




## Article

# Cleaning Phenolic Compounds Present in Water Using Salting-Out Effect with DCA-Based Ionic Liquids

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**Abstract:** Water is an essential natural resource, and its contamination is an important issue at present. This study aimed to increase the techniques that can be used to clean and reuse industrial wastewater by studying the feasibility of an aqueous two-phase system to eliminate phenolic compounds from aqueous systems. The system was prepared using two hydrophilic ionic liquids based on dicyanamide anion, 1-ethyl-3-methylimidazolium dicyanamide [EMim][DCA], and 1-butyl-3-methylimidazolium dicyanamide [BMim][DCA], and one inorganic salt,  $K_3PO_4$ , at three different concentrations (20, 30, and 40%). The process was tested for the removal of phenol, o-cresol, 2-chlorophenol, and a mixture of them (PCM) at initial concentrations from 0.003 to 15 g·L<sup>-1</sup> in water. The extraction efficiencies for all the studied systems were calculated. The influence of the structure of the cation, the concentration of salt, and the initial concentration of the extracted compounds in the extraction yields were recorded. In general, the obtained results were high for all the studied systems, with extraction efficiencies of more than 90% representing the highest removal of the 2-chlorophenol compound using [EMim][DCA] at the highest concentration of salt.

**Keywords:** phenolic compound; ionic liquids; salting-out



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## 1. Introduction

Water is an essential natural resource, and due to over-consumption and its scarcity, it is necessary to establish systems that allow the recovery of industrial wastewater with the aim of reusing it and developing more sustainable and environmentally friendly processes. The World Health Organization (WHO) and the European Union (EU) have established a list of priority pollutant substances in water, in which some phenolic compounds were included, and the Environmental Protection Agency (EPA) has fixed their limit concentration in wastewater as 1 mg·L<sup>-1</sup> [1,2]. Due to their high toxicity, it is necessary to clean this water by removing these compounds before they reach the environment, with the aim of complying with the legislation [3]. Phenolic compounds are organic substances that have at least one aromatic ring with a hydroxyl group in their structure. They are naturally present in fruits and vegetables, but they can also be found in industrial wastewater, such as petrochemical, coal, paper, pharmaceutical industries, or coke plants, as pollutant substances (Table 1). A large part of industrial waste ends up polluting water, and therefore, it must be treated to obtain reusable water or water that can be discharged into the environment. The presence of these compounds in water, even at low concentrations, causes contamination because some types of phenols are very toxic to human health and aquatic life [4–7].

Liquid–liquid extraction (LLE) is a common technique that is used to remove phenols from water due to its effectiveness. It presents some advantages over other techniques, such as distillation, chemical oxidation, and adsorption, among others (Table 2). Since its consumption of energy is lower, it is a simple process and allows the removal of contaminants even at low concentrations [6–8].

**Table 1.** The concentration of phenolic compounds found in the wastewater of some industries.

Industry	Phenol Concentration (mg·L <sup>-1</sup> )	Reference
Paper	79.5	[2]
Textile	155	[3]
Coal	551	[4]
Coke	200	[5]

**Table 2.** Advantages and disadvantages of techniques used to remove phenolic compounds from water [9–12].

Technique	Advantages	Disadvantages
Biological degradation	Substitution of chemicals by microorganisms	Growth control, use of co-solvent for low phenol concentrations
Oxidative process	Simple process	Expensive, hazardous substances, high pressure, and temperature
Electrochemical	Not an expensive chemical	High consumption of energy, toxic chemicals
Adsorption	Economic process, simple equipment	Difficult to regenerate, not suitable for low concentrations
Liquid–liquid extraction	Easy operation, extraction agents can be recycled	Volatile organic solvents, low selectivity

The most commonly used solvents to remove substances from aqueous systems by liquid–liquid extraction are volatile organic compounds (VOCs); these solvents is volatile, flammable, and toxic—all undesirable properties—therefore, they must be replaced by other solvents with more suitable characteristics [13,14].

Due to their versatility, ionic liquids (ILs) have been widely applied as extraction agents in recent years since they can be used as solvents for the dissolution of both organic and inorganic compounds, as well as chemical or electrochemical synthesis [15–17]. ILs are organic salts formed by bulky organic cations and small organic or inorganic anions, which remain in a liquid state below 373 K [18–20]. They have suitable properties such as high thermal and chemical stability and negligible vapor pressure, and it is possible to design them for a specific task, combining the cations and anions used in their obtention [21–23]. Hence, they are presented as a great option to replace VOCs as extraction agents for the removal of phenolic compounds from aqueous media.

ILs can be obtained by mixing different cations (imidazolium, pyridinium, piperidinium, pyrrolidinium) and anions ((bis(trifluoromethylsulfonyl)imide [NTf<sub>2</sub>], bis(fluorosulfonyl)imide [Nf<sub>2</sub>], acetate [OAc], dimethylphosphate [DMP], thiocyanate [SCN], methylsulfate [MeSO<sub>4</sub>], triflate [TfO], dicyanamide [DCA]). The nature of the anion has a greater influence on its properties, being more hydrophilic than those based on [TfO] or [DMP] and is more hydrophobic than those based on [NTf<sub>2</sub>] or [Nf<sub>2</sub>], among others. Different studies on their application to the extraction of phenolic compounds have been published. Thasneema et al. [24] studied the extraction of chlorophenols, nitrophenols, and methylphenols, among others, using hydrophobic phosphonium-based ILs with good extraction results. The extraction efficiencies of phenolic compounds using [NTf<sub>2</sub>] and [Nf<sub>2</sub>]-based ILs were published by our research group. In these studies, high extraction efficiencies were obtained, and the influence of both the cation and anion structure of the ILs was studied in the extraction process [11,25]. González et al. [26] studied the efficiency of one aromatic cation (imidazolium) and one non-aromatic cation (pyrrolidinium) [NTf<sub>2</sub>]-based ILs to remove three phenolic compounds from aqueous systems; all the extraction efficiencies were high. It is important to note that the structure of both the cation of the IL and the substance to be extracted influenced the extraction efficiency.

Hydrophobic ILs are usually formed by anions with fluorinated ions, which are more expensive and less environmentally friendly than hydrophilic ones. Nevertheless, these kinds of solvents are miscible with water, so it is not possible to carry out a liquid–liquid

extraction directly. It is necessary to obtain an aqueous two-phase system (ATPS) using some reactive to produce the separation of both phases, aqueous and organic [27].

There are several published works about the use of liquid–liquid extraction and aqueous two-phase systems (ATPS) to remove phenols from water using hydrophilic ILs as extraction agents. In one of these studies, sugar (glucose) was used to promote the separation of phases using  $[C_n\text{Mim}][\text{BF}_4]$  as an extraction agent to remove phenol from water. In general, Chen et al. [28] concluded that ATPS formed with these ILs and glucose were good extraction agents, and the obtained results showed that an increase in the sugar concentration increased the extraction efficiency. However, it must be considered that this increase also produces an increase in the viscosity of the mixture. In the other study, Wang et al. [29] used salt ( $\text{NaH}_2\text{PO}_4$ ) to produce the salting out effect and obtain the ATPS system formed with  $[\text{BMim}][\text{BF}_4]$ . They studied the capability of this system to remove 4-chlorophenol, 2,4-dichlorophenol, and 2,6-dichlorophenol from water. In all the studied systems, the obtained results produced a greater than 90% recovery of phenolic compounds. They explained that the presence of salt in the water reduced the capacity of water to establish hydrogen bonds with phenolic compounds. This behavior increased the extraction process, and it was higher when the concentration of salt was increased.

Dicyanamide (DCA)-based ILs are hydrophilic and present lower viscosities than those based on  $\text{NTf}_2$  (bis(trifluoromethylsulfonil)imide), and they have adequate extractive properties as well. This low viscosity favors the mixture of the substances and, therefore, the extraction processes [30–32]. In some published works, DCA-based ionic liquids were used to recover naphthenic acid from crude oil; the ability of the anion to attract the acid is crucial, as well as the number of the anion molecules available for the removal [14]. These ionic liquids are widely used for the separation of compounds derived from fuels, the desulfurization of fuel oils, and the separation of olefins and paraffin or alcohols from fermentation media [5,15,33,34].

Based on the improvement of the properties of this kind of ILs (low cost, more environmentally friendly, lower viscosity values), in this work, the capability of two DCA-based ILs to remove phenolic compounds from the water was studied, and the influence of the concentration of salt ( $\text{K}_3\text{PO}_4$ ) in the extraction efficiency was evaluated. This salt was selected based on its favorable properties, such as its low price as a non-pollutant substance, and due to the fact that it is a trivalent salt with a stronger salting out ability than divalent or monovalent salts [27]. For this investigation, phenol, o-cresol, and 2-chlorophenol samples prepared at different initial concentrations (from 0.003 to 15  $\text{g}\cdot\text{L}^{-1}$ ) in water were used as extractable substances, and a phenolic compound mixture (PCM) was prepared, and the feasibility of the two extraction agents to remove this mixture from the water was analyzed. Three different concentrations of salt in water 20, 30, and 40% ( $w/v$ ), with respect to the water volume, were prepared, and their influence on the extraction process was discussed.

## 2. Experimental Section

### 2.1. Materials

1-ethyl-3-methylimidazolium dicyanamide  $[\text{EMim}][\text{DCA}]$  (purity > 98%), 1-butyl-3-methylimidazolium dicyanamide  $[\text{BMim}][\text{DCA}]$  (purity > 98%) were supplied by Iolitec (Germany). Ionic liquids were vacuum dried ( $p = 0.2$  Pa) at a moderate temperature and stored under inert gas (argon). Phenol with 99.5% purity was supplied by Sigma-Aldrich (Germany). O-cresol and 2-chlorophenol with 99% purity were purchased from Sigma-Aldrich (Germany) and Merck Scuclart (Germany), respectively. For the 4-amineantipyrine method, the reagents used were potassium hexacyanoferrate (III) with 99% purity, potassium sodium L(+)-tartrate tetrahydrate and ammonium chloride with 99% purity, and 4-amineantipyrine with 97% purity; all these reagents were supplied by VWR Prolabo Chemicals (Belgium). Ammonium hydroxide solution (25% wt  $\text{NH}_3$ ) was purchased from Sigma-Aldrich (Germany). All the systems were prepared using Milli-Q water.

## 2.2. Methods

### 2.2.1. Determination of the Solubility Curves of Ternary Mixture: {Water + Salt + IL}

The cloud point method was used to obtain the binodal curve; a known mass fraction mixture was prepared using two compounds of the ternary system (water and salt). Consecutively, the IL was added drop by drop until turbidity was reached, indicating the formation of two liquid phases. Then, water was added drop by drop until the turbidity disappeared, which indicated the formation of one liquid phase [35]. These experiments were carried out at 298.15 K: the same temperature at which the phenolic compound extraction was studied. The composition of all compounds was calculated by weighing, and the % of IL versus % of salt was plotted, obtaining a binodal curve. These graphs can be consulted in the Supplementary Information (Figures S1 and S2).

### 2.2.2. Liquid–Liquid Extraction

The experimental conditions used in this study were the same as in the previous work published by our research group. In these studies, the temperature, stirring, settling time, and the IL/aqueous phase ratio was optimized, and the established conditions were 298.15 K, 2 h of stirring and settling time, and a 1:3 (*v/v*) IL/aqueous phase ratio [25].

The extraction capability of the two studied solvents was evaluated; for this, the quaternary mixture {water + phenolic compound + IL + K<sub>3</sub>PO<sub>4</sub>} was prepared. All the reagents used to prepare the samples were weighed using an analytical balance (Mettler Toledo Excellent plus XP205, Columbus, OH, USA) with an uncertainty of  $\pm 3 \cdot 10^{-4}$  g. The mixtures were stirred using a Phoenix Instrument RSM-03-10 K (Garbsen, Germany) in a thermostatic bath (Polyscience, Niles, IL, USA) for 2 h at 298.15 K (uncertainty  $\pm 0.1$  K), and the temperature was controlled using a thermometer (digital thermometer ASL model F200) (uncertainty  $\pm 0.01$  K). After this time, to ensure the correct separation of both formed phases, the mixtures were left for 2 h to settle down. Then, a sample was collected, and these aqueous phases were analyzed with a Jasco V-630 UV-Vis spectrophotometer (Japan) (uncertainty of  $\pm 0.002$  Abs (from 0 to 0.5 Abs) and  $\pm 0.003$  Abs (from 0.5 to 1 Abs)) to measure the phenolic compound concentration. The 4-amineantipyrine method was used with the aim of giving color to the aqueous phases [36]. This method is based on the formation of a colored complex between phenol and 4-amineantipyrine at a basic pH when potassium ferricyanide is present in the mixture. The absorbance was measured at 510 nm, and then the extraction efficiency was calculated using the next equation:

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

where  $C_i$  and  $C_f$  are the initial and the final concentration ( $\text{mg} \cdot \text{L}^{-1}$ ) of phenolic compound in the aqueous phase, respectively.

The UV-Vis spectra obtained for phenol, o-cresol, and 2-chlorophenol, before and after the 4-amineantipyrine reaction can be consulted in the Supplementary Information (Figure S3).

### 2.2.3. Phenolic Compound Mixture (PCM)

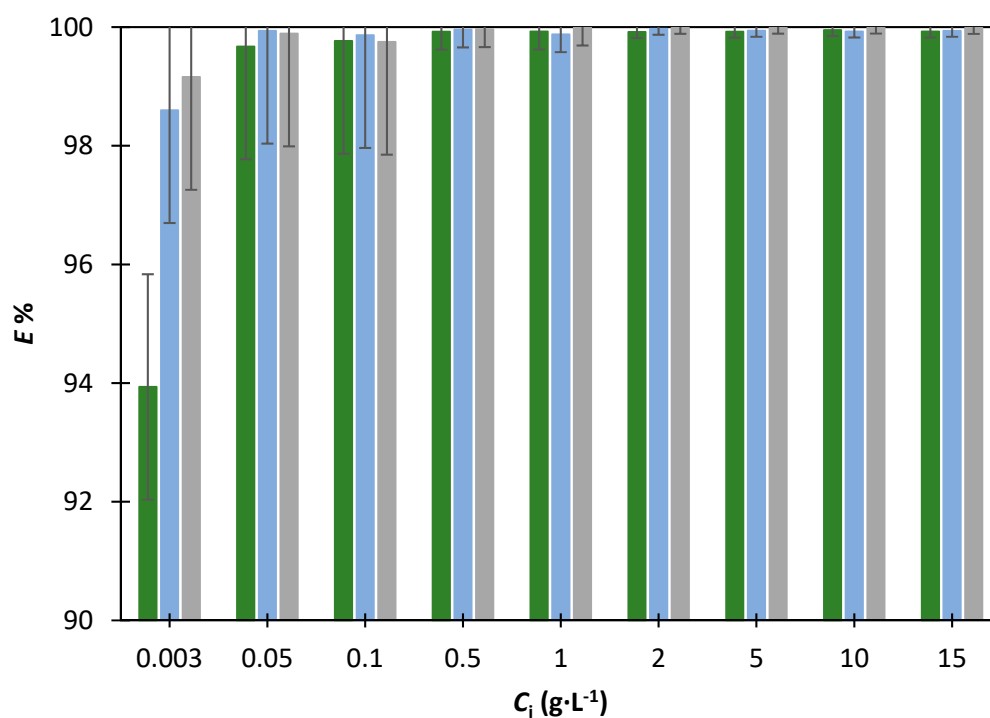
Wastewater usually contains more than one phenolic compound, so to study the feasibility of the ILs as extraction agents for a mixture of phenolic compounds in water, an equal amount of each compound was used to prepare the samples by weighing, and the extraction efficiency was determined using the experimental procedure described in the previous section.

## 3. Results and Discussion

The efficiency of the two abovementioned ILs to eliminate phenol, o-cresol, and chlorophenol, and a mixture of them from the water, was studied. The experimental procedure was carried out by liquid–liquid extraction and K<sub>3</sub>PO<sub>4</sub> as a salt that produces the salting out effect and, therefore, the separation of both aqueous and organic phases.

Four different concentrations, 10, 20, 30, and 40% (*w/v*) of salt, with respect to the volume of the aqueous phase, were studied. Nevertheless, at 10% with [EMim] [DCA], the two phases were not separated, so only the other three concentrations were used to study the extraction of phenols. All the experiments were carried out at atmospheric pressure and constant temperature (298.15 K). The final concentration of each phenolic compound, and the mixture (PCM) in water, as well as the extraction efficiencies, were calculated, and the results can be consulted in the Supplementary Information, Tables S1 and S2, respectively.

In general, for all the initial studied concentrations of phenolic compounds in water (from 3 to 15,000  $\text{mg}\cdot\text{L}^{-1}$ ) with both ILs as extraction agents, the extraction efficiencies were high and greater than 90%. The 2-chlorophenol compound presented the best extraction efficiency with both ILs at all initial concentrations and with all percentages of salt. These results are in agreement with the results obtained for the extraction of 2-chlorophenol with [NTf<sub>2</sub>] and [Nf<sub>2</sub>]-based ILs published for this research group in previous works [11,25]. The extraction efficiency for the phenolic compounds from water followed the next trend, as it is possible to observe in Figure 1:

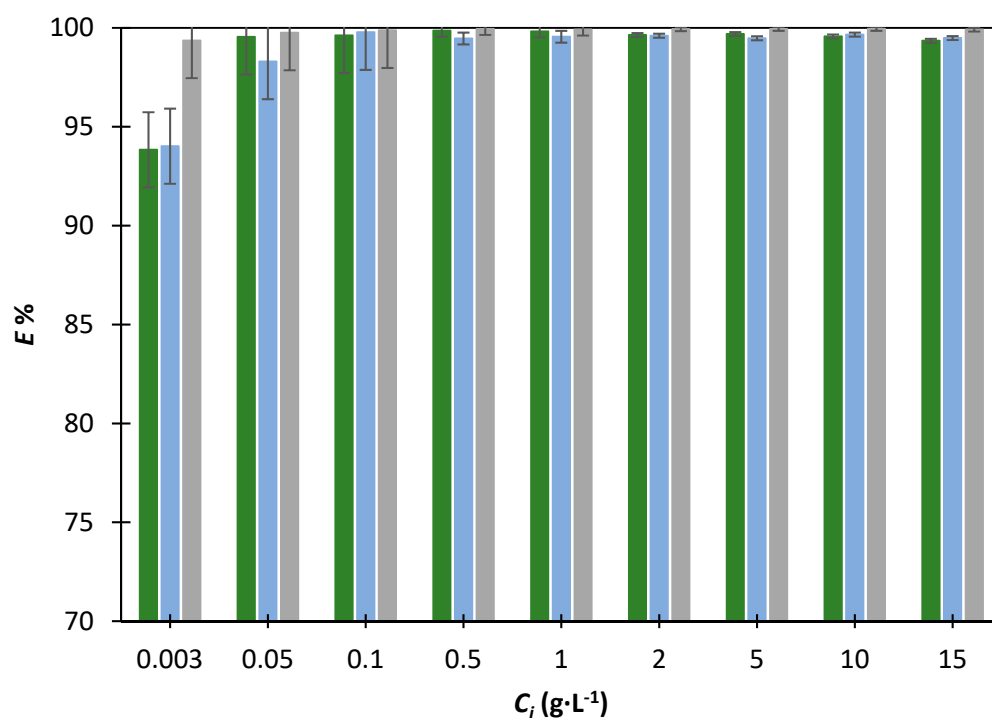


**Figure 1.** Extraction efficiency ( $E\%$ ) versus initial concentration ( $C_i$ ) of phenol (—), o-cresol (—) and 2-chlorophenol (—) for the extraction using [EMim] [DCA] and 30% of  $\text{K}_3\text{PO}_4$ .

The legal limit, established in  $1 \text{ mg}\cdot\text{L}^{-1}$ , was reached with only one extraction process for all initial concentrations below  $500 \text{ mg}\cdot\text{L}^{-1}$  for phenol and o-cresol with all studied percentages of salt. For higher initial concentrations, one more extraction step would be needed to achieve the legal limit. For the extraction of 2-chlorophenol, the legal limit was reached with one extraction step for initial concentrations below  $1000 \text{ mg}\cdot\text{L}^{-1}$  using 20% of salt with both ILs, and this value increased to 10,000 using 30% and 40% of salt. Only one more extraction cycle was needed when the initial concentration of 2-chlorophenol was  $15,000 \text{ mg}\cdot\text{L}^{-1}$ . For the extraction of PCM with 20% of salt, the legal limit was reached for initial concentrations below 500 in one cycle with 30% of salt, this value reached initial concentrations below  $1000 \text{ mg}\cdot\text{L}^{-1}$ , and with 40% of salt, concentrations were below  $10,000 \text{ mg}\cdot\text{L}^{-1}$  using both ILs. For the other systems, one more extraction cycle was necessary.

### 3.1. Effect of Initial Concentration in the Extraction Yield

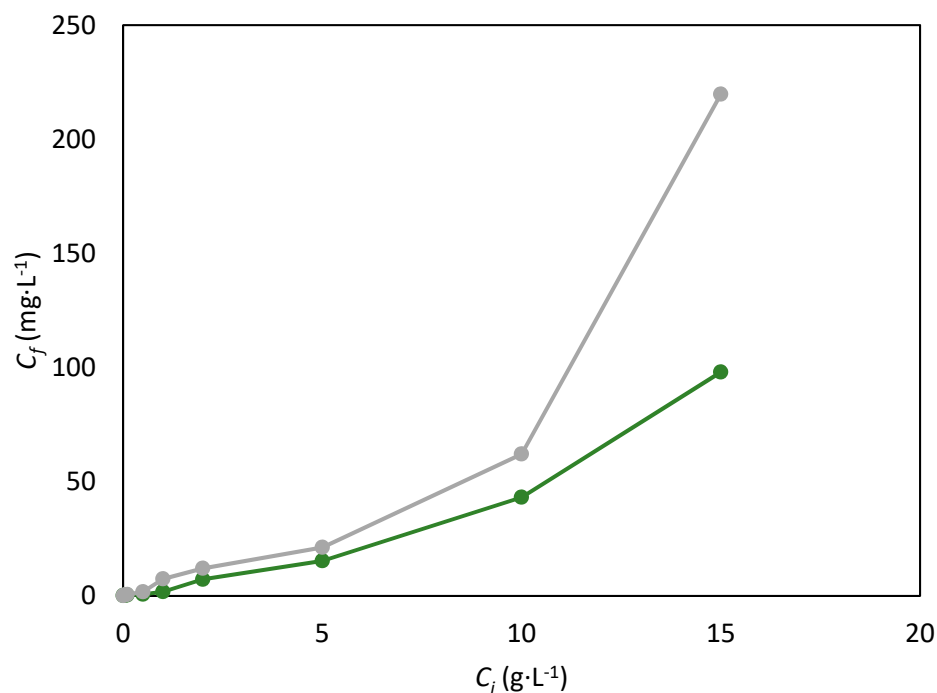
The initial concentration of the compound that wanted to be extracted significantly influenced the extraction efficiency since a lower amount of the compound meant more difficult extraction. Regarding the obtained results, for the removal of 2-chlorophenol and PCM, the extraction yields were higher than for phenol and o-cresol, even at the lowest initial concentration. This behavior can be observed in Figure 2, where the extraction efficiency for the removal of the three phenolic compounds at all initial concentrations was plotted using [EMim] [DCA] as an extraction solvent with 20% of salt. Nevertheless, all data were higher than 92%, and the extraction efficiencies increased as the initial concentration increased.



**Figure 2.** Extraction efficiency ( $E\%$ ) versus initial concentration ( $C_i$ ) of phenol (—), o-cresol (—) and 2-chlorophenol (—) for the extraction using [EMim] [DCA] and 20% of  $K_3PO_4$ .

### 3.2. Effect of the Cation Structure of the IL in the Extraction Yield

Ionic liquids are salts formed by anions and cations, and both have an important role in their properties as extraction agents. The influence of the structure of the anion is usually greater than the cation. However, there are studies that showed the influence of the extraction efficiency as a function of the length of the alkyl chain of the cation since this increase increased the hydrophobicity of the solvent [37]. In the present work, the influence of the alkyl chain length of the cation was not significant, and all the results were high. Nevertheless, it is possible to note a slightly better difference in the extraction when [EMim] [DCA] was used as an extraction agent (Figure 3). This is in line with the conclusions obtained by Neves et al. [37], which indicate that the more hydrophilic the cation of the IL is, the greater its ability for extraction.



**Figure 3.** Final concentration ( $C_f$ ) versus initial concentration ( $C_i$ ) for the extraction of phenol using [EMim] [DCA] (—) and [BMim][DCA] (—) with 20% of salt.

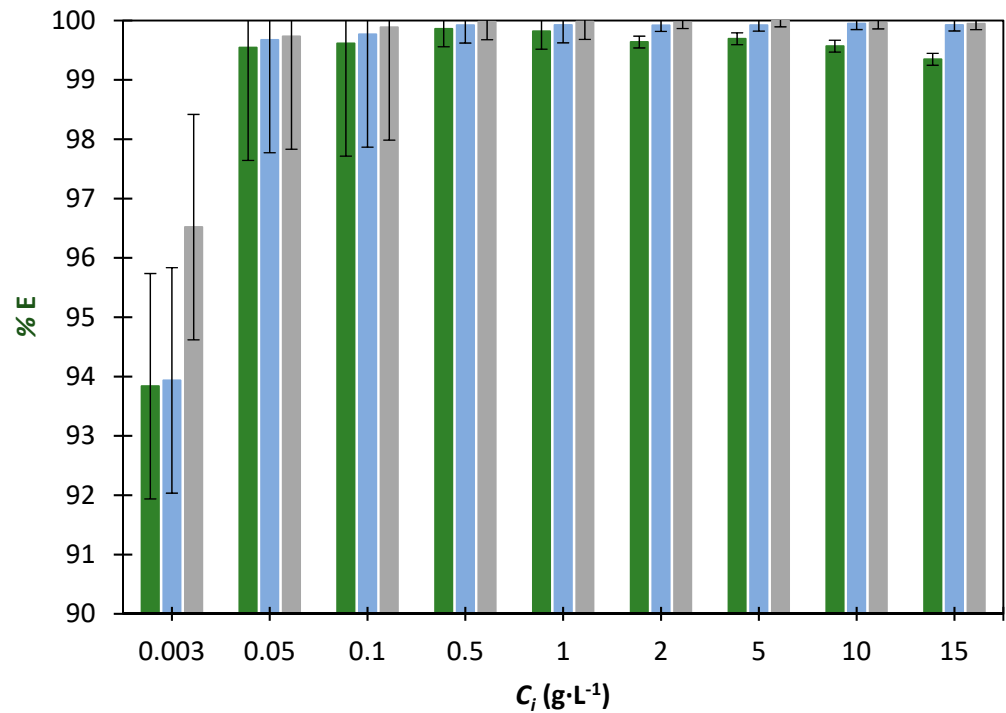
### 3.3. Effect of the Salt Concentration in the Extraction Yield

Regarding the study carried out, three different concentrations of salt were studied at 20, 30, and 40% ( $w/v$ ). Regarding the obtained results, an increase in the salt concentration slightly improved the extraction efficiency. It is possible to observe this behavior in the initial concentrations, as is shown in Figure 4, for the extraction of phenol, where at the lowest initial concentration, the extraction efficiency increased from 93.84% to 96.52%, increasing the % of the salt. This increase was higher for the results obtained using [EMim] [DCA], as can be observed in Figure 5, where the final concentration of o-cresol using both IL [EMim] [DCA] (a) and [BMim] [DCA] (b) is represented, at the three studied concentrations of salt, for all initial concentrations. For the extraction using 30% and 40% of salt, the final concentration of o-cresol was lower than  $10 \text{ mg}\cdot\text{L}^{-1}$  for all the initial studied concentrations using [EMim] [DCA], and these results were higher for the extraction using [BMim] [DCA].

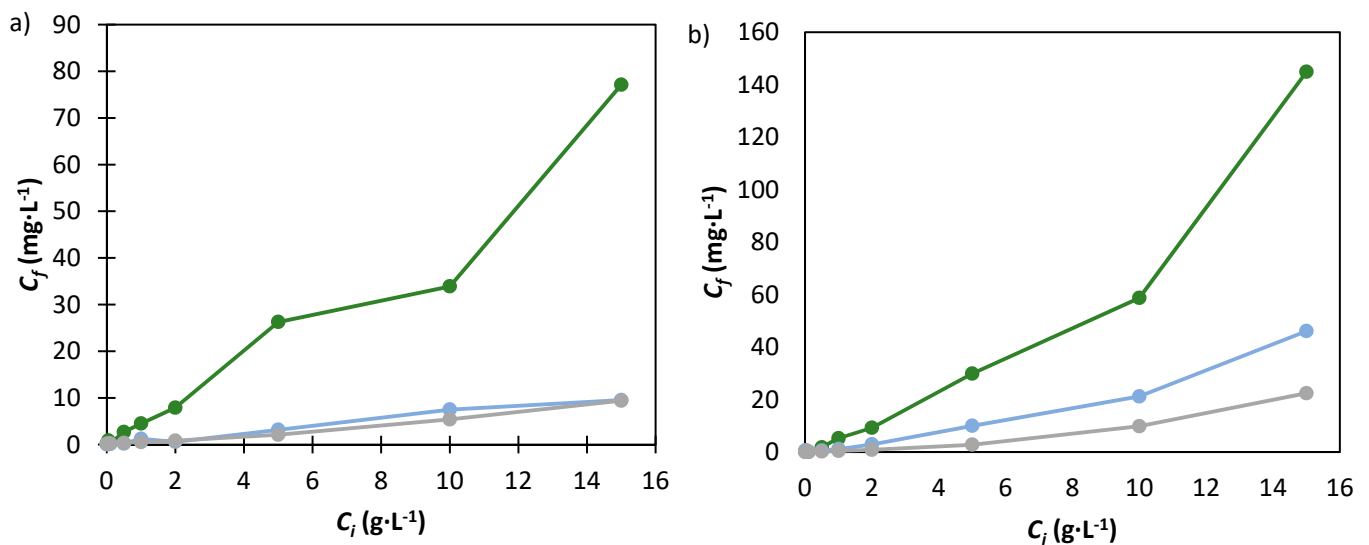
In work published by Fan et al. [7], it is explained that the presence of salts in water generally increases extraction efficiency. This behavior is explained by the lower “free water” available in the aqueous medium, and thus, the apparent phenolic compound concentration increases.

### 3.4. Extraction of Phenolic Compound Mixture (PCM)

The extraction of the multi-component system, formed by phenol, o-cresol, and chlorophenol, was carried out under the conditions described above. As it is possible to observe in both figures for the extraction of PCM using [EMim] [DCA] and [BMim] [DCA] (Figure 6a,b, respectively), an increase in the salt concentration increased the extraction of the mixture. Once more, the extraction efficiencies were higher for the removal of PCM using [EMim] [DCA] than using [BMim] [DCA]. These results are in agreement with the observations carried out by Mohammadi et al. [38], where the increase in the concentration of the salt increased the extraction efficiency.



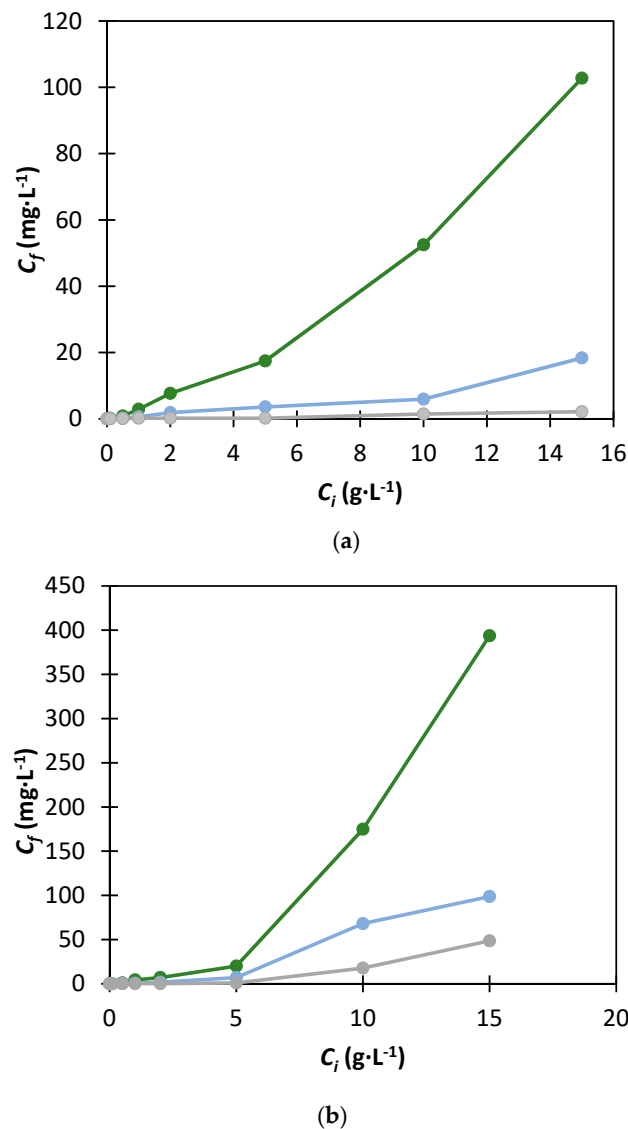
**Figure 4.** Extraction efficiency ( $E\%$ ) versus initial concentration ( $C_i$ ) of phenol for the extraction using [EMim] [DCA] and 20% (—), 30% (—) and 40% (—) of  $K_3PO_4$ .



**Figure 5.** Final concentration ( $C_f$ ) versus initial concentration ( $C_i$ ) of o-cresol for the extraction using (a) [EMim] [DCA] and (b) [BMim] [DCA] and 20% (—), 30% (—) and 40% (—) of  $K_3PO_4$ .

Considering the results presented in this work for the extraction of phenolic compounds presented in aqueous systems, it can be concluded that ATPS, formed by ILs based on the [DCA] anion  $K_3PO_4$ , allowed their removal with high extraction yields.





**Figure 6.** Final concentration ( $C_f$ ) versus initial concentration ( $C_i$ ) for the extraction of PCM using (a) [EMim] [DCA] and (b) [BMim] [DCA] with 20% (—●—), 30% (—●—) and 40% (—●—) of  $K_3PO_4$ .

#### 4. Conclusions

In this work, the extraction capability of two hydrophilic ILs, [EMim] [DCA] and [BMim] [DCA], was evaluated for the removal of three phenolic compounds, phenol, o-cresol, and chlorophenol, and a mixture of these compounds (PCM) from water using three different concentrations of salt, (20, 30 and 40% of  $K_3PO_4$ ), and ATPS.

For all the studied systems, the extraction efficiencies were generally high, with extraction yields greater than 90% for all the initial studied concentrations of phenolic compounds at all concentrations of salt.

The legal limit established for these compounds in water is  $1 \text{ mg}\cdot\text{L}^{-1}$ , and it was reached in only one extraction cycle for 2-chlorophenol and PCM for initial concentrations lower than  $1000 \text{ mg}\cdot\text{L}^{-1}$  and for  $500 \text{ mg}\cdot\text{L}^{-1}$  of phenol and o-cresol. For the other systems with two extraction cycles, it was possible to obtain dischargeable water.

It was observed that an increase in the salt concentration increased the extraction efficiencies, and an increase in the initial concentration of the phenolic compound increased the efficiencies.

Regarding the alkyl chain length of the cation of the IL, there were slight differences between the extraction results—both are good extraction agents for phenolic compounds in

water—nevertheless, in this work, better results were observed when [EMim][DCA] was used as the extraction solvent.

Both ILs presented high extraction efficiencies when the mixture of phenols (PCM) was extracted from the water, which means that they could be applied in real industrial wastewater where these compounds are normally present as a mixture.

The best result was obtained for the extraction of 2-chlorophenol with 40% salt using [EMim][DCA] as an extraction agent.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/app13032009/s1>.

**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 and editing, B.G. and Á.D. All authors have read and agreed to the published version of the manuscript.

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

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