Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Correia, Paulo M. M. and de Carvalho, Jorge R.(2005) 'Salt Effects on the Recovery of Phenol by Liquid-Liquid Extraction with Cyanex 923', Separation Science and Technology, 40: 16, 3365 — 3380
To link to this Article: DOI: 10.1080/01496390500423722
URL: http://dx.doi.org/10.1080/01496390500423722

Separation Science and Technology, 40: 3365–3380, 2005
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ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390500423722

Salt Effects on the Recovery of Phenol by Liquid-Liquid Extraction with Cyanex 923

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Abstract: In this work, the effect of salt addition on the recovery of phenol from a 46 g/L aqueous solution simulating a phenolic resin plant effluent by liquid-liquid extraction at 298 K has been studied by using an organic phase containing 0.6 M Cyanex 923 extractant in ShellSol T. Addition of sodium sulfate, potassium nitrate, and sodium chloride to the aqueous phase was tested and sodium chloride was selected. Based on the obtained results, a study of phenol recovery process was undergone by taking advantage of the salting-out effect. Equilibrium curves are presented for liquid-liquid extraction with and without salt addition to the aqueous phase. An integrated process involving salting-out and liquid-liquid extraction was proposed. The stripping concentrates can be reused for phenolic resin production.

Keywords: Phenolic resins, liquid-liquid extraction, phenol, salt addition, salting-out

INTRODUCTION

Phenolic resins are polymeric compounds of phenols and aldehydes characterized by their high shear and heat resistance. These resins are produced by a batch process consisting of the loading of a reactor with a phenol and formaldehyde mixture in certain proportions, catalyst addition, pre-heating or continuous heating to achieve polymerization conditions and consequent resin formation and drying until the desired resin water content is reached.

Received 8 April 2005, Accepted 10 October 2005

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Phenolic resins are mostly used in molding compounds, coatings and industrial bond resins for grinding wheels, coated abrasives, brake lining, clutch facing, laminates, plywood adhesives, glass-wool thermal insulation, bonded organic-fiber padding, foundry-sand bonding, wood-waste, cork bonding and other miscellaneous applications (1).

In this work, the recovery of phenol by liquid-liquid extraction from a 46 g/L aqueous solution simulating the effluent resulting from phenolic resins production has been studied.

The processes for phenolic compounds removal from industrial effluents can be classified in destructive processes (that lead to the degradation of phenolic compounds, converting them into other compounds) or non destructive processes (that allow the separation of phenolic compounds from the aqueous effluent and its posterior recovery) (2). Examples of phenol destructive processes are incineration, chemical oxidation, and biological degradation. Since the scope of this work is the recovery of phenol for its reuse in phenolic resins production, non destructive processes must be used. Examples of phenol non destructive processes are liquid-liquid extraction, activated carbon adsorption (it could be destructive, depending on regeneration process), adsorption in resins, ion exchange, membrane processes, and mixed processes involving liquid-liquid extraction and adsorption.

The range of application of the different technologies must be considered. As a general guideline the following can be taken into account (2):

i. To deal with highly concentrated phenolic effluents (tens of g/L or higher), it is possible to apply incineration and, eventually, liquid-liquid extraction;
ii. For the treatment of moderately concentrated phenolic effluents (of the order of the thousands of mg/L), liquid-liquid extraction, resin adsorption, hydrogen peroxide oxidation, and liquid membranes can be considered;
iii. The treatment of aqueous effluents with phenols in low concentrations (of the order of the hundreds of mg/L or lower) can be achieved by activated carbon adsorption, biological degradation processes, chemical oxidation, or liquid membranes.

These limits cannot be taken as compulsory. For example, Wan et al. (3) have reported the treatment of highly concentrated phenolic waste waters (phenol concentration range 7 to 47 g/L) by liquid surfactant membranes technology by using an appropriate membrane phase formulation and a suitable electrocoalescer for demulsification of the loaded emulsion that allowed to reuse the organic membrane phase at least seven times. However the present authors tried the same technology with commercially available diluents and surfactants to two effluents from phenolic resin production (one with 46 g/L phenol and 41 g/L formaldehyde and other less concentrated with 787 mg/L phenol and 3487 mg/L formaldehyde) and only could obtain interesting results with the less concentrated effluent as published in (4, 5), due to the low stability of the liquid membrane composition that led to the occurrence of swelling and to a difficult demulsification step.

Taking the above information into account to deal with an effluent with 46 g/L phenol content, in order to recover and concentrate it, liquid-liquid extraction seems to be the proper choice. Despite the fact that the process of liquid-liquid extraction applied to simple phenols has been extensively studied, most of the studies used volatile and water-soluble solvents. In this process, the aqueous effluent is contacted with an organic solvent in which phenols are dissolved preferentially. Isopropyl ether, benzene, methylisobutylketone, butyl acetate and isoamyl alcohol (6–8) and also mixtures of solvents (9) have been widely used. This technology has the drawbacks of solvent stripping, usually by distillation, in order to reuse it and to allow phenols recovery. The separation of the solvent, eventually dragged by the effluent, after their mutual contact in the extractor (either by entrainment or due to some solubility in the aqueous phase) is also a limiting factor.

As an alternative to these conventional solvents, extractants with low solubility in the aqueous phase have been developed, such as tertiary amines (10). The extractant reacts with phenols during the extraction stage, forming a complex soluble in the organic phase. This allows obtaining a great increase of the capacity of the organic phase for phenols. Solvent stripping stage can also be achieved by distillation and the phenols are obtained as the distillate. Due to their high boiling point (181.4°C for phenol (11)), chemical stripping by contacting the extract with a concentrated aqueous solution of a strong base is more interesting economically. The respective phenolates are formed, which, due to their ionic character, have a larger solubility in the aqueous stripping phase and concentrate in it by using a convenient phases ratio. Studies with salts of tertiary amines (namely chlorides and sulphates) as extractants for the extraction of phenol, chlorophenols and nitrophenols (12–14) have been published in the literature.

Besides amine extractants, liquid-liquid extraction was also applied with good results to phenol extraction by using Cyanex 923 (a mixture of four trialkylphosphine oxides) as the extractant (15, 16). The extraction mechanism occurs, in this case, by solvation (17), since the compounds present in the extractant form relatively strong and reversible hydrogen bonds with phenols. Szymanowski and co-workers (18–20) have also studied the recovery of phenol with Cyanex 923 in several membrane-extraction systems, both dispersive and non-dispersive. These researchers also compared the efficiency of Cyanex 923 with other extractants such as Amberlite LA-2 and trioctylamine in the recovery of phenol from aqueous streams in hollow fiber modules and verified that Cyanex 923 performance is better both in the extraction and in the stripping step, due to higher capacity of the solvent phase.

In the case of solvating extractants, such as Cyanex 923, extraction depends often on the ion strength. It plays a role in the relative strength of the solute-water and solute-extractant bonds, which leads to competition between water and the extractant for the solvation sites (17). Thus the presence of ionic species in the aqueous phase will compete with the solute for solvation water, that the hydration degree of the solute will decrease and its bond to the solvating extractant will be benefited.

The main objective of this research work is to depurate the effluent of a Portuguese phenolic resin plant containing approximately 46 g/L phenol and 41 g/L formaldehyde (the detailed composition is presented elsewhere (4, 21)) and obtain a phenolic resin concentrate with phenol content higher than 300 g/L, which can be reused in phenolic resin production as raw material. Studies of phenol and formaldehyde extraction from phenolic resin plant effluents with several extractants and solvents were presented elsewhere (4, 21). Cyanex 923 was chosen as a selective extractant for phenol towards formaldehyde, because it presented both the highest extraction degree for phenols and the highest selectivity towards formaldehyde among the tested extractants. In this paper the effect of salt addition is studied in order to optimize phenol recovery.

EXPERIMENTAL

Liquid-liquid extraction equilibrium studies at 298 K were performed by agitation of the aqueous and organic phases in an Aralab Agitorb 160E orbital agitator, with temperature and agitation speed control. This equipment was connected to a Aralab Refri 320E cooling unit that allowed pumping cooling water to the orbital agitator, in the tests at temperature lower than room temperature.

Organic phases were prepared by diluting the extractant Cyanex 923 (a mixture of 4 trialkylphosphine oxides; purity higher than 93 wt.%; average molar weight: 348 g/mol, produced by Cytec (22)) in the isoparaffinic hydrocarbon solvent ShellSol T, of Shell Chemicals Ltd. (paraffin content higher than 99 wt.%; average relative molecular weight: 169 (23)).

For preparing the aqueous stripping and scrubbing solutions, sodium hydroxide (MERCK p.a., purity higher than 99 wt.%) and HCl (MERCK p.a., purity higher than 37 wt.%) were used, respectively.

For the study of the effect of salt addition, a salt was introduced in the initial aqueous phase before extraction and stripping cycles. Sodium sulfate (MERCK p.a., purity higher than 99 wt.%), potassium nitrate (MERCK p.a., purity higher than 99 wt.%) and sodium chloride (MERCK p.a., purity higher than 99.5 wt.%) were tested.

Salting-out experiments were undergone by preparing the aqueous phase with several salts at different concentration in a calibrated volumetric flask. Its content was introduced in a separator funnel and shaked at 298 K for 15 minutes in an Aralab Agitorb 160E orbital agitator, with temperature and agitation speed control. After shaking, the phases were allowed to settle for

180 minutes at 298 K. An upper layer highly concentrated in phenol separated by salting-out effect from the salty aqueous phase whose phenol content has consequently lowered. Both phases were analyzed for phenol content. The same salts as the ones used in the effect of salt addition were used.

Analysis of phenols in the aqueous phase samples was made by 4-aminoantipyrine reaction colorimetric method (24). The analyses were performed in a double beam ultraviolet/visible spectrophotometer Hitachi U2000. Phenol used for standards and synthetic effluent preparation was analytical grade (MERCK p.a., purity higher than 99.5 wt.%). In the spectrophotometrical analysis no effect was noticed from the presence of salts in the aqueous phase. This was checked against a blank composed by deionized water and others containing salts in several concentrations.

pH measurement was performed by using a Metrohm 632 pH Meter with a Metrohm combined electrode.

RESULTS AND DISCUSSION

The results of the studies with a 46 g/L phenol aqueous solution used to simulate the effluent of a Portuguese phenolic resin plant containing approximately 46 g/L phenol and 41 g/L formaldehyde involving the effect of salt addition at several concentration ranges are presented below.

Effect of Salt Addition to the Synthetic Effluent in the Overall Process of Phenol Recovery

To study the effect of salt addition to the aqueous phase to increase its ion strength in the global process, cycles of extraction and stripping with several concentrations of sodium sulfate, potassium nitrate, and sodium chloride were carried out.

The study of the effect of sodium sulfate addition in the global process was accomplished through an extraction stage of phenol solutions with several concentrations of sodium sulfate with 0.6 M Cyanex 923 in ShellSol T at 298 K. The phase ratio, V_{aq}/V_{org}, of 3/1 was used. After the extraction studies, the loaded organic phases were stripped with 3 M NaOH and a phase ratio, V_{aq}/V_{org}, of 1/3 was used. The results are presented in Fig. 1.

There is a linear relationship between the extraction percentage increase and the concentration of sodium sulfate, due to the effect of ion strength. Results as high as 87.5% were obtained. However, the presence of Na_2SO_4 in the extraction stage had a deleterious effect in the stripping stage. Therefore, a commitment solution should be used that would allow simultaneously the largest extraction and stripping percentages.

For trying to solve this problem, the introduction of a scrubbing stage of the organic phase with 0.008 M HCl between the extraction and stripping steps

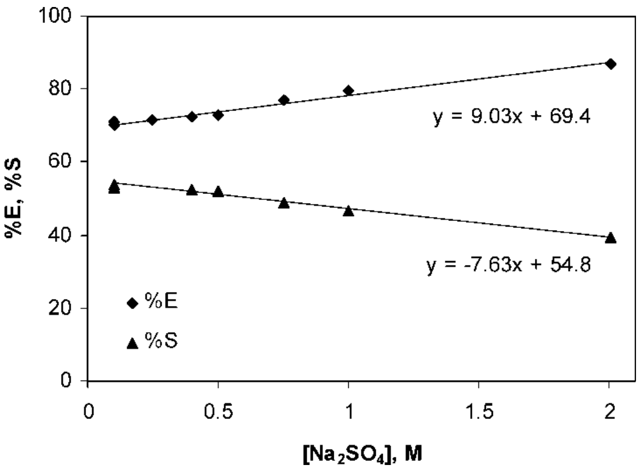

Figure 1. Effect of sodium sulfate addition in a cycle of extraction and stripping (Operating Conditions for Extraction: $V_{aq}/V_{org} = 3/1$, $T = 298$ K, agitation speed: 150 rpm; agitation time: 2 h. Operating Conditions for stripping: $V_{aq}/V_{org} = 1/3$, 3 M NaOH, $T = 298$ K, agitation speed: 130 rpm; agitation time: 2 h). The separation of phases was immediate in all of the tests.

was tested. Since the salt has a higher solubility constant than phenol, it would be transferred preferentially to the aqueous phase than phenol, which would remain in the organic phase. Then, it would be possible that the subsequent stripping would be as efficient as the stripping in the absence of salt. However scrubbing studies with 0.008 M HCl undergone between extraction and stripping did not improve very much the stripping extent. Thus this procedure was abandoned.

Another limitation of salt addition is the possibility to obtain a salty effluent, when the subsequent removal of the salt is not economically viable. In order to reuse the effluent, further extraction/stripping tests were undergone with potassium nitrate so that the effluent could be used as chemical fertilizer, if it is completely clean of phenol.

Extraction studies of 46 g/L phenol solutions containing several concentrations of potassium nitrate with 0.6 M Cyanex 923 in ShellSol T were undergone. From the observation of Fig. 2, it is verified that the increase of phenol extraction percentage with KNO_3 concentration increase was not so noticeable as in the study accomplished with Na_2SO_4 (as one can see through the line slopes). Since Cyanex 923 (assigned below as S) is a solvating extractant, the reaction could be expressed by

$$C_6H_5OH \cdot (H_2O)_{p(aq)} + qS_{(org)} \rightarrow C_6H_5OH \cdot S_{q(org)} + pH_2O_{(aq)}$$

As shown above, during extraction water molecules in the solvation sphere of phenol are exchanged by extractant molecules, so that a complex with higher

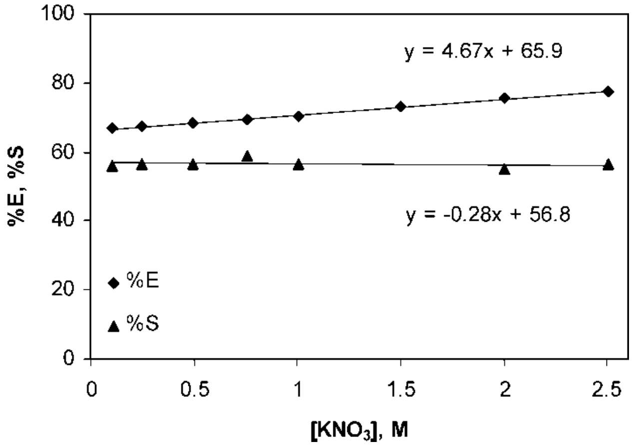

Figure 2. Effect of potassium nitrate addition in a cycle of extraction and stripping (Operating Conditions for Extraction: $V_{aq}/V_{org} = 4/1$, $T = 298\,K$, agitation speed: 134 rpm; agitation time: 2 h. Operating Conditions for stripping: $V_{aq}/V_{org} = 2/5$, 3 M NaOH, $T = 298\,K$, agitation speed: 135 rpm; agitation time: 2 h). The separation of phases was immediate in all of the tests.

solubility in the organic phase is obtained. The presence of salts in the aqueous phase causes a competition of its cations with phenol for solvating water molecules, thus reducing the degree of hydration of phenol and facilitating its bonding to extractant molecules. Since potassium cation has a higher ionic radius than sodium cation, it is not so easily hydrated than Na^+. Thus it cannot compete so effectively with phenol for the hydration water molecules present in the aqueous phase that would lead to phenol solvation by the extractant molecules. The increase of the distribution coefficient with the decrease of the cationic radius, in any one periodic group and with the increase of cation valence has also been reported by Cox (17).

Relatively to stripping, it is verified that it does not have a very steep slope. Thus no great alterations are verified in the percentage of stripping of the organic phase with the increase of KNO_3 concentration.

Since the presence of potassium nitrate was not very relevant for the improvement of the process, no further studies with this salt were made.

A study was made on the effect of the ionic strength by using sodium chloride because sodium cation already proved its efficiency and because sodium chloride could be obtained from inexpensive sources, *e.g.*, as a by-product from the tanning industry (since the hides used as raw material in this industry are often preserved in sodium chloride).

To study the effect of salt addition with sodium chloride, extraction tests of phenol solutions with several concentrations of this salt were undergone. Subsequently the organic phases were stripped with 3 M NaOH and the obtained results are shown in Fig. 3.

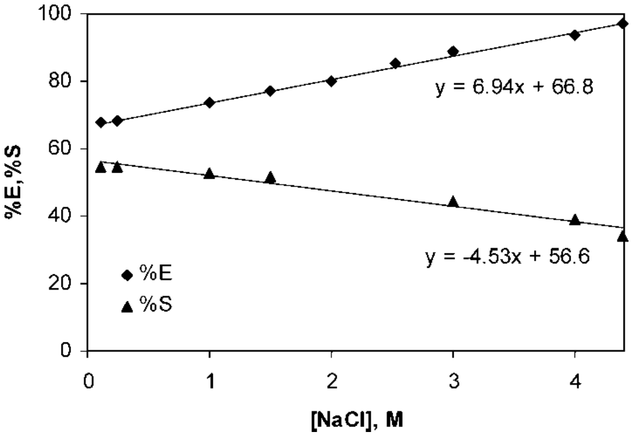

Figure 3. Effect of sodium chloride addition in a cycle of extraction and stripping (Operating Conditions for Extraction: $V_{aq}/V_{org} = 4/1$, $T = 298$ K, agitation speed: 132 rpm, agitation time: 2 h. Operating Conditions for stripping: $V_{aq}/V_{org} = 2/5$, 3 M NaOH, $T = 298$ K, agitation speed: 135 rpm, agitation time: 2 h). The separation of phases was immediate in all of the tests.

As shown in Fig. 3, phenol extraction percentage reached 97.3% in the concentration of salt saturation (approximately 4.4 M). A raffinate with 1.3 g/L phenol resulted. On the other hand, that salt concentration allowed a stripping percentage of only 34.2% (which corresponds to a loss of 22.4% in the stripping percentage, relatively to the same situation in the absence of sodium chloride). Thus a commitment solution must also be reached in this case.

Effect of Salting-Out in Phenol Synthetic Solutions

The salting-out effect in the synthetic aqueous solutions of phenol, due to the formation of two liquid phases, after the addition of salts was studied. The separation of both phases and respective analysis for phenol in solutions with concentrations of Na_2SO_4 of 0.5 M, 0.75 M, 1 M and 3 M was carried out (for 3 M Na_2SO_4, the dissolution of the salt in the 46 g/L phenol solution was not complete). The results of this study are shown in Fig. 4.

As can be seen, from a feed solution containing 46 g/L of phenol and 3 M Na_2SO_4, two layers are obtained from the salting-out effect after mixing and settling: a lower layer consisting of a phenol in water fraction with a phenol concentration of 4.4 g/L and an upper layer consisting of a concentrated phenolic fraction with a concentration of 883 g/L in phenol, *i.e.*, about three times more concentrated in phenol than the intended objective of phenol reuse.

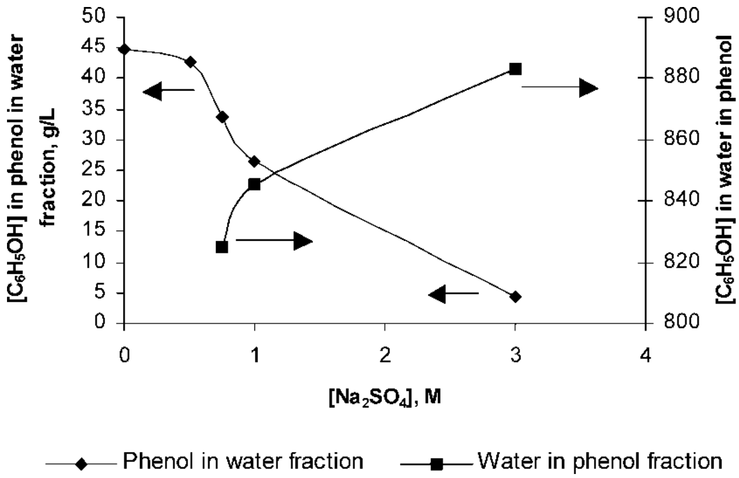

Figure 4. Salting-out effect in a 46 g/L synthetic solution of phenol due to the presence of sodium sulfate (Operating conditions: contact time: 180 min; $T = 298$ K).

The addition of potassium nitrate did not cause any separation of layers by salting-out effect.

After the addition of sodium chloride to 46 g/L phenol solutions, the formation of two liquid phases occurred again. As shown in Fig. 5, this value of concentration was twice the value obtained in the studies with sodium

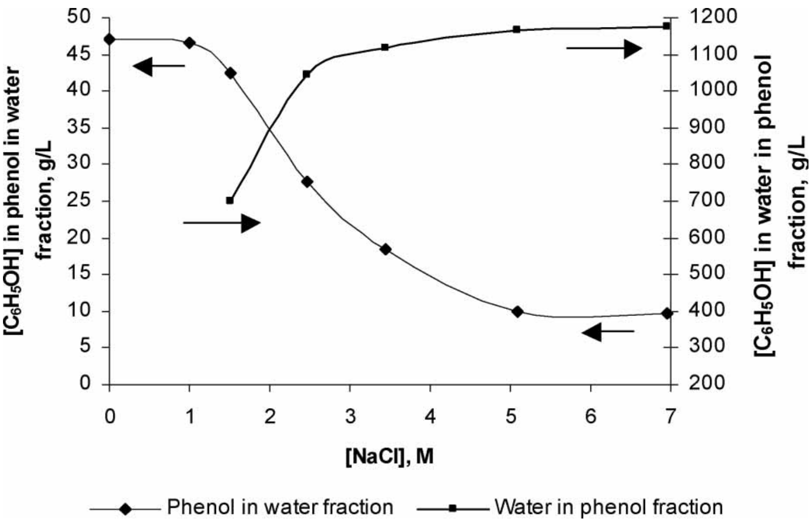

Figure 5. Salting-out effect in a 46 g/L synthetic solution of phenol due to the presence of sodium chloride (Operating conditions: contact time: 180 min; $T = 298$ K).

sulfate, since each Na_2SO_4 molecule contains two sodium ions. This confirms that the salt cation is the one responsible for most of the salting-out effect.

It should be noted that the saturation point for 41 g/L phenol solutions containing sodium chloride is 4.8 M. Thus, in Fig. 5, the curves stabilize for higher values of salt concentration due to solubility limitations.

Establishment of an Equilibrium Curve for the Extraction of Phenol after the Salting-Out Effect

Based on the results presented for the salting-out effect, a study was conducted by submitting the synthetic effluent to the addition of sodium chloride for subsequent separation of the most concentrated phase in phenol followed by the recovery of phenol from the least concentrated fraction by liquid-liquid extraction. It was decided to use 3.5 M sodium chloride in the synthetic solutions of phenol, for subsequent extraction, since for higher concentrations, phenol content in fraction with highest phenol concentration no longer rises in a significant way and also due to higher difficulties in NaCl dissolution.

The most concentrated fraction in phenol formed in a solution containing 46 g/L phenol and 3.5 M sodium chloride was separated. The fraction least concentrated in phenol (containing 16.81 g/L phenol) was used in extraction studies with 0.6 M Cyanex 923 in ShellSol T at several phase ratios. The results are compared in Fig. 6 with the case of a 16.81 g/L phenol solution

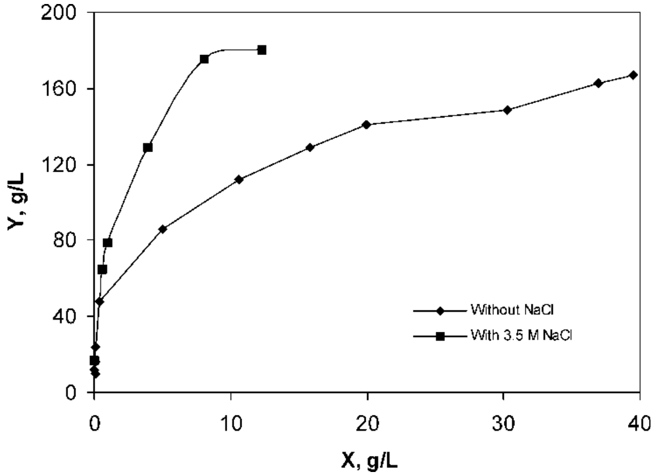

Figure 6. Phenol extraction isotherm from a solution containing 16.81 g/L phenol and 3.5 M sodium chloride with 0.6 M Cyanex 923 in ShellSol T (Operating Conditions: V_{aq}/V_{org} variable, $T = 298$ K, agitation speed in orbital agitator: 145 rpm, agitation time: 2 h) and comparison with the same process in the absence of salt. *X* and *Y* represent the solute concentration in the aqueous and organic phase after reaching equilibrium, respectively.

without NaCl addition. The extraction of phenol in the presence of sodium chloride is more efficient than in its absence.

Through the reading of the extreme points of the bold curve in Fig. 6, is verified that the capacity of the organic phase is of 180.4 g/L phenol (without NaCl addition it was of 167.1 g/L). On the other hand, by considering 4 counter-current equilibrium theoretical stages, the raffinate concentration of phenol is 10.5 mg/L.

Establishment of an Equilibrium Curve for the Stripping of the Organic Phase Loaded with a Saline Solution of Phenol

For the establishment of an equilibrium curve for the stripping of the organic phase, a solution with 46 g/L phenol and 3.5 M NaCl was prepared with the separation of the fraction with the highest phenol concentration (containing 960 g/L phenol). The organic phase was contacted with the fraction with the least phenol concentration in two stages in order to carry it up to the value of the organic phase capacity (180.4 g/L). A phase ratio V_{aq}/V_{org} of 10 was used. After the extractions, the loaded organic phase was stripped with 3 M NaOH at several phase ratios. The results of these tests are summarized in Fig. 7.

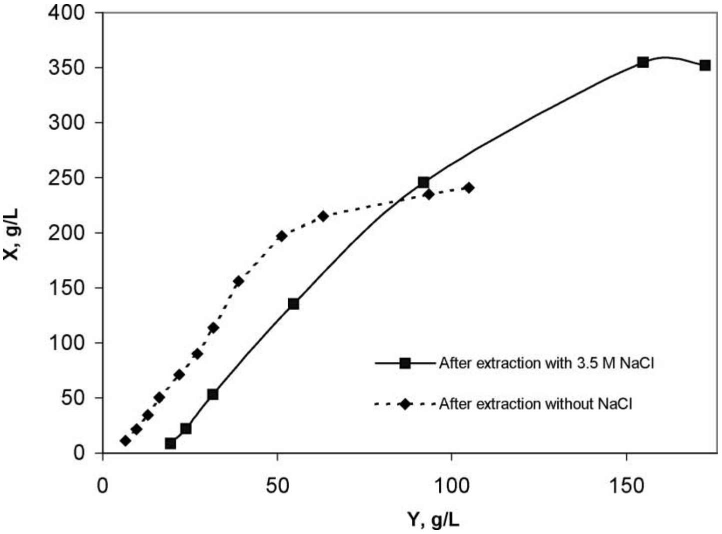

Figure 7. Stripping isotherms, with 3 M NaOH, from the organic phases containing 0.6 M Cyanex 923 in ShellSol T, loaded with phenol, with and without salt in the extraction step. (Operating Conditions: V_{aq}/V_{org} variable, $T = 298$ K, agitation speed: 130 rpm (in orbital agitator), agitation time: 2 h). X and Y represent the solute concentration in the aqueous and organic phase after reaching equilibrium, respectively.

The curves plateaus happen when the aqueous phase (composed by 3 M NaOH) becomes saturated. Thus, the plateau of the stripping equilibrium curve after extraction of the aqueous phase containing NaCl is higher, since the loaded organic phase was more concentrated in phenol. From the reading of the extreme point on the right side of the curve, it is obtained that the aqueous phase contains 352.1 g/L phenol. Once this concentration will correspond approximately to the composition of the aqueous phase at the exit of a stripping column, then the intended concentration factor was reached. For initial stripping condition, it is expected that from the curve the organic phase content in phenol after counter-current stripping is 19 g/L.

Integrated Process of Phenol Recovery by Liquid-Liquid Extraction

Based on the results of the present study, the operating conditions proposed for the integrated process of liquid-liquid extraction of 46 g/L phenol solutions are presented in Fig. 8.

The recovery process starts with the addition of sodium chloride to the phenolic resin wastewater in order to have 3.5 M NaCl concentration. The separation of two liquid phases by salting-out effect occurs. One is about 20 times more concentrated in phenol than the initial solution. It has approximately 3.3% of the initial solution volume, pH of about 6 and can be directly reused in the phenolic resin manufacture process. The other fraction is about 3 times more diluted than the initial solution, with about 96.7% of the initial volume. It was treated by liquid-liquid extraction with 0.6 M Cyanex 923 in ShellSol T in a phase ratio V_{aq}/V_{org} of 10.

An aqueous solution containing about 10 mg/L in phenol and an organic phase loaded with about 180 g/L phenol are obtained. The raffinate with about

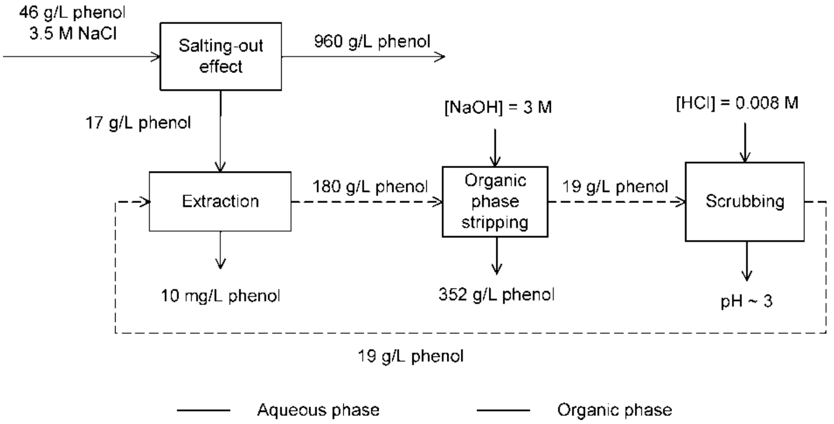

Figure 8. Schematic diagram of an overall extraction cycle proposed in this study.

10 mg/L phenol will be directed for a process of treatment of formaldehyde and dilute solutions of phenol (*e.g.*, oxidation with ultraviolet radiation and hydrogen peroxide, adsorption, etc.) that will be presented elsewhere.

The organic phase is directed for the stripping process, at 298 K, with 3 M NaOH at the phase ratio V_{aq}/V_{org} of 1/2, to obtain an aqueous solution with about 352 g/L phenol and pH of 14, and an organic phase with about 19 g/L in phenol that is directed for the scrubbing of the organic phase with 0.008 M HCl at phase ratio V_{aq}/V_{org} of 3/1. An aqueous solution with pH of about 3 is obtained and the organic phase can be reused for a new extraction. The aqueous phase resulting from the scrubbing step has still some phenol content and it will be directed for the treatment process of phenol dilute solutions.

The phenolic concentrate obtained in stripping can be directly reused in the phenolic resin manufacture process or submitted to acidification, in order to concentrate phenol again and to precipitate it before it is reused in phenolic resins manufacture process.

CONCLUSIONS

A brief description of phenolic resins and of their production process has been presented. Liquid-liquid extraction has been applied to a phenol solution with the same concentration as the effluent resulting from their production.

From the results of the present study, the selective separation of phenol in concentrated solutions through liquid-liquid extraction technology with chemical reaction, using 0.6 M Cyanex 923 in ShellSol T as solvent, has benefited by the previous addition of a salt to the phenol solution due to the salting-out effect. This allows separating a phenol concentrated phase in the beginning of the treatment process.

The use of NaCl has shown more advantages than the one of Na_2SO_4 and KNO_3 because it is more effective in causing a beneficial ion strength effect and it can be obtained from an inexpensive source, *e.g.*, as a by-product from tanning industry.

Based on these results, an integrated process was proposed that included NaCl addition to the phenolic resin effluent and separation of the layer with highest phenol concentration (960 g/L phenol) for reusing in phenolic resin production. Additional phenol was recovered from the layer with lowest phenol concentration by liquid-liquid extraction. A concentration higher than 300 g/L phenol was reached in the stripping phase, which allowed its use in phenolic resins production. For reusing the organic phase, scrubbing with HCl is undergone so that the pH reduces to about 3. Dilute solutions of phenol and formaldehyde are submitted to chemical oxidation. The resulting NaCl aqueous stream can be mixed with the other plant waste waters. Alternatively studies of NaCl recovery and reuse by evaporation-crystallization are being considered in order to make the process self-sustainable in NaCl requirements.

Since the real phenolic resin wastewater effluent contains salts that were used to catalyze the reaction of resins synthesis, the accomplishment of further studies in order to adjust NaCl concentration in the effluent must be undergone, so that the intended concentration of about 300 g/L in the phenol concentrate after stripping is reached with the minimum of NaCl concentration in the system.

During the study of ion strength and salting-out effects, the effect of the formaldehyde presence in solution was not considered, so the study of its influence in the system will be done in future work.

The economical viability of this process depends on the availability of a cheap source of salt. The possibility of making the process self-sufficient in NaCl by the evaporation-crystallization of the saline effluent resulting from the treatment process, after removal of phenol and formaldehyde, could also be considered. However this option is not so economically interesting due to the high energy costs involved.

Anyway, the use of liquid-liquid extraction, even without the previous addition of a salt to the effluent, is a selective and efficient process for phenol recovery from the phenolic resin plant waste water allowing phenol reuse in the phenolic resin production.

Further work including studies in several types of liquid-liquid extraction columns (such as packed, pulsed plate, RDC and Kühni columns) must be done in order to analyze the effect of the presence of salts in a continuous process and how the system would behave after several cycles of extraction, stripping and scrubbing. Also, modeling of the results by considering the equilibrium solvation reaction and the understanding of the salt effects both qualitatively and quantitatively by studying the dependence of phenol extraction constants on ionic strength and the variation in the equilibrium constant with the ionic strength is previewed in future work. Also, the activities of the different species in solution will be considered.

LIST OF SYMBOLS

$\% E$	percentage of extraction (%)
$\% S$	percentage of stripping (%)
T	temperature (K)
V_i	phase *i* volume (see subscripts) (m^3)
X	solute concentration in the aqueous phase after reaching equilibrium (g/L)
Y	solute concentration in the organic phase after reaching equilibrium (g/L)

Subscripts

0	initial
aq	aqueous

f	final
org	organic

ACKNOWLEDGEMENTS

The authors would like to thank Eng. Francelino Fernandes for his helpful comments, the company FUNDIPOR–Production of Products for Foundry, Lda. (Oporto) for the phenolic resins effluent given to be studied in this work, Margarida Sampaio for her help in part of the experimental work and Shell Chemicals, Ltd. and Cytec Inc. for providing the reagent samples. The financial support of FCT and AdI (Portuguese Government Funding Agencies) is also acknowledged.

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