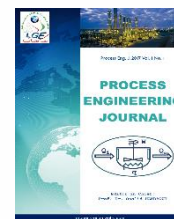# Extraction of organic pollutants from water by emulsion liquid membrane

Oualid Hamdaoui *

Laboratory of Environmental Engineering, Department of Process Engineering, Faculty of Engineering, Badji Mokhtar – Annaba University, P.O. Box 12, 23000 Annaba, Algeria

ARTICLE INFO

ABSTRACT

Emulsion liquid membrane (ELM) or surfactant liquid membrane has gained much attention as an advanced extraction process for the removal of pollutants present in wastewater. In the ELM technique, both extraction and stripping stages are combined in one step, which leads to simultaneous purification and concentration of the solute. ELM is not only an important technique for concentration, separation and recovery, but also is of fundamental importance from a process engineering point of view in understanding the transport mechanisms. In this work, the results obtained by our research group on the removal of several classes of organic pollutants from water by emulsion liquid membrane were presented. The selected organic contaminants are priority pollutants (4-nitrophenol and aniline), cationic dyes (methylene blue, rhodamine b, malachite green and basic red 29), anionic dyes (Congo red and acid blue 25), pharmaceuticals (paracetamol, ibuprofen and ketoprofen) and endocrine disrupting compounds (propylparaben, 4-cumylphenol and bisphenol A).

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1. Introduction

Most frequently, conventional treatment processes applied at wastewater treatment plants fail to remove completely organic contaminants such as priority pollutants, dyes, pharmaceuticals and endocrine disrupting compounds. Therefore, the integration of conventional wastewater treatments with advanced technologies has become of great interest [1]. From this point of view, liquid membrane processes have gained much attention as an advanced extraction techniques and attractive alternative treatments for the removal of organic contaminants present in wastewater.

The term liquid membrane is given to a system in which the membrane that divides the aqueous feed and product phases consists of a thin film of organic reagent [2]. Liquid membranes function as solution-diffusion barriers, providing the very high diffusivity to permeants characteristic of the liquid state. Consequently, selective mass transport is expected to be governed by the rules of solute distribution (partition) between immiscible liquid phases in contact. Facilitated transport makes use of mobile carriers incorporated in the liquid membrane phase to provide species-specific selectivity [3].

Emulsion or surfactant liquid membrane (ELM) consists of a water-in-oil (WO) emulsion formed from droplets of the aqueous strip solution contained in an organic phase. The latter consists of a diluent, an organic extractant to combine with the solute, and a surfactant to stabilize the emulsion. This emulsion is then suspended in the aqueous feed solution in a suitable contactor. The solute of interest in the feed aqueous phase react with the organic extractant at the aqueous–organic interface and migrate across the organic membrane to the inner aqueous strip interface where they are stripped. The regenerated extractant then migrates back to the feed interface, and the extraction process continues. When the extraction is complete, the loaded emulsion phase is removed from the aqueous raffinate, and the emulsion is broken to separate the aqueous strip and the organic phase. The recovered organic phase is then contacted with fresh strip solution in an emulsifier, and the process repeated.

In this work, some experimental results on the removal of various organic pollutants in water by ELM were presented and discussed.

* *Corresponding author.* E-mail addresses: ohamdaoui@yahoo.fr; oualid.hamdaoui1@gmail.com

2. Background

Since its invention, ELM has been used to separate a variety of solutes from aqueous solutions. ELM could be competitive when the targeted species is present at low concentrations in the aqueous solution. The mechanism of separation by ELM is mass transfer. Any mass transfer operation which produces a modification in composition of a given feed mixture without permanently altering the identity of its components inherently is a separation. Any such operation yields at least two product mixtures which differ in composition from one another and from the original feed. If one of the products is considered the target fraction of the separation, the other, by necessity, is the original feed devoid of the target fraction. The separation effect or selectivity of the process is assessed by comparing the analytical composition of the two products, or by relating the composition of either one of the products to that of the original feed. The objective of ELM process design usually is to render one of the products as pure as possible.

ELM processes are those involving a selective liquid membrane phase in which simultaneous extraction/stripping occurs. An ELM can be considered as a double emulsion consisting of three phases: the external, membrane and internal phases. Separation is achieved by permeation of solute through this liquid phase from a feed phase to a receiving phase. The feed and receiving phases are normally miscible while the membrane phase is immiscible in both. An aqueous internal (stripping) phase is stabilized by a surfactant and dispersed, using high-speed agitation (stirrer, colloid mill, mixer and valve homogenizer) or ultrasound, as very fine droplets (in the range of 1−3 μm [4,5]) inside a membrane (organic) phase. The resulting liquid membrane, or water-in-oil (W/O) emulsion, is then dispersed as emulsion globules of a diameter of 100–2000 μm [6,7] in external feed phase (a second aqueous phase) with constant agitation. Target solute in the external feed phase is transferred across the membrane phase into the internal aqueous phase during an extraction process. In this water-in-oil-in-water (W/O/W) ELM, the organic phase serves a dual purpose of permitting selective transfer of one or more components through it from external phase to internal droplets and vice versa and functions as a barrier by preventing mixing of external and internal phases. The ELM process is schematically shown in Fig. 1.

In non-facilitated transport, the solute mass transfer is driven by the concentration difference between the external feed phase and the internal stripping phase.

For facilitated transport mechanism, the effectiveness of separation is improved by maximizing the flux through the membrane phase and the capacity for the diffusing species in the receiving phase. This may be achieved by two mechanisms:
- The solute is converted to ion state which cannot transfer through the membrane phase back to the external phase by the internal phase agent.
- The efficiency and selectivity of transport across the membrane may be markedly enhanced by the presence of a mobile complexation agent (carrier) in the liquid membrane. Carrier in the membrane phase reacts rapidly and reversibly with the desired solute to form a complex. This reversible reaction provides a means of enhancing the solute flux and improving the selectivity at the same time. This process is known as facilitated or carrier-mediated liquid membrane separation. It is easy to make the feed and strip solutions with different pH thus that ion exchange processes on the two membrane surfaces will be shifted in opposite directions. This creates a concentration gradient of different forms of the carrier (with and without ions) in the membrane, and results in the directed ion flux through the membrane. Evidently the process leads to the transport of targeted ionic species across the membrane against their concentration gradient. The facilitated transport is combined with coupling counter- or co-transport of different ions through the liquid membrane. The coupling effect supplies the energy for uphill transport of the solute or active transport will continue until one driving factor (difference of chemical potentials) is balanced by the difference between chemical potentials of another transported ion [8].

Four points demonstrate the benefits of using carriers in ELM process [9]:
- High fluxes are possible.
- Very selective separations much better than those obtained solely are possible.
- Ions can be concentrated since the coupled transport mechanism can pump one ion against its concentration gradient due to a gradient in the coupled ion.
- Expensive complexing agents can be used. Only small amounts of carrier are required because of the small solvent inventory in the membrane.

After the subsequent separation of the external phase from the W/O emulsion by gravity (settling), splitting of the emulsion (demulsification) is carried out. Demulsification is performed in order to separate the phases that makeup the emulsion, the internal aqueous phase and the organic membrane phase. At the end of the process, the membrane phase can be reused and the receiving phase (enriched in the recovered solute) can be recycled or recovered for solute.

For breaking W/O emulsion in wastewater treatment, electrostatic demulsification techniques are generally used [10]. Other methods of demulsification have been tried to include heat treatment, phase dilution, high shear [10] and ultrasound [11].

ELM has gained much attention as an advanced extraction process for the removal of contaminants present in wastewater. Compared to conventional processes, the main advantages of ELM techniques are [12]:
- simple operation, high extraction efficiency and scope of continuous operation;
- high interfacial area resulting in enhancement of mass transfer rate, especially at the inner membrane–water interface, due to the small size of the aqueous phase droplets;
- simultaneous performance of extraction (at the outer interface) and stripping (at the inner interface) in the same system, which implies that in practice there would be no need to construct separate circuits for stripping and extraction;
- capability of treating a variety of elements and compounds in industrial setting at a greater speed and with a high degree of effectiveness, with varying contaminant concentrations and volume requirements;
- relatively low cost and energy conservation due to its cycling usage and non-dependence on heating consideration;
- requirement of expensive extractant and organic solvent, necessary to form an oil membrane, in small quantities.
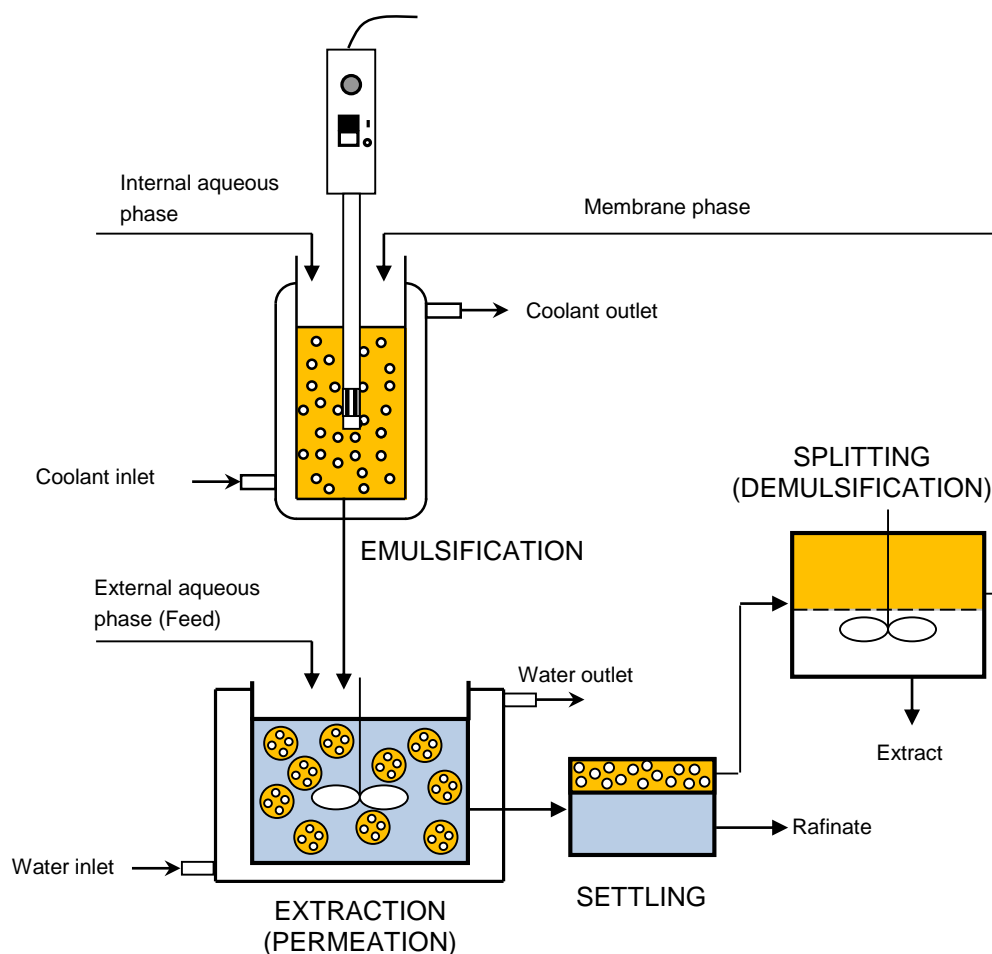
Fig. 1 – The ELM process.

3. Extraction of organic pollutants by ELM

The extraction of organic pollutants using liquid emulsion membrane involves three steps: preparation of liquid membrane emulsion, extraction of the solute from feed by contacting the emulsion and separation of liquid emulsion from the external phase by settling.

Analytical reagent grade chemicals, purchased from Sigma-Aldrich, were used throughout this work. The liquid membrane phase is composed of a surfactant and a diluent for the extraction of 4-nitrophenol, aniline, Congo red, acid blue 25, ibuprofen, ketoprofen, bisphenol A and 4-cumylphenol. For the separation of the other of organic pollutants, carriers are added to the membrane phase: trioctylphosphine oxide (TOPO) for propylparaben, Aliquat 336 for paracetamol and di(2-ethylhexyl) phosphoric acid (D2EHPA) for cationic dyes (methylene blue, rhodamine b, malachite green and basic red 29). The non-ionic surfactant used for stabilizing the emulsion is sorbitan monooleate which is a product of Sigma and commercially known as Span 80.

Internal aqueous solutions were prepared by taking the required amount of stripping agents in distilled water. The organic membrane phase was prepared by dissolving the appropriate amount of Span 80 as a surfactant and the adequate quantity of extractant (if necessary) in a diluent under a gentle mixing by a magnetic stirrer.

The emulsion was prepared by mixing the internal aqueous solution with the organic membrane phase using a high-speed disperser (Ultra-Turrax IKA T18) for a fixed mixing time. For the emulsion prepared for the removal of cationic dyes, emulsification was conducted using ultrasonic irradiation (22.5 kHz) carried out with a commercial supply Microson XL 2000 equipped with a titanium horn (3 mm diameter) mounted at the top of the cylindrical glass cell.

A volume of the prepared W/O emulsion was added to a fixed volume of external aqueous solution, containing the organic pollutants, in a cylindrical thermostated vessel that was attached to an overhead mechanical stirrer. The agitator used was a 45° pitch four blades down pumping impeller (diameter 5 cm). The content of the vessel was stirred in order to disperse the W/O emulsion in the external phase to make the W/O/W double emulsions. The external phase solution was periodically sampled at various time intervals. The concentration of pollutant in the solutions was determined by a UV–visible spectrophotometer set at the wavelength corresponding

to maximum absorbance of the studied pollutant. Each experiment was repeated at least two times in order to verify the reproducibility. The maximum standard deviation was 2−3%.

For stripping experiments, the double emulsion (W/O/W) is allowed to be spontaneously separated by gravity and the demulsification of W/O emulsion was achieved by adding 10 mL of 2-methyl-2-propanol (tert-butyl alcohol). The mixture (W/O emulsion and tert-butyl alcohol) was stirred and poured in a separating funnel. The membrane phase and the internal phase receiving the extracted solute were separated by gravity in the separating funnel. The concentration of extracted solute in the internal aqueous phase was determined using a UV-visible spectrophotometer. Each experiment was performed twice at least and the mean values were presented.

3.1. Priority pollutants

Extraction of priority pollutants, 4-nitrophenol (4-NP) and aniline (AN), from aqueous solutions by ELM was examined. An ELM system composed of Span 80 as the surfactant, hexane as the diluent and Na_2CO_3 as the stripping aqueous solution. Optimum experimental conditions, determined in our previous papers [6,13], are summarized as: emulsion volume: 30 mL; external phase volume: 250 mL; volume ratio of internal phase to organic phase: 1/1; emulsification time: 4 min; stirring speed: 300 rpm; concentration of Span 80: 3% (w/w); volume ratio of W/O emulsion to external phase: 30/250; internal phase concentration (Na_2CO_3): 0.1N; diluent: hexane; concentration of H_2SO_4 in the external feed phase: 0.1N.

The extraction kinetics of 4-NP and AN in aqueous solution at the optimum operational conditions is shown in Fig. 2. It was observed that the removal of priority pollutants increases progressively with contact time and reached a plateau afterward. After only 5 min, the extraction efficiency was about 90%. An extraction efficiency of 99.7% and 98.0% for, respectively, 4-NP and AN was attained after 30 min.

The main efforts in ELM process are devoted to overcome the instability or lifetime of the liquid membrane which has limited their industrial application. Formulation of the emulsion membrane was optimized to provide emulsion with good stability during extraction, but which could be easily broken under mild conditions. Usually, a tracer method is used to determine the stability of liquid membrane. In the present work, Na_2CO_3 was used as the internal phase. The pH of the external phase was continuously measured in order to follow its evolution against time. The leakage of carbonate ions in the external feed phase increases the pH and indicates a rupture of the W/O emulsion.

The influence of stripping agent concentration (Na_2CO_3) in the inner phase on the stability of the membrane and the removal of 4-NP by ELM was investigated (Fig. 3). From this figure, it was found that when the Na_2CO_3 concentration in the internal phase increased, the stability of the emulsion decreased. Though emulsion stability decreases with the increase in internal phase concentration, the membrane is still quite stable in the concentration range of 0.005−0.1N. However, higher stripping agent concentrations (0.5 and 1N) conduct to greater breakage, which may be due to the reaction between Na_2CO_3 and the surfactant that engenders a partial loss of its surfactant properties and, therefore, the destabilization of

the emulsion [14]. For a concentration of 0.1N Na_2CO_3, W/O emulsion was stable and this concentration is also beneficial for the extraction (Fig. 3) and stripping of the pollutant (see ref. [6]).
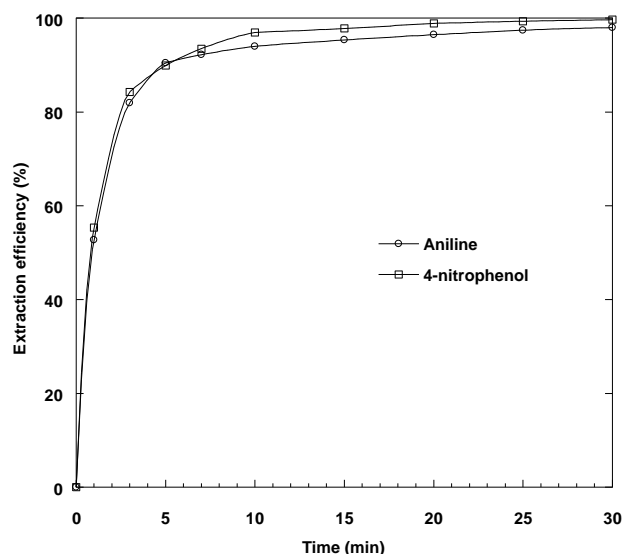

Fig. 2 – Extraction kinetics of 4-NP (25 mg/L) and AN (25 mg/L) by ELM (experimental conditions ̶ emulsion volume: 30 mL; external phase volume: 250 mL; volume ratio of internal phase to organic phase: 1/1; emulsification time: 4 min; stirring speed: 300 rpm; concentration of Span 80: 3% (w/w); volume ratio of W/O emulsion to external phase: 30/250; internal phase concentration (Na_2CO_3): 0.1N sulfuric acid concentration in the external phase: 0.1N; diluent: hexane).
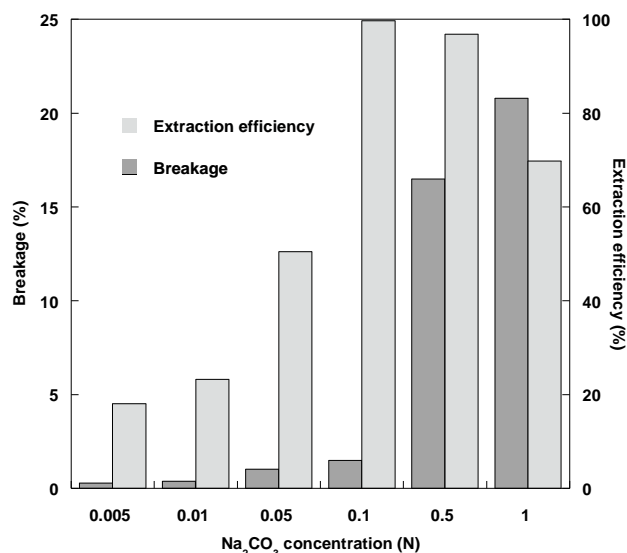

Fig. 3 – Effect of Na_2CO_3 concentration in internal phase on the stability of the emulsion and the extraction of 4-NP (25 mg/L) by ELM (experimental conditions ̶ emulsion volume: 30 mL; external phase volume: 250 mL; volume ratio of internal phase to organic phase: 1/1; emulsification time: 4 min; stirring speed: 300 rpm; concentration of Span 80: 3% (w/w); volume ratio of W/O emulsion to external phase: 30/250; sulfuric acid concentration in the external phase (extraction only): 0.1N; diluent: hexane).

The pKa value of 4-NP is 7.15. Consequently, the overall extraction was significantly affected by the feed phase pH. When the pH was kept low, 4-NP is present in neutral protonated form. Strong basic agent used inside the emulsion droplets as internal stripping phase (Na_2CO_3) serves to convert unionized 4-NP, which had diffused through the liquid membrane, into ionized form (4-nitrophenolate). The latter compound, that is charged species in basic aqueous phase, could not diffuse back to the external phase and thus were retained in the internal aqueous phase (Fig. 4). However, the difference of electrolyte concentrations between the internal and external phases is increased by increasing Na_2CO_3 concentration, which causes an osmotic pressure between these two phases. Water in the external phase is then transferred to the internal phase that results in swelling and breakage of the emulsion, and thus decreasing in extraction efficiency. Therefore, sulfuric acid is used in the feed phase in order to avoid swelling phenomenon and enhance the removal efficiency.
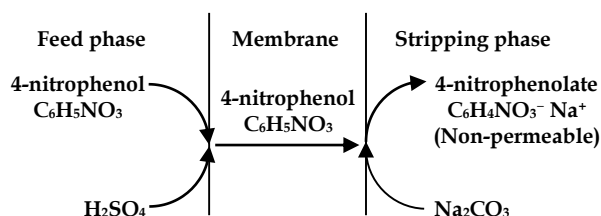

Fig. 4 – Extraction mechanism of 4-NP by ELM.

3.2. Cationic dyes

The effectiveness of emulsification by low frequency (22.5 kHz) ultrasonic irradiation was examined for the preparation of water–in–oil (W/O) emulsions. The formed W/O emulsions will be used for the extraction of cationic dyes by ELM. The membrane phase contained Span 80 as emulsifying agent, di(2–ethylhexyl)phosphoric acid (D2EHPA) as carrier, and hexane as diluent. Sulfuric acid solution was used as stripping internal aqueous phase. Effect of experimental parameters that affect the stability such as ultrasonic power, emulsification time, extractant, surfactant, and internal phase concentrations, volume ratios of internal phase to organic phase and of external phase to W/O emulsion, stirring speed, diluent, and contact time was examined. The obtained results showed that the production of W/O emulsions by using low frequency ultrasound is a very attractive and effective technique and an excellent stability was attained [15]. The operating conditions leading to an excellent stability of the W/O emulsions were [15]: emulsification time: 3 min; ultrasonic power for the production of 60 mL of emulsion: 20 W; concentrations of carrier and surfactant: 10 and 5 % w/w, respectively; internal phase concentration (H_2SO_4): 0.5 M; volume ratio of internal phase to organic phase: 1/1; volume ratio of W/O emulsion to feed external phase: 0.3; stirring speed: 200 rpm; diluent: hexane.

The W/O emulsion prepared by ultrasound (22.5 kHz) was used for the removal and recovery of cationic dyes (methylene blue (MB), malachite green (MG), basic red 29 (BR29) and rhodamine b (RhB)) from aqueous solutions by ELM containing di(2–ethylhexyl)phosphoric acid (D2EHPA) as extractant. The significant

parameters governing the extraction behavior of dyes were investigated.

Under most favorable operating conditions, practically all the dye cations present in the feed aqueous phase were extracted. Fig. 5 shows the MB and RhB solutions (10 mg/L) before and after extraction by ELM.

Fig. 5 – MB and RhB solutions (10 mg/L) before and after extraction by ELM under most favorable experimental conditions.

The permeation mechanism of cationic dyes by ELM is illustrated in Fig. 6. Dye cation diffuses at the external interface between feed phase and membrane phase. A cation exchange reaction occurred between the carrier (D2EHPA) and dye ion. Dye cation (Dye^+) reacts with the carrier [$(HR)_2$], dimerized D2EHPA, at the external interface to form Dye–D2EHPA complex [Dye–R(HR)] and hydrogen ion (H^+). The dye–carrier complex then diffuses through the membrane phase to the internal interface. Dye cation is released into the internal aqueous phase by the stripping reaction at the internal interface and the extractant reacts with H^+ ion provided by sulfuric acid solution. The dye is, finally, in the receiving phase and the carrier is ready for another cycle.
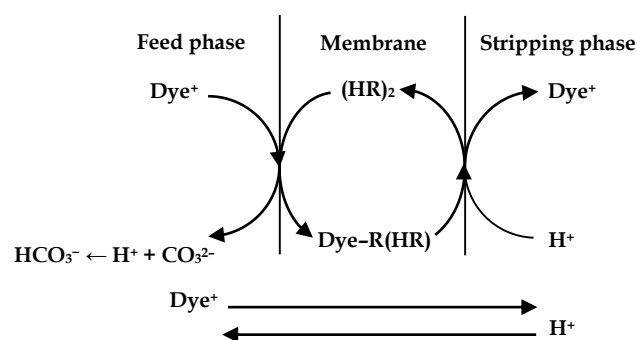

Fig. 6 – Extraction mechanism of cationic dye by ELM using D2EHPA (($HR)_2$ is the dimerized D2EHPA).

Owing to the fact that real dye-laden wastewaters consists of a mixture of several dyes, dye mixture was prepared in objective to simulate a real effluent. The simulated effluent used is composed of the mixture between four cationic dyes: MB, RhB, MG and BR29. The concentration of each dye in the mixture is 10 mg/L. Emulsification and permeation experiments were carried out in the most favorable operational conditions previously mentioned. The mixed dye solution before and after separation by ELM is shown in Fig. 7. The extraction efficiency of dye mixture after 7 min of contact time was excellent (about 99%) [16].

Fig. 7 – Dye mixture solution containing MB, RhB, MG and BR29 before and after extraction by ELM under most favorable experimental conditions (the concentration of each dye in the mixture is 10 mg/L).

After the separation of the external phase from the W/O emulsion by settling, chemical demulsification of the emulsion was conducted by adding 10 mL of tert-butanol. Then, the phases that makeup the emulsion, the internal aqueous phase and the organic membrane phase were separated (Fig. 8) and the membrane phase was reused. In all cases, the recovery of the organic phase was total and the extraction of dyes was not decreased up to 7 runs.
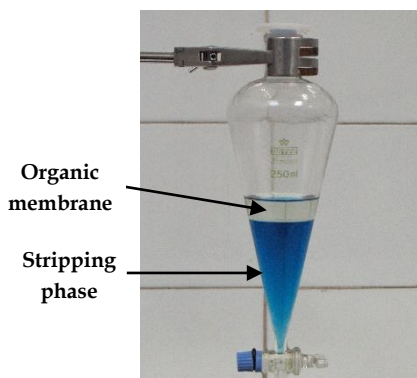

Fig. 8 – Separating funnel containing the receiving phase charged by MB and the organic membrane phase.

3.3. Anionic dyes

The extraction of an anionic diazo direct dye, Congo red (CR), from water by ELM was investigated. The important operational parameters governing emulsion stability and extraction behavior of CR dye were studied. The operating conditions leading to an excellent stability of the W/O emulsion were [17]: emulsification time: 5 min; stirring speed: 200 rpm; concentration of Span 80: 4% (w/w); volume ratio of internal phase to organic phase: 1/1; internal phase concentration (Na_2CO_3): 0.1 N; volume ratio of W/O emulsion to external phase: 50/400; diluent: hexane. The removal of CR was influenced by a number of parameters such as surfactant concentration, stirring speed, acid concentration in the feed solution and volume ratios of internal phase to organic phase and of emulsion to feed solution. Under the best experimental conditions, practically all the CR molecules present in the feed phase were

extracted even in the presence of salt (NaCl). Under the most favorable experimental conditions, total removal of antharaquinonic dye Acid Blue 25 was attained after only 10 min.

Effect of sodium carbonate concentration as internal receiving phase on the membrane stability, removal percentage and stripping efficiency of CR was studied (Fig. 9). The best sodium carbonate concentration in the stripping phase that conducted to excellent permeation percentage and stripping efficiency and stable emulsion was 0.1 N. The recovery of the membrane phase was total and the extraction of CR dye was not decreased up to seven runs (Fig. 10).
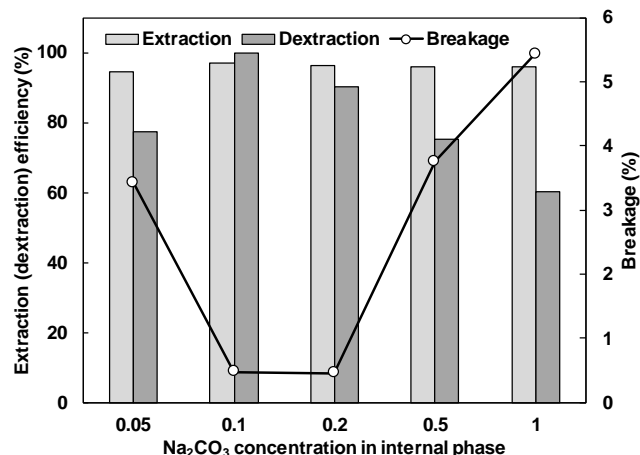

Fig. 9 – Effect of Na_2CO_3 concentration in the stripping phase on extraction and dextraction of CR and stability of the membrane (experimental conditions — emulsion volume: 50 mL; external phase (dye solution or distilled water) volume: 400 mL; volume ratio of internal phase to organic phase: 1/1; emulsification time: 5 min; stirring speed: 200 rpm; concentration of Span 80: 4% (w/w); volume ratio of W/O emulsion to external phase: 50/400; sulfuric acid concentration in the feed phase: 0.1 N; diluent: hexane; CR concentration: 10 mg/L).
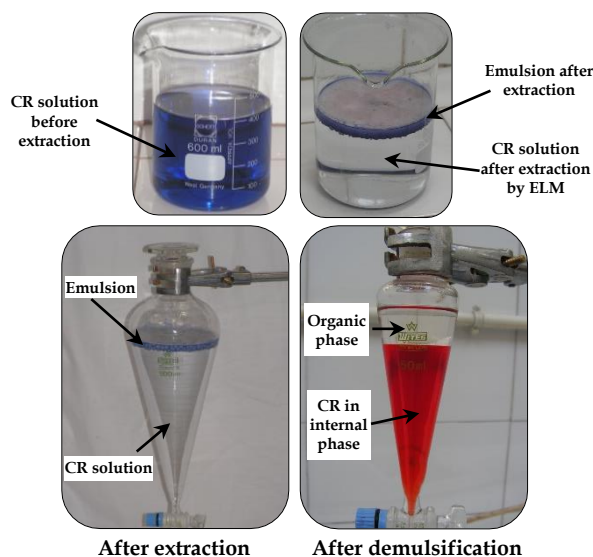

Fig. 10 – CR solution before extraction, after extraction and settling (in beaker and in separating funnel) and after demulsification.

3.4. Pharmaceuticals

An ELM process for the permeation of acetaminophen (ACTP), currently named as paracetamol, from aqueous solutions by ELM using Aliquat 336 as extractant was developed. The ELM system is made up of potassium chloride as the inner aqueous phase, Span 80 as the surfactant and hexane as the diluent. Effect of experimental parameters which affects the permeation of ACTP was examined. Optimum operating conditions for higher extraction efficiency of ACTP and excellent stripping percentage were summarized as follows [4]: emulsion volume: 30 mL; feed external phase volume: 250 mL; volume ratio of internal phase to organic phase: 1/1; emulsification time: 4 min; stirring speed: 250 rpm; concentration of Span 80: 8% (w/w); concentration of Aliquat 336: 5% (w/w); volume ratio of W/O emulsion to external phase: 30/250; internal phase concentration (KCl): 0.5N; diluent: hexane; concentration of H_2SO_4 in the external feed phase: 1N. Under the best operating parameters, it was possible to extract closely all of ACTP molecules from the external feed solution (see Ref. [4]).

Extraction mechanism of ACTP by ELM using Aliquat 336 as carrier was given in Fig. 11.
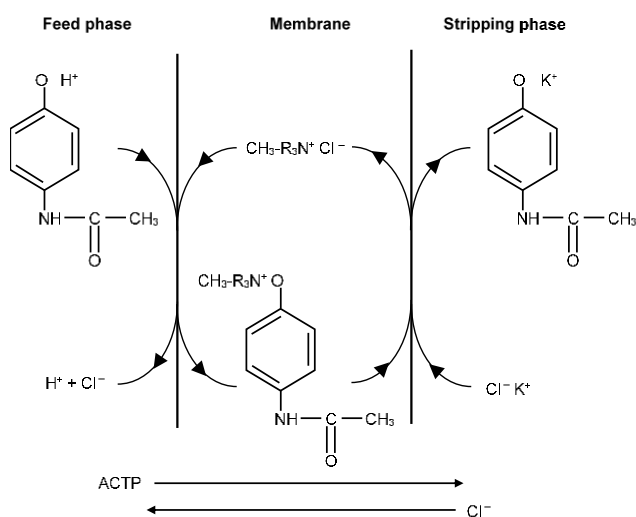

Fig. 11 – Extraction mechanism of ACTP by ELM using Aliquat 336 as carrier.

Influence of KCl concentration in the internal aqueous phase on the extraction and stripping of ACTP was presented in Fig. 12. From this figure, it was shown that the best extraction efficiency of ACTP can be achieved by using 0.5N KCl. At lower concentration (below 0.5N), there was insufficient stripping agent (KCl) to remove the ACTP from the membrane phase resulting in lower extraction efficiency. When the concentration of KCl in the stripping solution was varied from 0.5 to 2N, the extraction of ACTP was reduced. It was expected that increasing the amount of stripping agent in the internal phase decreased the difference of densities and increased the emulsion viscosity. The increasing of emulsion viscosity reflected in an increasing in the size of droplets. Furthermore, difference in ionic strength between external and internal phase led to internal phase volume increasing, which promotes excess emulsion leakage [15,17]. The increasing of emulsion viscosity

reflected in an increasing in the size of droplets. Therefore, 0.5N KCl solution was the best internal phase concentration.
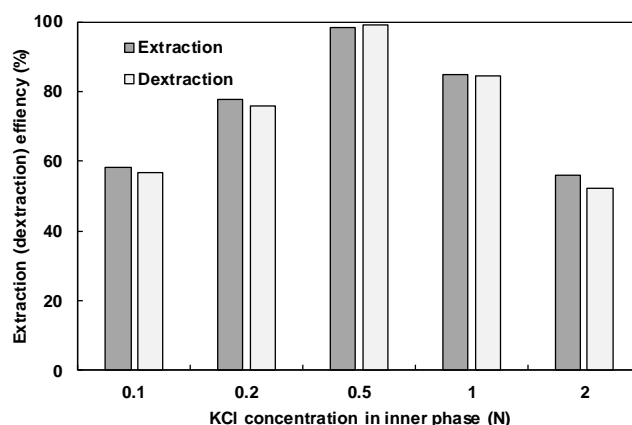

Fig. 12 – Effect of KCl concentration in the inner phase on extraction and dextraction of ACTP (experimental conditions — emulsion volume: 30 mL; external phase (ACTP solution) volume: 250 mL; volume ratio of internal phase to organic phase: 1/1; emulsification time: 4 min; stirring speed: 250 rpm; concentration of Span 80: 8% (w/w); concentration of Aliquat 336: 5% (w/w); volume ratio of W/O emulsion to external phase: 30/250; sulfuric acid concentration in the feed phase: 1 N; diluent: hexane; ACTP concentration: 10 mg/L).

The worldwide non-steroidal anti-inflammatory drugs ibuprofen (IBP) and ketoprofen (KTP) was removed from aqueous solutions by an ELM system made up of hexane as diluent, Span 80 as the surfactant and sodium carbonate as the stripping aqueous solution. Influence of operating conditions that affect the extraction of IBP was investigated. The appropriate operational parameters for the permeation of IBP were summarized as [1]: emulsion volume: 60 mL; external phase volume: 600 mL; volume ratio of internal phase to organic phase: 1/1; emulsification time: 3 min; stirring speed: 250 rpm; concentration of Span 80: 3% (w/w); volume ratio of W/O emulsion to external phase: 60/600; internal phase concentration (Na_2CO_3): 0.1N; diluent: hexane; concentration of H_2SO_4 in the external phase: 0.1N. Under the best operating conditions, it was possible to extract nearly all of IBP and KTP molecules from the feed aqueous solution (Fig. 13). About 99.3 % IBP and 97.4% KTP was removed in less than 20 min of contact time.

The removal efficiency of IBP from distilled water, a natural mineral water and sea water was investigated and the obtained results are shown in Fig. 14. The main characteristics of the natural water were: pH 7.2, Ca^{2+}: 81 mg/L, Mg^{2+}: 24 mg/L, Na^+: 15.8 mg/L, Cl^-: 72mg/L, SO_4^{2-}: 53mg/L, HCO_3^-: 265 mg/L. The seawater has a high salinity (~35 g/L), which is composed mainly of Na^+: 11 g/L, Mg^{2+}: 1.3 g/L, Ca^{2+}: 0.4 g/L, Cl^-: 20 g/L, SO_4^{2-}: 3 g/L. The efficiencies of IBP extraction from distilled water (99.3%), natural mineral water (97.3%) and sea water (94.0%) were comparable, which shows that the ELM treatment process in comparison with other techniques that are hindered by the presence of salts is a promising process for the elimination of non-steroidal anti-inflammatory drugs from complex matrices such as natural and sea waters.
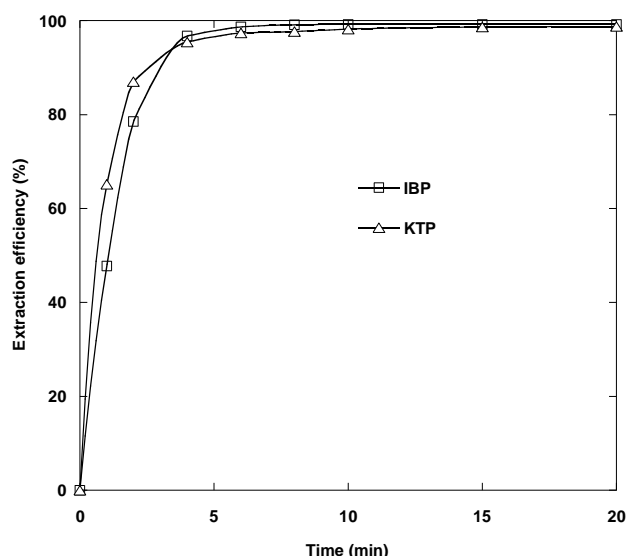
Fig. 13 – Removal of IBP (50 mg/L) and KTP (50 mg/L) by ELM (experimental conditions— external phase volume: 600 mL; volume ratio of internal phase to organic phase: 1/1; emulsification time: 3 min; stirring speed: 250 rpm; concentration of Span 80: 3 % (w/w); volume ratio of W/O emulsion to external phase: 60/600; internal phase concentration (Na_2CO_3): 0.1 N; sulfuric acid concentration in the feed phase: 0.1 N; diluent: hexane).

Fig. 14 – Extraction of IBP (50 mg/L) from distilled water, natural mineral water and sea water by ELM (experimental conditions— external phase volume: 600 ml; volume ratio of internal phase to organic phase: 1/1; emulsification time: 3 min; stirring speed: 250 rpm; concentration of Span 80: 3 % (w/w); volume ratio of W/O emulsion to external phase: 60/600; internal phase concentration (Na_2CO_3): 0.1 N; sulfuric acid concentration in the feed phase: 0.1 N; diluent: hexane).
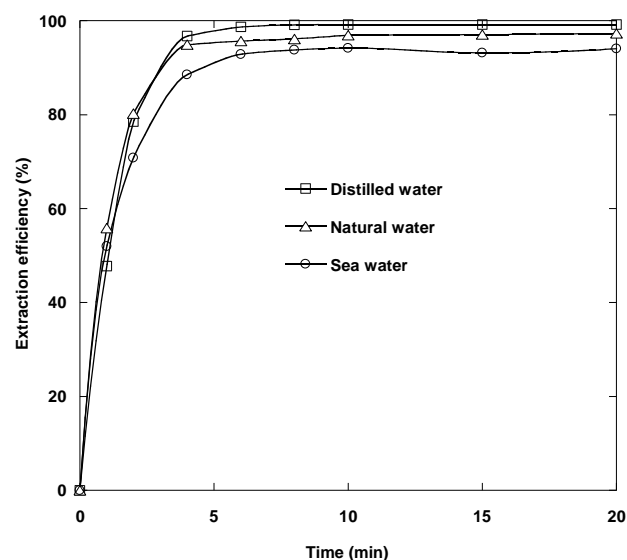
3.5. Endocrine disrupting compounds

Endocrine disrupting compound propylpraben (PP) from aqueous solution was extracted by ELM that contains trioctylphosphine oxide (TOPO) as extractant, n-hexane as solvent and Span 80 as surfactant. Na_2CO_3 was employed as inner stripping aqueous phase. Best experimental conditions for higher removal efficiency are [12]: emulsion volume: 30 mL; external phase (PP solution) volume: 250 mL; surfactant concentration: 5%(w/w); TOPO concentration: 4% (w/w); volume ratio of internal phase to organic phase: 1/1; emulsification time: 4min; stirring speed: 300 rpm; volume ratio of W/O emulsion to external phase: 30/250; internal phase concentration (Na_2CO_3): 0.1N; sodium sulfate concentration in the feed phase: 0.1N; diluent: hexane. By using the optimal operating parameters, it was possible to wholly remove all of PP molecules from the external feed solution. The recovery of the membrane phase was total and the extraction of PP was not decreased. The extraction mechanism of PP by ELM is detailed in Fig. 15.
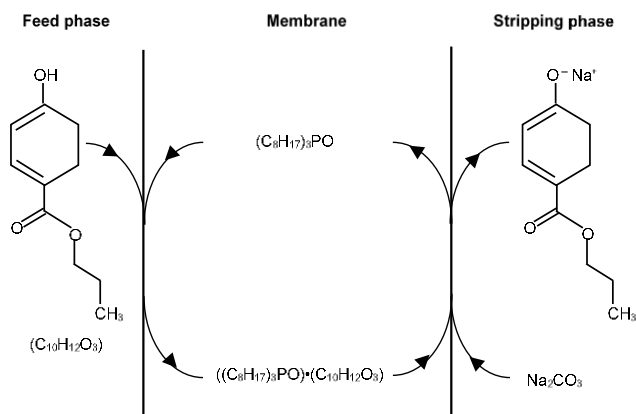

Fig. 15 – Extraction mechanism of PP by ELM using TOPO as carrier.

The removal of endocrine disrupting chemicals, bisphenol A (BPA) and 4-cumylphenol (4-CyP), from water by ELM was investigated. Liquid membrane consists of a diluent (hexane) and a surfactant (Span 80). 0.05N sodium hydroxide solution was used as internal aqueous phase. The important variables governing the stability of W/O emulsion as well as the permeation of BPA were examined [18,19]. The operating conditions conducting to an excellent stability of the W/O emulsion were: emulsification time: 5 min; stirring speed [18,19]: 200 rpm; concentration of Span 80: 3% (w/w); volume ratio of internal phase to organic phase: 1/1; internal phase concentration (NaOH): 0.05N; volume ratio of W/O emulsion to external phase: 50/400; diluent: hexane.

Experimental results showed that by appropriate selection of the extraction and stability conditions, the prepared W/O emulsion was capable of extracting almost completely the total BPA (20 mg/L) and 4-CyP (20 mg/L) molecules present in the external feed phase within a few minutes (Fig. 16). The best sodium hydroxide concentration in the internal phase that conducted to very good stripping efficiency (98%) and excellent emulsion stability was 0.05 N.
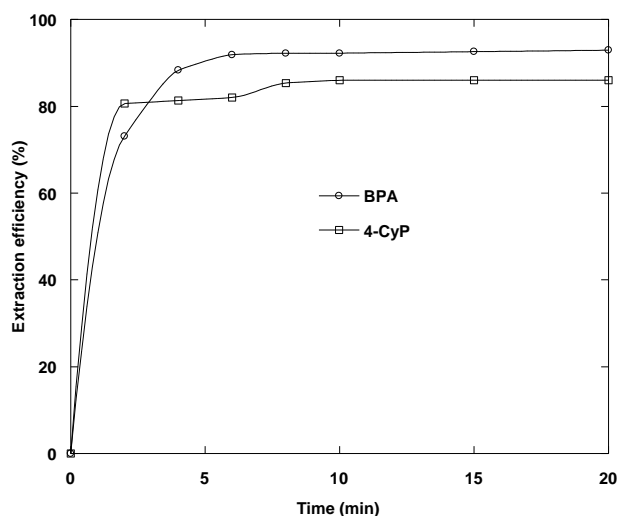
Fig. 16 – Extraction of BPA (20 mg/L) and 4-CyP (20 mg/L) by ELM (experimental conditions—emulsion volume: 50 mL; external phase volume: 400 mL; volume ratio of internal phase to organic phase: 1/1; emulsification time: 5 min; stirring speed: 200 rpm; concentration of Span 80: 3% (w/w); volume ratio of W/O emulsion to external phase: 50/400; internal phase concentration (NaOH): 0.05N; sulfuric acid concentration in the external phase: 0.1 N; diluent: hexane).

4. Conclusion

This paper reports a brief review on the removal of organic pollutants from water by ELM. ELM treatment process represents an interesting advanced separation procedure for the removal of priority pollutants (4-nitrophenol and aniline), cationic and anionic dyes (methylene blue, rhodamine b, malachite green, basic red 29, Congo red and acid blue 25), pharmaceuticals (paracetamol, ibuprofen and ketoprofen) and endocrine disrupting compounds (propylparaben, 4-cumylphenol and bisphenol A) even from complex matrices such as natural water, sea water and sewage treatment effluent.

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