5 M NaOH .

Author Contributions: Investigation, O.G.S.; Methodology, B.G. and Á.D.; Supervision, B.G. and Á.D.; Writing—original draft, O.G.S.; Writing—review & editing, B.G. and Á.D.

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Conflicts of Interest: The authors declare no conflict of interest.

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