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# Simultaneous extraction and stripping of 4-chlorophenol from aqueous solutions by emulsion liquid membrane

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ABSTRACT

Chlorophenols (CPs) are hazardous phenolic compounds that are produced by direct chlorination of phenol in water treatment systems. They are among the most harmful substances in water and wastewater. They are toxic even in very low concentrations. So recovery and reuse methods for the treatment of effluents containing CPs (instead of destructive methods such as chemical oxidation and incineration) should be urgently developed. In the present study, the extraction of 4-CP from aqueous solutions by using emulsion liquid membrane (ELM) technique has been investigated. An effective ELM technique was used for extraction and recovery of 4-CP from aqueous solutions. The effect of feed concentration, initial pH value, internal reagent concentration, and stirring speed has been studied. The results showed at the ELM system is able to extract the solute from a feed containing 100 ppm of 4-CP within less than 5 min, completely.

*Keywords:* 4-Chlorophenol; Emulsion liquid membrane; Extraction; Stripping

## 1. Introduction

Chlorophenols (CPs) are chemical species known to be highly toxic and a potential threat to public health. CPs are generated from phenols during the treatment of tap water with chlorine and are considered to be one of the most obnoxious contaminants because they deteriorate taste and produce an unfavorable smell [1].

According to the Environmental Protection Agency classification, the so-called primary pollutants are a series of 129 organic and inorganic toxic substances. Due to their high toxicity, they are subject to specific regulations, and their industrial use is increasingly avoided by substituting them with harmless compounds. Among these, 11 are phenols (phenol or CPs), hence demonstrating the high toxicity of such a class of organic compounds. Since these chemicals are commonly employed in several industrial processes, a significant number of organic pollutants encountered in the environment belong to this class. In particular, they are abundant in the effluents of CPs producing and utilizing industries as well as cookeries and oil refineries [2].

The mono-CPs have been used as antiseptics, although in this role other chemicals have mostly replaced them. 4-CP has been used as a disinfectant for homes, hospitals, farms, and as an antiseptic for root canal treatment [3]. Phenolic wastewaters are usually treated by biodegradation, thermal decomposition, and adsorption. Under aerobic or anaerobic conditions, phenols can be degraded to harmless compounds by micro-organisms. Some aerobic bacteria and fungi utilize phenols as a source of carbon and energy, and degrade it [4]. However, the major disadvantage of biological treatment is that the micro-organisms cannot survive in high concentrations of phenol. Many researchers [5] have reported inhibition of micro-organisms by high concentrations of phenol. Thermal decomposition can be used to treat wastewater with concentrations of phenol as high as 15,000 mg/l, but it is only used in small scale for the high energy demand. Adsorption is an effective method of treating dilute phenolic wastewater. However, for the relatively high cost of activated carbon or other sorbents, adsorption cannot be used to treat high-concentrated phenolic wastewater [6].

Among the different membrane-based extraction of phenols, emulsion liquid membrane (ELM) technique is the most attractive method because of unique specifications such as very high mass transfer area, possibility of using nonselective and efficient solvents, simultaneous extraction and stripping in one step, and applicability for very low (few ppms) to very high concentrations (several thousands ppms) of phenols. Recently performed researches show that extraction of phenol from aqueous wastes is an up-to-date subject for scientists and industries [6–19].

ELM or liquid pertraction is a three-phase extraction system consists of a double emulsion with either O/W/O or W/O/W type depending on the nature of the feed. This emulsion typically made by first dispersing the internal phase in an immiscible liquid and then dispersing this emulsion in a third phase (called the external phase) so that the internal and the external phases are miscible, but both are immiscible with the membrane phase separating them. Generally, the emulsion consists of encapsulated droplets about 1–10 μm in diameter, while the dispersed emulsion in the continuous phase has the globules of the order of 0.1–2 mm in diameter. The solute is selectively being transported from the external continuous phase to the internal droplets [20–25]. Fig. 1 shows the structure of an emulsion globule.

Extraction of 4-CP from aqueous solutions, including the study of the effect of various operating parameters on the extraction efficiency, is completely new. In order to separate the 4-CP from wastewater, some solvents can be selected, in which the solubility of the solute is higher than that in water. A set of batch experiments has been carried out in this study in order to evaluate the influence of process parameters on the extraction of 4-CP from aqueous solutions.

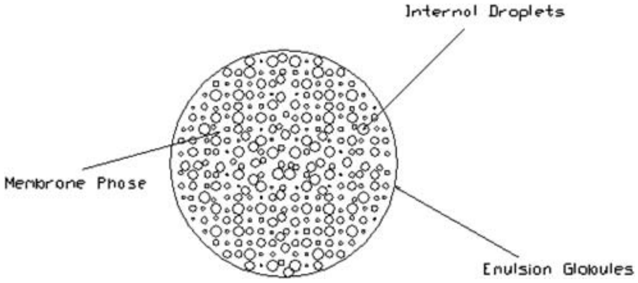

Fig. 1. A schematic presentation of an ELM (emulsion globule).

## 2. Experimental

### 2.1. Apparatus

All experiments were performed at constant temperature of 25 ± 0.2°C using a water bath equipped with a P-type controller and an agitator. Extraction experiments were carried out in a cylindrical glass container with 100 mm diameter and 150 mm height equipped with four round glass baffles with 8 mm diameter. The stirrer for the extraction experiments was made of glass with 47 mm diameter and had four pitched blades with 45° angle. Stirring driver was a laboratory mixer model RE-166 from Ika-Werk Germany with variable speed from 50 to 6,000 rpm. Fig. 2 represents the experimental set up.

A high-speed homogenizer (Ultra Turrax T-25 digital-IKA, Germany) was used for primary emulsion preparation. The speed of the homogenizer varies in the range of 0–24,000 rpm. The stirrer for the secondary emulsion preparation was Teflon® coated to minimize contamination of emulsion. It had six pitch blades with 45° angle and 63 mm diameter.

Sampling were done at the predetermined time intervals by disposable sanitary syringes and centrifuged by a laboratory centrifuge in order to separate emulsion phase from external phase.

To determine the concentration of phenol in the external phase, an UV spectrophotometer of Cecil CE-1010 was used. pH measurements were carried out by a Metrohm 780 Herisau, Switzerland, pH meter.

### 2.2. Reagents

4-CP, sodium hydroxide, hydrochloric acid, potassium ferricyanide, chloroform, and ammonia were of reagent grade and purchased from Merck. Emulsifier LK-80 was purchased from local market. The HLB value for LK-80 was 4.5. The emulsifier LK-80 is a natural product and consists of a complex mixture of acids, fatty alcohols, and esters, from $C_7$ to $C_{41}$. Iso-kerosene from Isomax® unit was supplied from Tehran petroleum refinery. Table 1 shows the specification of the Iso-kerosene. Distilled water was used throughout.

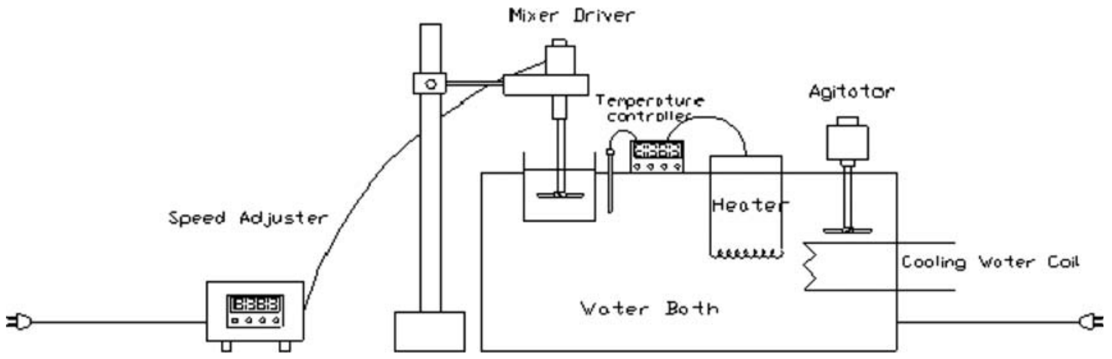

Fig. 2. A scheme of experimental set up.

Table 1
Tehran Refinery Isomax® unit kerosene (Iso-kerosene) specification [26]

| Property | Value | Unit |
|---|---|---|
| Density @ 15℃ | 0.82 | $kg/dm^3$ |
| *Distillation* | | |
| Recovered @ 185℃ (max) | 50 | %vol |
| Recovered @ 200℃ (min) | 70 | %vol |
| Recovered @ 210℃ (max) | 90 | %vol |
| Recovered @ 235℃ (max) | 95 | %vol |
| F.B.P (max) | 275 | ℃ |

### *2.3. Procedure*

All experiments were performed at 25 ± 0.2℃. Emulsions were prepared by mixing the kerosene and the emulsifier under moderate heating. Then, the internal phase was added to the mixture and homogenized for 20 min at 11,000 rpm to form a stable primary emulsion.

The external phases were prepared by dissolution of 4-CP in water followed by dilution with distilled water and pH adjustment. The external phases were placed into water bath for 20 min, and then the emulsion was added to the external phase with stirring. The external phase solution was periodically sampled at certain time intervals. The concentration of phenol in the solution was determined after separation of the emulsion phase, by sensitive 4-amino antipyrine method using UV–Visible spectrophotometer at 460 nm [27].

## 3. Results and discussion

### *3.1. Effect of external phase concentration*

Pertraction is a complex process. It is a combination of different chemical- and mechanical-related properties and operations. In pertraction operation, the internal phase reagent concentration is one of the most important parameters determining the final extraction performance. On the other hand, stability of the emulsion is vital for a successful operation. If the emulsion is less stable, the extraction operation will fail due to emulsion breakage and leakage of the internal reagent into the external phase; and if the emulsion is too stable, the emulsion breakage and recovery of the internal depleted aqueous phase is far difficult. Then a reasonable stability for the emulsion is expected.

As the extraction operation proceeds, the transfer of the solute from the external phase into the organic membrane phase lowers the viscosity of the emulsion and the emulsion starts to break. At this point, the emulsion should be separated from aqueous external phase and sent for the solute recovery process.

The effect of 4-CP concentration in the external phase, at speed of agitation of 500 rpm, is shown in Fig. 3. It is reasonable that by increasing the 4-CP concentration in the external phase, the time for extraction also increases. The figure shows that the time for extraction increases by increasing the external phase concentration. This is true for all extraction processes.

The figure shows that the pertraction system removes nearly 98% of the phenolic species within 5 min. At this point, equilibrium is established between the extraction and emulsion breakage rate, and then the extraction efficiency is remained constant. At higher feed concentration, such a behavior is observable but the amount of internal reagent was not sufficient to react with the solute and then the extraction efficiency decreases considerably.

### *3.2. Effect of agitation speed*

The effect of agitation speed on the extraction efficiency is shown in Fig. 4. By increasing agitation speed, the shear forces which act on the emulsion globules

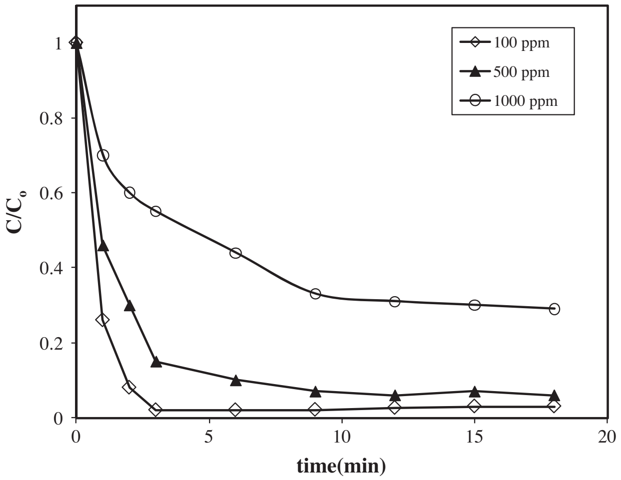

Fig. 3. The effect of the external phase concentration on the extraction efficiency. $C_i = 0.5$ M NaOH; $R_{ew} = 0.1$; pH $= 1.61$; 500 rpm.

increase and this makes the globules smaller. As other authors have pointed out, the external surface area of globules rather than the internal phase droplet surface area controls the extraction process with ELMs, so by increasing the speed of agitation the area for mass transfer increases and the extraction efficiency increases. Increasing the speed of agitation above a critical value, not only does not increase the extraction efficiency considerably, but also affects the stability of the emulsion and increases the breakage of the membrane and makes the emulsion unstable. The results in Fig. 4 show a critical speed of agitation in the range of 600–650 rpm, namely 625 rpm.

### 3.3. Effect of the internal phase reagent concentration

The effect of sodium hydroxide aqueous solution concentration as the internal phase reagent on the extraction efficiency is shown in Fig. 5. Increase in the internal phase reagent concentration increases the ability of the internal phase for stripping the membrane phase at the external surface of the internal droplets and reduces the concentration polarization at the surface that increases the driving force for the extraction.

### 3.4. Effect of the external phase pH

4-CP is a week acid and dissociates in aqueous solutions to form ionic components as follow:

$$\mathrm{PhCl{-}OH} \leftrightarrows \mathrm{PhCl{-}O^-} + \mathrm{H^+} \qquad (1)$$

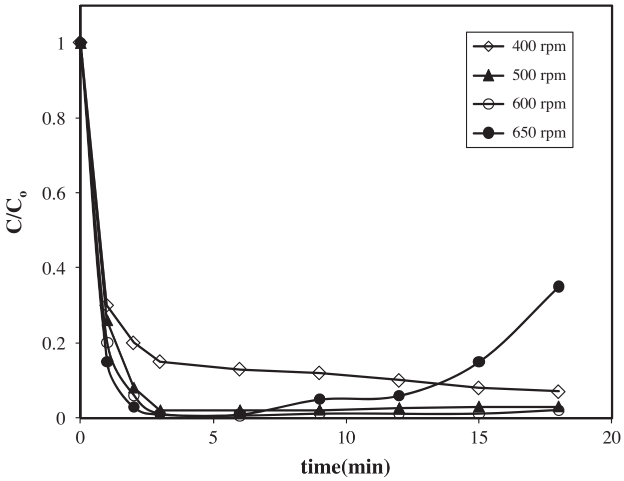

Fig. 4. The effect of speed of agitation on the extraction efficiency. $C_e = 100$ ppm; $C_i = 0.5$ M NaOH; $R_{ew} = 0.1$; pH $= 1.61$.

The molecular form of 4-CP as PhCl-OH is oil soluble where the ionic form is oil insoluble. Decrease in pH value or increase in H$^+$ concentration reverses the dissociation of 4-CP and remains it in its molecular form and consequently in an oil soluble state, which is desirable for ELM extraction. Fig. 6 shows the effect of pH on the extraction rate of 4-CP from aqueous solutions. Any decrease in pH of the external phase increases the extraction efficiency which is in agreement with Eq. (1).

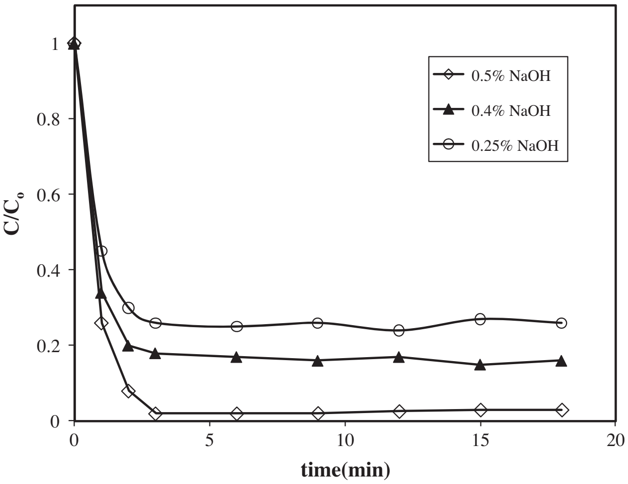

Fig. 5. The effect of internal phase reagent concentration on the extraction efficiency. $C_e = 100$ ppm; $R_{ew} = 0.1$; pH $= 1.61$; 500 rpm.

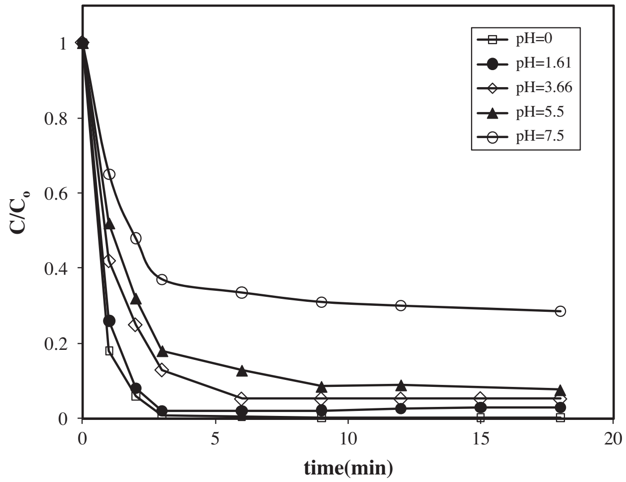

Fig. 6. The effect of external phase pH on the extraction efficiency. $C_e = 100$ ppm; $C_i = 0.5$ M NaOH; $R_{ew} = 0.1$; 500 rpm.

## 4. Conclusion

An efficient method for treatment of aqueous solutions and wastewaters containing 4-CP with high concentrations has been introduced. The most important parameter for the extraction of phenol from aqueous solutions by ELM method is the pH of the external phase. By proper selection of the parameters and the process conditions, almost all of the 4-CP present in a feed solution (up to 100 ppm) can be extracted within less than 5 min.

## References

[1] Z. Es'haghi, Extraction and determination of three chlorophenols by hollow fiber liquid phase microextraction—spectrophotometric analysis, and evaluation procedures using mean centering of ratio spectra method, Am. J. Anal. Chem. 2 (2011) 1–8.

[2] M.S.A. Palma, J.L. Paiva, M. Zilli, A. Converti, Batch phenol removal from methyl isobutyl ketone by liquid–liquid extraction with chemical reaction, J. Chem. Eng. Process. 46 (2007) 764–768.

[3] V. Glezer, Environmental effects of substitute phenols, in: Z. Rappoport (Ed.), The Chemistry of Phenols, Wiley, Chichester, 2003, pp. 1347–1368.

[4] M.M. Broholm, A. Erik, Biodegradation of phenols in a sandstone aquifer under aerobic conditions and mixed nitrate and iron reducing conditions, J. Contam. Hydrol. 44 (2000) 239–273.

[5] M. Kibret, W. Somitsch, Characterization of a phenol degrading mixed population by enzyme assay, Water Res. 34 (2000) 1127–1134.

[6] H. Jiang, Y. Fang, Y. Fu, Q.X. Guo, Studies on the extraction of phenol in wastewater, J. Hazard. Mater. B101 (2003) 179–190.

[7] Z. Lazarova, S. Boyadzhieva, Treatment of phenol-containing aqueous solutions by membrane-based solvent extraction in coupled ultrafiltration modules, Chem. Eng. J. 100 (2004) 129–138.

[8] A.M.Y. Jaber, S.A. Ali, G.O. Yahaya, Studies on phenol permeation through supported liquid membranes containing functionalized polyorganosiloxanes, J. Membrane Sci. 250 (2005) 85–94.

[9] I. Rodrguez, M.P. Llompart, R. Cela, Solid-phase extraction of phenols, J. Chromatogr. A 885 (2000) 291–304.

[10] Y.D. Wang, Q. Gan, C.Y. Shi, X.L. Zheng, S.H. Yang, Z.M. Li, Y.Y. Dai, Separation of phenol from aqueous solutions by polymeric reversed micelle extraction, Chem. Eng. J. 88 (2002) 95–101.

[11] J. Sawai, N. Ito, T. Minami, M. Kikuchi, Separation of low volatile organic compounds, phenol and aniline derivatives, from aqueous solution using silicone rubber membrane, J. Membrane Sci. 252 (2005) 1–7.

[12] M.K. Purkait, S.D. Gupta, S. De, Separation of aromatic alcohols using micellar-enhanced ultrafiltration and recovery of surfactant, J. Membrane Sci. 250 (2005) 47–59.

[13] E. Erhan, B. Keskinler, G. Akay, O.F. Algur, Removal of phenol from water by membrane-immobilized enzymes: Part I. Dead-end filtration, J. Membrane Sci. 206 (2002) 361–373.

[14] G. Akaya, E. Erhan, B. Keskinler, O.F. Algur, Removal of phenol from wastewater using membrane-immobilized enzymes: Part II. Cross-flow filtration, J. Membrane Sci. 206 (2002) 61–68.

[15] W. Kujawski, A. Warszawski, W. Ratajczak, T. Porebski, W. Capala, I. Ostrowska, Removal of phenol from wastewater by different separation techniques, Desalination 163 (2004) 287–296.

[16] P.F.M.M. Correia, J.M.R. de Carvalho, Recovery of phenol from phenolic resin plant effluents by emulsion liquid membranes, J. Membrane Sci. 225 (2003) 41–49.

[17] T. Dobre, A. Guzun-Stoica, O. Floarea, Reactive extraction of phenols using sulfuric acid salts of trioctylamine, Chem. Eng. Sci. 54 (1999) 1559–1563.

[18] K. Trivunac, S. Stevanovic, Efficiency of membrane extraction of phenol-4-aminoantipyrine complex with n-alcohols, Desalination 163 (2004) 61–67.

[19] A. Kargari, T. Kaghazchi, G. Kamrani, T. Forouhar, Pertraction of phenol from aqueous wastes using emulsion liquid membrane system, FILTECH Conference, October 2005, Wiesbaden, Germany.

[20] T. Kaghazchi, A. Kargari, R. Yegani, A. Zare, Emulsion liquid membrane pertraction of L-lysine from dilute aqueous solutions by D2EHPA mobile carrier, Desalination 190 (2006) 161–171.

[21] A. Kargari, T. Kaghazchi, M. Soleimani, Application of emulsion liquid membrane in the extraction of valuable metals from aqueous solutions, in: 4th European Congress of Chemical Engineering, September 2003, Granada, Spain.

[22] A. Kargari, T. Kaghazchi, M. Soleimani, Role of emulsifier in the extraction of gold(III) ions from aqueous solutions using emulsion liquid membrane technique, Desalination 162 (2004) 237–247.

[23] A. Kargari, T. Kaghazchi, M. Sohrabi, M. Soleimani, Batch extraction of gold(III) ions from aqueous solutions using emulsion liquid membrane via facilitated carrier transport, J. Membrane Sci. 233 (2004) 1–10.

[24] M. Takht Ravanchi, A. Kargari, New advances in membrane technology, in: K. Jayanthakumaran (Ed.), Advanced technologies, Intech publication, Rijeka, 2009, pp. 369–394, ISBN 978-953-307-009-4.

[25] M. Takht Ravanchi, T. Kaghazchi, A. Kargari, Application of membrane separation processes in petrochemical industry: A review, Desalination 235 (2009) 199–244.

[26] B. Nabieyan, A. Kargari, T. Kaghazchi, A. Mahmoudian, M. Soleimani, Bench-scale pertraction of iodine using a bulk liquid membrane system, Desalination 214 (2007) 167–176.

[27] M.B. Ettinger, C.C. Ruchhoft, R.J. Lishka, Sensitive 4-aminoantipyrine method for phenolic compounds, Anal. Chem. 23 (12) (1951) 1783–1788.