

Separation of Chlorophenols using Inverse Emulsion with Carrier

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In this work we aimed to test the effectiveness of the chlorophenols extraction method using inverse emulsions with carrier in the presence of kerosene as organic solvent. We also considered the identification of the main operational parameters (source phase pH, phase source / emulsion volume ratio, contact time, concentration of carrier) influence on the extraction yield. The experimental results showed that the studied method can be used to separate the chlorophenols from ideal diluted solutions to concentrations that allow their discharge into surface waters. From the three carriers studied: Aliquat 336, fatty amine C18-C14 and trioctyl amine, fatty amines have been found to be the most effective. Also, the source phase pH is a parameter that plays a major role in the achievement of high extraction efficiency due to the protonation process.

Keywords: chlorophenols, extraction, kerosene, inverse emulsions

Phenols are present in large quantities in petroleum products from oil refineries. An important source of phenols is the waste water discharged from coal, wood processing and distillation plants, tar, coke ovens and petrochemical industry [1, 2].

The presence of phenols in water induce toxicity, persistence and bioaccumulation in animal and vegetable bodies and represents a risk factor for human health. The phenol is a toxic compound for fish nervous system. The toxicity limit depends on the fish species and is between 6 and 20 mg / L. Phenol gives taste and odor to fish meat and causes a very sharp deterioration to water organoleptic properties. In the case of surface water, the disinfection was done with chlorine, taste and odor of the water is completely degraded [3].

Chlorophenols are organic compounds in which one or more hydrogen atoms of the phenol are substituted by one or more chlorine atoms. Thus, there are 19 types of chlorophenols grouped according to the chlorine atoms number: mono, di, tri, tetra and penta chlorinated [4].

Chlorophenols are mainly introduced into the environment during the manufacture of various products (pesticides, drugs, dyes), in the disinfection stage by chlorination of surface or waste water containing organic compounds, as by-products from paper bleaching step [2,3].

Most of the chlorophenols released in the environment end-up in the water, so that the population is exposed to very low concentrations (ppt order) by drinking water consumption which was subject to disinfection by chlorination [4].

The main chlorophenol pathways in human body are: oral with food, cutaneous by skin contact, respiratory with the inspired air [4,5].

These compounds are particularly accumulated in the kidney and liver, brain, muscle and fat. The toxic effect of chlorophenols is directly proportional to their degree of chlorination. An acute exposure to low-chlorination degree phenols results in: muscle spasms, tremors, weakness, ataxia, convulsions and collapse [6]

Concentration and separation using liquid membranes has experienced an explosive growth both for metal ions and organic substances recovery, in contrast to the separation, and in particular, the regenerative separation of anions or non-metals [8-17].

The treatment of waste waters using liquid membranes is an intensive process used as a viable alternative at the procedures mentioned above [18-22].

The use of liquid membranes presents a series of advantages: selective, simple in concept and operation, they are modular and easy to scale-up and they are low in energy consumption with a remarkable potential for low environmental impact and energetic aspects [23-31].

In this work we aimed to test the effectiveness of the chlorophenols extraction method using inverse emulsions with carrier in the presence of kerosene as organic solvent. We also considered the identification of the main operational parameters (source phase pH, phase source / emulsion volume ratio, contact time, concentration of carrier) influence on the extraction yield.

Experimental part

Materials and methods

Kerosene (Merck), H₂SO₄ (Merck), HCl 25% (Merck), NaOH (Merck), NaHCO₃ (Merck), Na₂CO₃ (Merck), and distilled water were analytical grade.

SPAN 80 (Sigma-Aldrich), nonylphenol ethoxylate with 4 moles of ethylene oxide and carriers (Aliquat 336, tri-octyl amine, fatty amines C₁₄-C₁₈) have a technical purity.

The removal of chlorophenols from the aqueous solution was carried out by contacting the inverse emulsion containing receiving phase, with source phase, under stirring, in order to make a contact area as large as possible. This way is produced a double emulsion A / U / A which exists as long as stirring is maintained.

The inverse emulsion dispersion into the source phase was performed using a multistage propeller-type stirrer, working at a stirring speed of 200 rpm which provides a good dispersion (the average particle size of the inverse emulsion was 0.25 mm).

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After a certain contact time, when stirring was stopped, the inverse emulsion was rapidly separated on the source phase surface, due to the density difference.

The inverse emulsion will be destroyed in order to recover the receiving phase, which contains the extracted phenol ions.

Synthetic phenols solution (10-50 ppm) analyses were carried out with a Perkin Elmer Spectrophotometer [22-24].

Results and discussions

The extraction experiments in which are used inverse emulsions took into account the following chloro phenol extraction parameters:

- the source phase pH;
- source phase/emulsion volume ratio;
- contact time timpul de contact;
- emulsion swelling.

The influence of source phase pH on the extraction yield

According to the accepted transport mechanism, source phase pH plays an important role in the extraction of phenols.

In the experiments, the source phase pH values ranged from 2 to 12, and the contact time between source phase and inverse emulsion was between five minutes and one hour.

The extraction results, expressed as the yield of chlorophenols removal from source phase using different surfactants (Span 80, nonylphenol ethoxylate with 4 moles of ethylene oxide) and carriers (Aliquat 336, tri-octyl amine, fatty amines C₁₄-C₁₈) in the presence of Merck kerosene as organic solvent are shown in figures 1-13.

For all the experiments, the extraction yield variation curve has a maximum around pH = 5, which corresponds to the approximately pKa of the target substance and which can be considered as the optimum value.

In carrying out the extraction experiments the receiving phase/source phase volume ratio 1:10, as well as receiving phase/organic phase 5:1 volume ratio in the inverse emulsion were kept constant. The source phase pH change was achieved with 98% sulfuric acid Merck.

The use of a sodium hydroxide 1M aqueous solution as receiving phase, in the case of Aliquat 336 0.1% concentration extracextraction conduced to an yield of about 63%, at an acid pH (pH = 5), after 35 min (fig. 1).

The extraction yields are maximum at pH = 5, and then are lowering at alkaline pH, their value being relatively small during the first 5 min (maximum 40%).

A maximum value (60-65%) is reached after 35 min of stirring, at a pH = 5, but after 35 min, the yield decreases due to breakage of the emulsion and / or mixing of the aqueous phases.

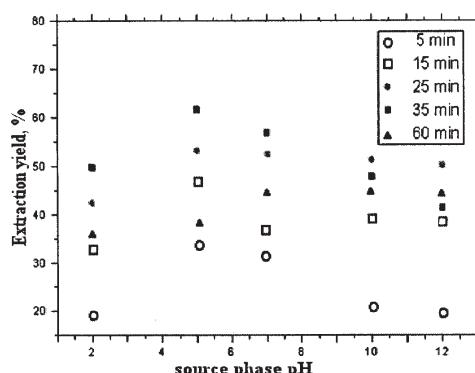


Fig. 1. pH influence on extraction yield (SPAN 80 1.5%)

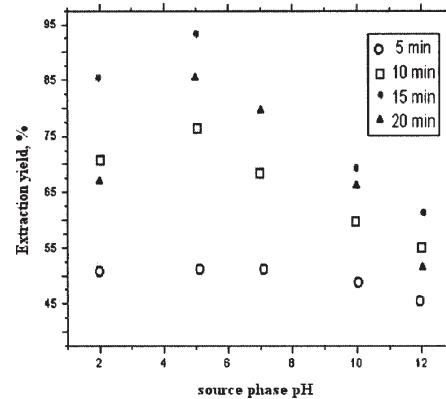


Fig. 2. pH influence on extraction yield (SPAN 80 1.5%)

Using a sodium bicarbonate 1M aqueous solution as receiving phase, Aliquat 336 concentration 0.1% as carrier is obtained a variation of the extraction yields whose progress is shown in figure 2.

The lowest values are obtained after the first 5 min (45-50%), the extraction yields are increased with the pH increase, reaching a maximum at pH = 5 and then are decreasing. At contact times greater than 20 min, the extraction yield decreases due to emulsion breakage.

The use of trioctyl amine 0.1% concentration as carrier and a NaOH 1M aqueous solution as receiving phase, does not lead to improved extraction efficiency (fig. 3). Extraction yields of up to 55% were obtained after a long period of time (35 min), at a pH also around 5.

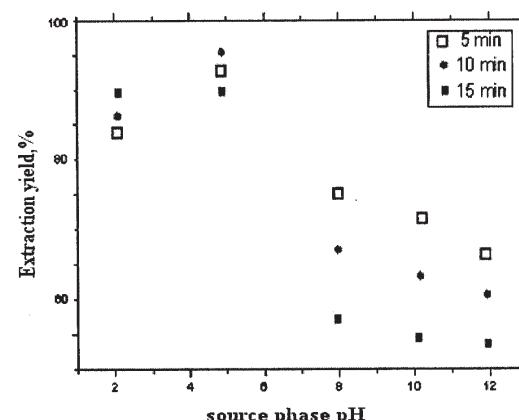


Fig. 3. pH influence on extraction yield

The best results are obtained when the fatty amines are used as carrier (fig. 3-6) for which the extraction yields values are reaching a maximum, as expected at pH 5, and then decrease in a basic medium.

At a concentration of fatty amines 1.5% a value of 90% for the extraction yield at pH = 5 is reached in the first 5 min, and then it drops in basic medium until to a value of 65% (fig. 3). As the contact time between the inverse emulsion and source phase increase, the yield gradually decreased, in the same way, due to partial breakage of the emulsion. After 10, 15 min of stirring, yields of about 90% are obtained at an acidic pH.

For a concentration of fatty amines 1%, the results are similar as in the case above, only that after a 15 min contact time, the yields are lower, the maximum at pH 5 being approximately 80% (fig. 4).

In the case of fatty amines 2% concentration yields over 95% are obtained at pH = 5 (fig. 5) starting from the first 5 minutes.

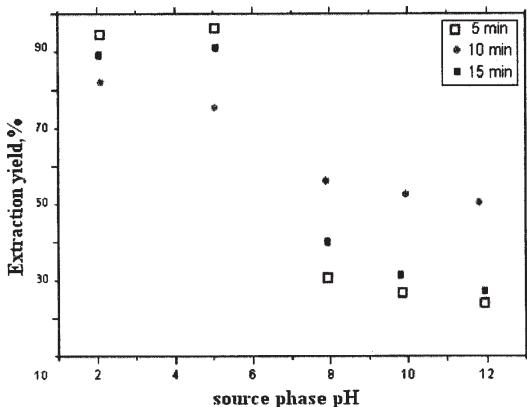


Fig. 4. pH influence on extraction yield

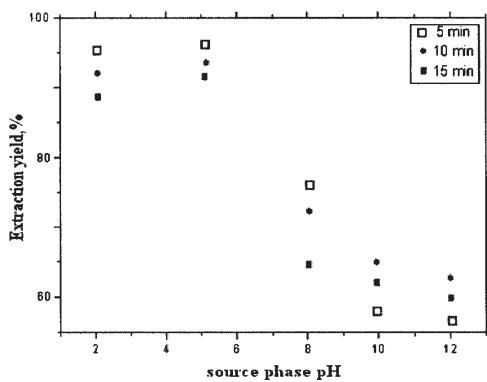


Fig. 5. pH influence on extraction yield

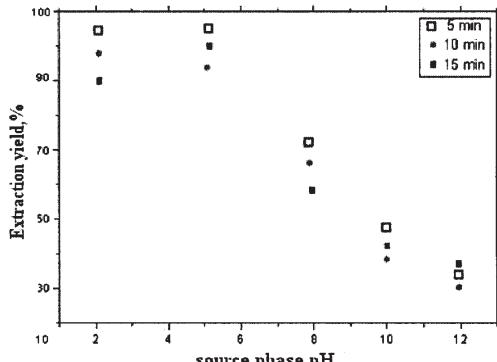


Fig. 6. pH influence on extraction yield

After 10, 15 minutes the extraction yields have reached a maximum between 80-90%, and then they sharply decrease in a basic medium until values between 20-45%.

A similar behaviour is also obtained in the case of fatty amines concentration 3 % (fig. 6).

In all cases of extraction using fatty amines according to figures 3-6, the curve allure substantially differs from the one obtained in the case of extraction using Aliquat 336, in the sense that maximum extraction yields are obtained at all pH values under 5.

The use of Aliquat 336 as carrier in the phenols removal from the water, results in obtaining extraction yields ranging from 60-80% at acid pH (fig. 1), followed by a decrease starting from a neutral to a basic source phase pH.

The best results (extraction yields over 95%) are obtained with fatty amine as carrier at a concentration 1.5-2%, at acid pH (fig. 3-6).

The chlorophenol's extraction yields have decreased with increasing the source phase pH.

This decrease is more evident in the case of using the amines (triethyl amine: fig. 5; fatty amines: fig. 3-6),

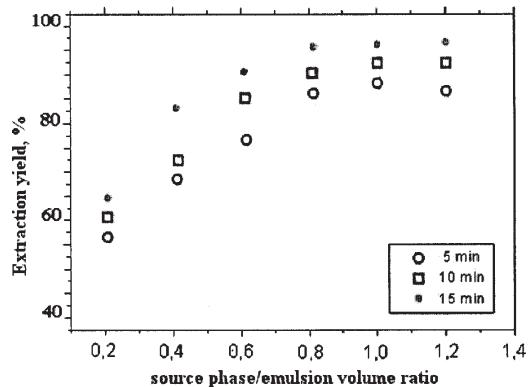


Fig. 7. Influence of source phase / emulsion volume ratio V_E / V_{SP} on extraction yield (SPAN 80 1.5%)

compared to Aliquat 336, due to carrier molecules „activation” process in the presence of protons, process which is not necessary in the case of Aliquat 336.

This represents quaternary ammonium salts which can transported phenol ions without an initial protonation into source phase.

The influence of source phase/emulsion volume ratio on extraction yield

Ideally, in the technological applications, the primary emulsion volume (receiving phase / kerosene) is desired to be minimized, for economic reasons (high cost of the surfactant, large volumes handled).

Through this study we aimed to investigate the influence of inverse emulsion / source phase volume ratio on the extraction yield.

At a ratio of 1:1.2 and a source phase pH = 5, using Aliquat 336 concentration 0.1% as carrier and NaHCO₃ 1 M aqueous solution as receiving phase, after 15 min high yields are obtained, their values approaching to 96% (fig. 7).

Increasing the source phase/emulsion volume ratio results in an increase of the extraction yield, with the occurrence of a cap phenomenon with increasing contact time (10 and 15 min).

Increasing the source phase / emulsion volume ratio involves an increase in yield; as such, it is possible to work with unit reports, which is not technologically advantageous. At a basic pH (pH = 8), using fatty amine 1.5% concentration as carrier and 1M NaHCO₃ aqueous solution as receiving phase, the extraction yields are increased slowly with an increase of the emulsion / source phase volume ratio and time contact (after 15 min of stirring, fig. 8).

At a concentration of 1% fatty amine, in a basic medium (the source phase pH is 8) and in the presence of a 1M NaHCO₃ aqueous solution as receiving phase, the

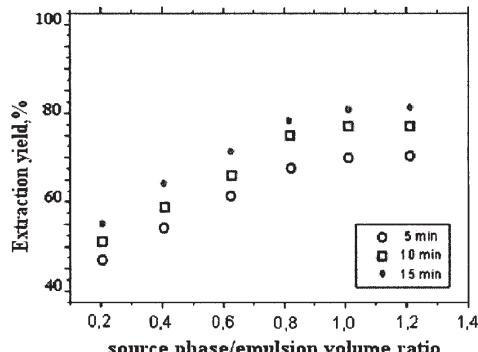


Fig. 8. Influence of source phase/emulsion volume ratio V_E / V_{SP} on extraction yield

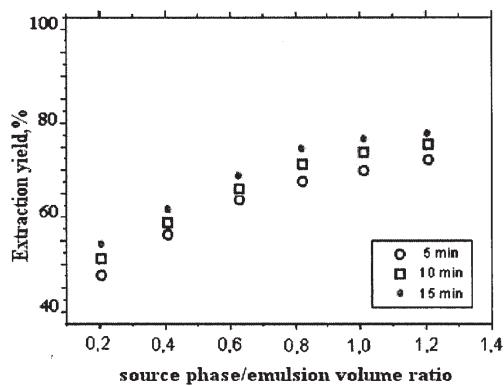


Fig. 9. Influence of source phase/emulsion volume ratio V_E/V_{SP} on extraction yield

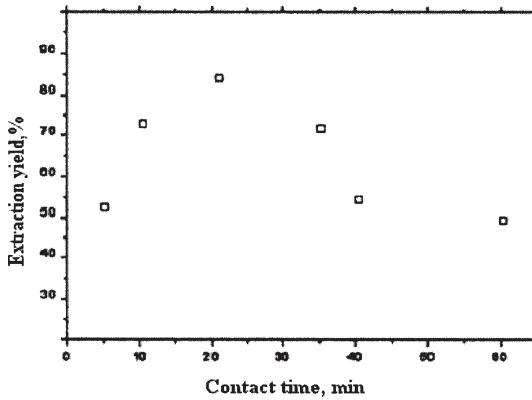


Fig. 10. Influence of contact time on extraction yield (SPAN 80 1.5%)

maximum yields (over 75%) are obtained, after 15 min (fig. 9), at an emulsion/source phase volume ratio of 1:1.2.

On the average, the chlorophenols extraction yields increase with increasing the source phase / emulsion volume ratio. The use of Aliquat 336 as carrier has the effect of achieving high yields (80-90%) at an emulsion / source phase volume ratio 1:1.2, after stirring for 15 min (fig. 7).

At a basic pH of the source phase, with fatty amines as carrier, lower yields (maximum 80%) are obtained compared to the case in which the source phase has acid pH, at emulsion / source phase volume ratios between 1:1.0-1 : 1.20, but after 15 minutes of stirring (fig. 8 and 9).

The influence of contact time on extraction yield

The parameter "contact time" between the source phase and inverse emulsion plays an important role in the efficiency of chlorophenols extraction process. It is desirable that this time to be minimized, especially in the case of application of this process to industrial scale.

The contact time between the source phase and inverse emulsion studied ranged from 5 to 60 min.

Using as carrier Aliquat 336 in an acid medium (source phase pH = 5), and NaHCO₃ 1M aqueous solution as receiving phase have the effect of increasing the extraction efficiency with contact time during the first 20-35 min when is reached a maximum (about 60%), followed by its lowering due to the partial breaking of the emulsion (fig. 10).

If nonylphenol 1.5% concentration is used as surfactant and a Na₂CO₃ 1M aqueous solution as receiving source, at a source phase pH = 5, the extraction yields are lower (about 25% after 15 min), because of higher packing density of nonylphenol ethoxylate molecules at the interface receiving phase / membrane, which act as a steric barrier, reducing the transport stream of the extracted species from the source phase (fig. 11).

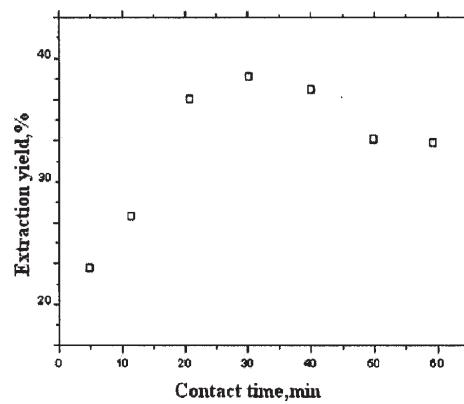


Fig. 11. Influence of contact time on extraction yield (SPAN 80 1.5%)

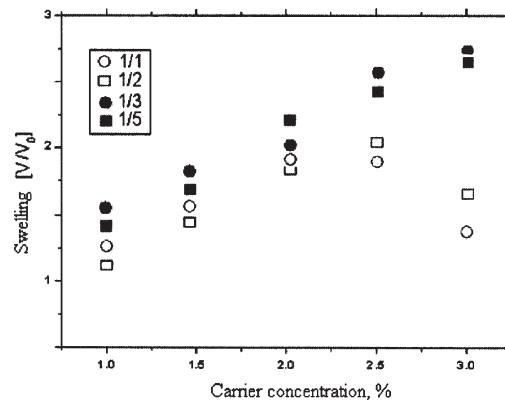


Fig. 12. Influence of carrier concentration on emulsion swelling

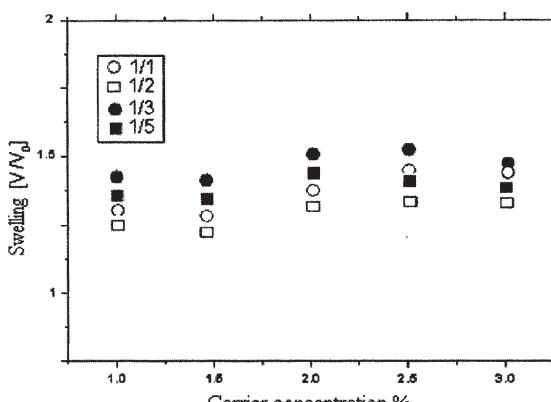


Fig. 13. Influence of carrier concentration on emulsion swelling

In an acid medium, maximum extraction efficiencies are obtained using a fatty amine concentration of 1.5%, as early 15 min, but in any case, the extraction yields for fatty amine concentration range 1-3% are over 80%.

On the average, extraction yield decreases with contact time increasing, but not below 50% value. The extraction yield increases with increasing contact time, but is not suitable for operation over 30 min.

In the first 5 min the yield values are in the range 20-50%, and then gradually increase up to 95% at a fatty amine concentration of 1.5%, but after 15 min.

The exception is represented by the fatty amines having a 3% concentration, their yield remains approximately constant (70%) in the interval 5-15 min.

In general, the extraction yield increases during the first 20-35 min and for Aliquat 336 carrier or 5-10 min, for fatty amines carrier, and then decreases due to partial breakage of the emulsion.

The type of organic solvent used has special influence in obtaining maximum extraction yields at lower contact times.

The influence of carrier concentration on emulsion swelling

An undesirable effect of emulsion liquid membrane is represented by the emulsion swelling. This is a process in which water is passed through osmosis from the external continuous phase in the internal phase.

The transfer causes a reduction of solute concentration opportunities in the internal phase and a decrease in driving force.

Swelling of the emulsion is given by the volumetric ratio V_f/V_o , where V_f is the final volume of the emulsion, after the extraction process, and V_o the inverse emulsion initial volume.

Swelling is due to either the difference in osmotic pressure between the aqueous phase or due to entrainment of the external aqueous phase within emulsion by stirring.

Swelling of the emulsion is an issue that leads to at least two drawbacks:

- lowering the concentration factor through water transportation into the receiving phase, so is diluted;
- inverse emulsion breaking due to receiving solution particle size increase from the organic solvent.

In the case of fatty amine carrier, the influence of concentration (from 1% to 3%) on emulsion swelling, at source phase pH 5 and 8 was studied.

The source phase / emulsion volume ratio was between 1:10 and 1:30, and receiving phase / organic phase (kerosene) volume ratio was 1:1.

At acidic pH (source phase pH = 5), source phase / emulsion optimum ratio producing a minimum swelling is 1:5 for carrier concentration of 1.5-2% and receiving phase: NaOH 1M aqueous solution (fig. 12).

The differences which appear in the emulsion swelling depending on the source phase/emulsion volume ratio become minimum in the case of a basic pH in the source phase.

This phenomenon is related to the low chlorophenols flow, compared with the acid medium from the source phase and thus minimum differences between the yields for the different experimental conditions.

The highest chlorophenols extraction yield is obtained for a source phase/emulsion volume ratio = 1:3, ratio at which the most powerful swelling of the studied system occurs. This result can be explained by chlorophenols transport with counter ions in their hydration sphere

Thus, the receiving phase expands its volume. The hydration sphere transport leads to concentration factor decrease.

In basic medium (pH = 8) at a fatty amine concentration of 1.5-2%, receiving phase: NaOH 1M aqueous solution, the situation is somewhat inverse in the sense that at source phase/emulsion volume ratio of 1:3 minimal swelling are obtained (fig. 13).

Conclusions

The aim of the experiments was to study the influence of various operating parameters on chlorophenols extraction process efficiency in the presence of Merck kerosene as organic solvent.

The results obtained from the studies carried out on three types of surfactants: Span 80, $C_{14}-C_{18}$ fatty amine and ethoxylated nonyl-phenol with 4 moles of ethylene oxide have revealed that the first two compounds form

sufficiently stable emulsions in order to be used in the extraction process.

Notable differences are observed between the first two compounds, in the first place in terms of process execution speed, as well as the extraction evolution.

From the studies done on three types of carriers: Aliquat 336, which is a quaternary ammonium salt, $C_{14}-C_{18}$ fatty amines and amine trioctyl we determined that in order to be efficient, the last compounds, require the protons presence, so an acid environment in the source phase to form sulphate - amine complex, which is actually the active transporter.

Comparing the results obtained for the three carriers results that fatty amines are more efficient than the other two studied compounds.

A parameter that plays a crucial role in achieving high extraction yields is the pH of source phase, due to protonation process.

In the case of carrier Aliquat 336, the extraction efficiency has a maximum value at pH 5, while the fatty amine extraction yields are maximum at any pH below 5.

In the phenol extraction process, another important parameter is the nature of the receiving phase. Thus, we have studied three aqueous solutions systems: hydroxide, carbonate and sodium bicarbonate 1M. Maximum efficiency was obtained for 1M sodium hydroxide aqueous solution.

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References

- 1.EL MHAMMEDI, M.A., ACHAK, M., BAKASSE, M., CHTAINI, A., J.Hazard Mat., **163**(1), 2009, p. 323
- 2.ALIZADEH, T., REZA GANJALI, M., NOROUZI, P., ZARE, M., ZERAATKAR, A., Talanta, **79**(5), 2009, p. 1197
- 3.P., MULCHANDANI, C. M., HANGARTER, Y., LEI, W., CHEN, A. MULCHANDANI, Biosens. Bioelectron., **21**(3), 2005, p. 523
- 4.Z., LIU, J., DU, C., QIU, L., HUANG, H., MA, D., SHEN, Y., DING, Electrochim. Com, **11**(7), 2009, p. 1365
- 5.HAN, S., FERREIRA, F.C., LIVINGSTON, A., J. Membr. Sci., **188**, 2001, p.219
6. CORREIA, P.F.M.M., DE CARVALHO, J. M.R., J.Membr.Sci., **225**, 2000, p. 41
- 7.R.P. CAHN, N.N. LI, Sep. Sci.Tech., **9**, 1974, p. 505
- 8.K., PROVAZI, B. A., CAMPOS, D., CROCCE, R., ESPINOSA, J. A. S., TENÓRIO, Waste Management, **31**, 2001, p. 59
- 9.NECHIFOR, A.C., RUSE, E., NECHIFOR, G., SERBAN, B., Rev. Chim. (Bucharest), **53**, no. 1, 2002, p. 20.
- 10 NICOL, S.K., GALVIN, K.P., ENGEL, M.D., **5**(10-12), 1992, p. 1259
- 11.MAVROV, V., ERWE, T., BLÖCHER, C., CHMIEL, H., Desalination, **157**(1-3), 2003, p. 97
- 12.GALVIN, K.P., NICOL S.K., WATERS, A.G., Colloids and Surfaces, **64**(1), 1992, p. 21-33.
- 13.STRZELBICKI, J., SCHLOSSER, S., Hydrometallurgy, **23**, 1989, p. 67
- 14.GHEORGHE, E., BARBU, L., NECHIFOR, G., LUCA, C., Rev. Chim. (Bucharest), **57**, no. 9, 2006, p. 940.
- 15.SOLDENHOFF, K., SHAMIEH, M., MANIS, A., J. Membr. Sci., **252**, 2005, p. 183
- 16.PEREIRA, F. P., LAVILLA, I., BENDICHO, C., Spectrochim. Acta B, **64**, 2009, p. 1
- 17.KUMBASAR, R. A., Sep. Pur. Technol., **63**, 2008, p. 599
- 18.SENGUPTA, B., BHAKHAR, M. S., SENGUPTA, R., Hydrometallurgy, **89**, 2007, p. 311
- 19.OKAMOTO, Y., NOMURA, Y., NAKAMURA, H., IWAMARU, K., FUJIWARA, T., KUMAMARU, T., Microchem. Journal, **65**, 2000, p. 341

- 20.SERBAN, B., RUSE, E., MINCA, M., PASARE, J., NECHIFOR, G., Rev. Chim. (Bucharest), **51**, no. 4., 2000, p. 249
- 21.CRACIUN, M.E., MIHAI, M., NECHIFOR, G., Environmental Engineering and Management Journal, **8**, 2009, p. 771.
- 22.DIACONU, I., NECHIFOR, G., NECHIFOR, A.C., RUSE, E., EFTIMIE TOTU, E., Rev. Chim. (Bucharest), **60**, no. 12, 2009, p. 1243
- 23.DIACONU, I., ABOUL-ENEIN, H. Y., AL-OMAR M. A., NECHIFOR, G., RUSE, E., BUNACIU, A.A., EFTIMIE TOTU, E., Arabian Journal of Chemistry, **4**(1), (2011), p. 99
- 24.DIACONU, I., GIRDEA, R., CRISTEA, C., NECHIFOR, G., RUSE, E., EFTIMIE TOTU, E., Romanian Biotechnological Letters, **15**(6), (2010), p. 5702
- 25.SASTRE, A.M., KUMAR, A., SHUKLA, J.P., SINGH, R.K., Sep. Purif. Meth., **27**, 1988, p. 213
- 26.NECHIFOR, A.C., DANCIOLESCU, V., MIRON, A. R., TANCZOS, S.K., BUTUCEA, O.D., Romanian Biological Letters, Vol. **17**(6), 2012, p. 7835
- 27.DOYLE, F.M., International Journal of Mineral Processing, **72**(1-4), 2003, p. 387
- 28.PO PIECH, B., WALKOWIAK, W., Sep. Pur. Technol., **57**(3), 2007, p. 461
- 29.LURDES, M., GAMEIRO, F., ROSINDA, M., ISMAEL, C., TERESA, M., REIS, A., CARVALHO, J.M.R., Sep. Pur. Technol., **63**(2), 2008, p. 287
- 30.NECHIFOR, A.C., SAVA, S., GALES, O., TANCZOS, S.K., MIRON, A. R., Rev. Chim. (Bucharest), **64**, no. 1, 2013, p. 11
- 31.BUSCHMANN, H. J., MUTIHAC, L., Anal. Chim. Acta., **466**, 2002, p. 101

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