Ibuprofen Recovery from Aqueous Solutions by Supported Liquid Membranes

Teresa A. Razo-Lazcano[1], Yessica López-Munive[2], M. Pilar González-Muñoz[1], Liliana Villafaña-López[1], Liliana Hernández-Perales[1] and Mario Avila-Rodriguez[1,*]

[1]Department of Chemistry. Universidad de Guanajuato, Mexico. Cerro de la Venada s/n. 36040, Guanajuato, Gto, Mexico

[2]Universidad Politécnica de Tlaxcala.San Pedro Xalcaltinco, 90180 Tepeyanco, Tlax., Mexico

Abstract: Pharmaceuticals recently have acquired a big importance because of its growing detection in wastewater. The propionic acid derivatives, such as ibuprofen, are among the most commonly anti-inflammatories used by population. For this reason it is necessary to develop a friendly separation technique with environment, like the Supported Liquid Membranes (SLM). In this work, SLM have been prepared in order to recover ibuprofen from aqueous solutions. Two different organic phases were evaluated (dodecane and Parleam 4), as well as trioctylamine as carrier, and Abil EM 90 as surfactant in the preparation of SLM. The SLM prepared was tested in the IBP transfer process through the membrane, from feed phase to stripping phase. The results showed that it is possible to recover almost 98% of IBP, this using the SLM and a phosphate buffer solution of pH 7 like stripping phase.

Keywords: Ibuprofen, Supported liquid membranes, Permeability, Molar flux, Wastewater.

INTRODUCTION

Pharmaceuticals recently have acquired a big importance because of its growing detection in wastewater. The use of prescribed or over counter drugs is estimated worldwide in thousands of metric tons per year [1, 2]. The main sources of emissions of these compounds are: domestic, hospital, livestock (fecal and urinary excretions both from humans and animals after drug use) and industrial (accidental spillages) effluents [3]. They represent a grave problem due to their bioaccumulation may occur and provoking different adverse effects on organisms and environmental in spite of the low concentration at which they are found (mg.L^{-1} or ng.L^{-1})[2, 4-10].

There are several techniques utilized to wastewater treatment which are: bioremediation, physicochemical treatments such as activated sludge, coagulation, volatilization, adsorption (activated carbon), sedimentation and filtration, and advanced oxidation process (ozonation, UV irradiation, Fenton oxidation, photocatalysis and sonolysis). However, these methods are little effectives for the removal of organic compounds, such as drugs [1, 3, 4, 7].

The drugs most commonly found in wastewater are: anti-inflammatories, analgesics, antibiotics, antihypertensives, hormones, lipidic regulators, β-blockers, anxiolytics, anticonvulsants, anti-ulcer agents, diuretics, antidiabetics and bronchodilators [2, 4-7, 9, 11]. The propionic acid derivatives, such as ibuprofen, are among the most commonly used anti-inflammatories by population [3, 9, 12]. Ibuprofen has been detected in sewage treatment plants effluents and surface water at concentrations ranging from 674 – 85000 ng.L^{-1} in parts of USA, Canada and Europe [9, 13-17]. This drug does not represent any problem at acute exposure, but at long-term exposure it can be toxic both to humans and to animals [1].Toxic effects have been reported to bacteria, algae and *daphnia magna*, damaging the population growth rate and reproduction of this latter [18-20]. Since ibuprofen is a drug of wide human consumption, it can be found in sewage, its recovery from these effluents is very important.

There are reports about the ibuprofen elimination by oxidation techniques as ultrasound treatment [21] or with photo-Fenton oxidation process [22], and photo-transformation with low pressure mercury lamps [23] or using thermally activated persulfate (TAP) [24]. In the case of IBP recovery from aqueous solutions, one of the methods reported is by adsorption with activated carbon produced from wastes of *Agave Sisalana* [25], or using emulsion liquid membranes [10].

The supported liquid membranes (SLM) offer a useful alternative to separation and recovery of different compounds present in wastewater. They are a kind of non-dispersive liquid membranes where the

*Address correspondence to this author at the Department of Chemistry. Universidad de Guanajuato, Mexico, Cerro de la Venada s/n. 36040, Guanajuato, Gto. Mexico.; Tel: +524737327468; Fax: +524737327468; E-mail: avilam@ugto.mx

organic phase is embedded in pores of a polymer support. The organic phase consists of a diluent, a carrier and some times of a modifier. This modifier is added in order to favor the species extraction and avoiding the third phase formation [26, 27]. The advantages to use this technique (SLM) are that the extraction and stripping of the species is performed in one step, the volume of organic components is very small thus the pollution is very low, it is easy to scale-up, etc [28, 29]. The applications of SLMs include the recovery of metals and ions from effluents (Ni(II), Cu(II), Zn(II), Hg(II), Cd(II), Cr (VI), Pt(IV), Pd (II)) [29-34], of organic acids like citric acid [35], of drugs (cephalexin, macrolides, acetaminophen) [36-38], and as concentration method [39].

In this study a methodology for ibuprofen recovery from aqueous solutions by supported liquid membranes was developed. Dodecane and Parleam 4 were used like organic phases, trioctylamine (TOA) as carrier and Abil EM 90 as surfactant. The influence of different parameters such as, the surfactant and extractant concentrations, the nature of stripping solution, time transfer and surfactant presence have been analyzed.

THEORETICAL

The supported liquid membranes (SLM) consist of a microporous filter (polymer support) and an organic phase which is embedded in pores of this filter. The organic phase consists of a diluent, a carrier and sometimes of a modifier.

The mass transfer process through supported liquid membrane can divided in several steps (see Figure **1**) [27, 40]:

1.   IBP diffusion in the non-stirred boundary layer (feed phase-membrane interface, zone *a*).

2.   Formation of IBP-Extractant (E) complex at the feed phase-SLM interface, zone *b*.

3.   Diffusion of complex formed, IBP-Extractant through SLM, zone *c*.

4.   IBP stripping from IBP-Extractant complex at the SLM-stripping phase interface, zone *d*.

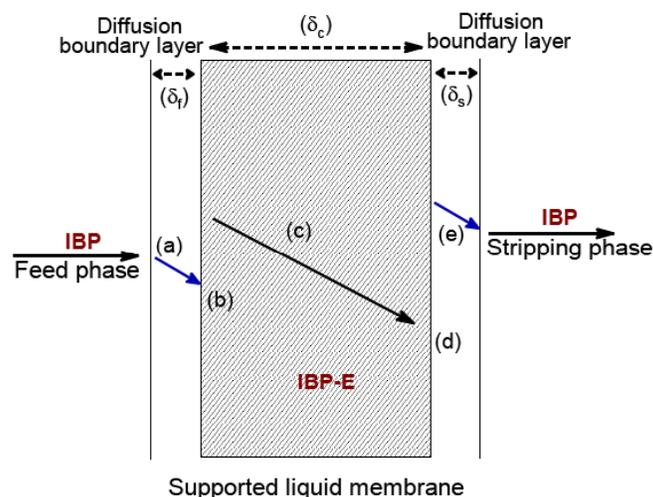5.   IBP diffusion in the non-stirred boundary layer (membrane-stripping phase interface, zone *e*).

Figure 1: Graphical representation of IBP transfer through SLM.

If it considered that chemical reactions between IBP and extractant are fast in the feed-membrane and membrane-strip interfaces, it is possible to say that the flux J is determined by the IBP diffusion in the limit zones of diffusion and in SLM. The IBP mass transport in zones *a*, *c* and *e* can be described as:

$$J_a = \frac{D_{IBM}}{\delta_a}\left\{\left[IBP\right]_{tot,f} - \left[IBP\right]_{i,f}\right\}$$

$$J_e = \frac{D_{IBM}}{\delta_a}\left\{\left[IBP\right]_{i,s} - \left[IBP\right]_{tot,s}\right\}$$

where

J_a and J_e (mol.cm^{-2}.min^{-1}) are the Molar Fluxes of IBP in the diffusion boundary layer of feed phase-membrane and membrane-stripping phase interfaces, respectively.

δ_a, δ_e are the thickness of the diffusion boundary layer of feed phase-membrane and membrane-stripping phase interfaces, respectively.

$\mathcal{D}_{IBP}$ is the IBP diffusion coefficient in feed phase-membrane and membrane-stripping phase interfaces.

$[IBP]_{tot,f}$ total concentration of IBP in feed phase.

$[IBP]_{i,fa}$ IBP concentration in feed phase-membrane interface.

$[IBP]_{i,s}$ IBP concentration in stripping phase-membrane interface.

$[IBP]_{tot,f}$ total concentration of IBP in stripping phase.

The flux can be defined by permeability. Permeability measures the quantity of transported solute through a specific area from the membrane surface into a given unit time [41]. This parameter can be determined experimentally by the equation (1):

$$\ln \frac{[IBP]t}{[IBP]t,o} = -P\frac{Q}{V}t \qquad (1)$$

where

P = SLM permeability (cm.min^{-1})

$[IBP]_t$ y $[IBP]_{t,0}$ = IBP concentration at time t and at time t = 0, respectively.

Q = SLM area (cm^2).

V = volume of feed phase (cm^3).

T = time (minutes).

Equation (1) has the form of straight line with –P as the slope. The variation of $\ln([IBP]_t/[IBP]_{t,0})$ as a function of (Q/V)t allows the determination of straight line slope and thus, of Permeability.

The IBP Flux through SLM is obtained by equation (2), in which permeability is related with the molar flux and initial concentration of drug in the feed phase:

$$P = \frac{J}{[IBP]t,o} \qquad (2)$$

where:

J = molar flux of drug (mol.cm^{-2}.min^{-1}).

$[IBP]_{t,0}$= initial concentration of IBP in feed phase (mol.cm^{-3}).

MATERIALS AND METHODS

The ibuprofen structure is showed in Figure **2**. Dodecane (Sigma Aldrich) was used like organic solvent, trioctylamine (TOA) (Sigma Aldrich) as a carrier to improve the transfer rate of IBP from the feed phase to stripping phase and Abil EM 90® (modified polyether-polysiloxane) (Evonik Industries) as surfactant.
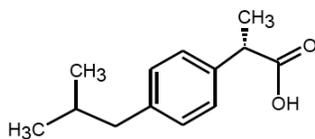

Figure 2: Ibuprofen (IBP) chemical structure.

The feed phase was composed by IBP dissolved in aqueous solution at pH 2 and the strip phase by phosphate buffer pH 7 or carbonate buffer pH 7.

The support used for the SLM preparation was a microfiltration filter (Millipore) of polyvinylidene difluoride (hydrophobic PVDF) with 47 mm of diameter, 0.22 μm of pore size, 125 μm of thickness and 75% of porosity.

In order to prepare the supported liquid membrane (SLM), the support (hydrophobic PVDF, polyvinylidene difluoride) was submerged in an organic solution containing the carrier (TOA, 1% w/V and 2% w/V) or the mix of the carrier + surfactant (Abil EM 90, 0.5% w/V and 1% w/V), diluted in dodecane or Parleam 4. The support was impregnated during 2 hours and then it was removed from the organic solution, allowing to drain off for 30 minutes. The device used in the SLM experiments is shown in Figure **3**. It consists in two cells (feed cell and stripping cell) communicated with a circular window. The SLM is placed on the circular window, between the cells 1 and 2, and the system is assembled. The feed and stripping solutions are added to cells 1 and 2, respectively. The cells are then covered and the system is stirred. Aliquots were taken from both cells at several different times and, finally the ibuprofen concentration was quantified by UV/Visible spectrometry (Varian Cary 50 Scan) at 222 nm.
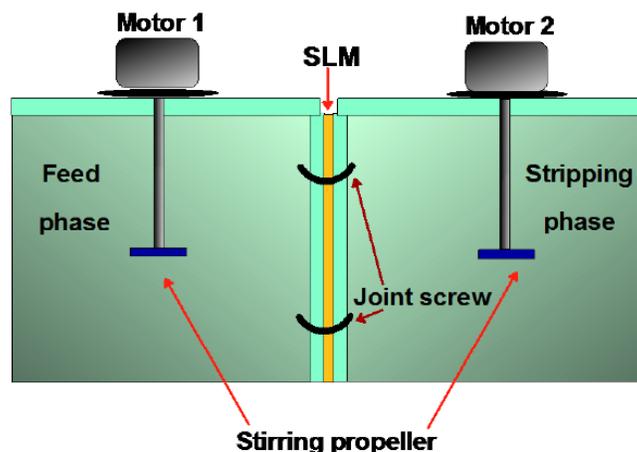

Figure 3: Schematic representation of equipment for IBP transfer by supported liquid membranes.

RESULTS AND DISCUSSION

The efficiency of IBP separation by the SLM was evaluated considering different parameters as the nature of stripping solution, the carrier concentration, the stirring rate and the surfactant presence. For each condition the curves of the variation of IBP

concentration as a function of time for the feed solution as well as the stripping solution were obtained.

Razo-Lazcano *et al*. [10] have been pointed out that the IBP distribution between an aqueous phase and an organic phase (dodecane or Parleam 4) is carried out by a simple partition mechanism. At low pH (2), high IBP extraction is reached, while at pH higher than 6.5 the IBP concentration in the organic phase is null. Then, dodecane and Parleam 4 were used like organic phases in the SLM preparation. However, because their viscosity values (1.34×10^{-3} Pa.s and 2.4521×10^{-3} Pa.s, respectively), Parleam 4 is able to impregnate better the membrane and, therefore, able to increase the stability of the SLM. Trioctylamine was used as carrier because its ability to extract organic acids [10, 42, 43]. On the other hand, the use of surfactant decrease the interfacial tension between the interface of aqueous-MLS phase, allowing a better wetting of the membrane and thus a greater solute flux [29, 31]. So, Abil EM 90 was chosen as surfactant, which is a non ionic surfactant with applications in cosmetic industry.

Effect of Strippant Nature on SLM Efficiency

The study of IBP transfer from a feed phase to a stripping phase across a SLM, was performed considering the acid-base properties of IBP as well as the conditions of feed phase and stripping phase. The IBP is extracted by dodecane or Parleam 4 in its neutral form, at the feed phase conditions (pH 2). In this way the IBP is transferred from the feed phase to the SLM. To make the transfer from MLS to the stripping phase, it is necessary to use a solution able to yield the IBP in its ionic form. So, NaOH was evaluated like stripping phase at two different concentrations (1×10^{-4} mol.L^{-1} and 1×10^{-2} mol.L^{-1}). The results obtained show that recovery percentages are 30% and 50%

respectively, after 3 hours of experiment. For this reason, we decided to use phosphate and carbonate buffers solutions at pH 7 as strippants to increase the system efficiency and to better regulate the pH changes. Figure **4** shows the $[IBP]_t/[IBP]_o$ variation as a function of time for both stripping solutions.

It is possible to see that the $[IBP]_t/[IBP]_o$ proportion decreases with the time in the feed solution while the relation ($[IBP]_t/[IBP]_o$) increases in the stripping phase. Therefore, there is an IBP transfer from the feed solution to the stripping solution across the SLM.

On the other hand, as it mentioned above, we can compare the SLM efficiency by the help of Permeability. The variation of ln $[IBP]_t/[IBP]_{t,0}$ as a function of t(Q/V)is represented in Figure **5**. It is possible to obtain the Permeability value (P) from the slope of the straight line.

From Figure **5**, it is possible to observe that the Permeability are quite similar for both phosphate and carbonate buffers (0.1005 and 0.1025 cm.min^{-1}, respectively). Thus, the IBP transfer has a similar behavior for the two stripping solutions. Thus, the ibuprofen transfer from the feed phase to the stripping phase is about 60% for both conditions after 3 hours; however, using phosphate buffer at pH 7, the drug transfer to membrane and from this one to stripping phase is slightly greater at less time. In addition, the buffer capacity of phosphates ($H_2PO_4^-/HPO_4^{-2}$) is bigger at pH close to 7. For these reasons, phosphate buffer was chosen like stripping phase.

Effect of Stirring Rate on SLM Efficiency

The stirring rate applied to feed phase was varied in order to observe the effect on the SLM transfer efficiency keeping the stirring rate of stripping phase as
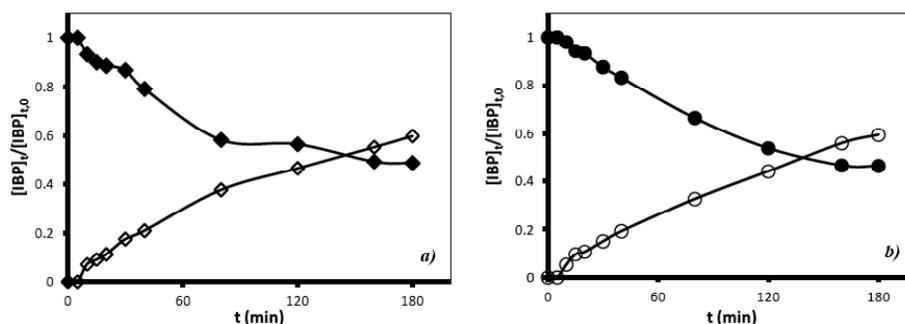

Figure 4: IBP transfer through the SLM. Feed phase: [IBP] = 50 mg.L^{-1} dissolved in solution at pH 2. Strip phase: a) Phosphate buffer at pH 7 (◆ feed, ◇strip), b) Carbonate buffer at pH 7 (● feed, strip○). SLM: hydrophobic polyvinylidene difluoride support (PVDF) impregnated with TOA 1% w/V dissolved in dodecane. Stirring rate for both cells: 1000 rpm; transfer time: 3 hours.
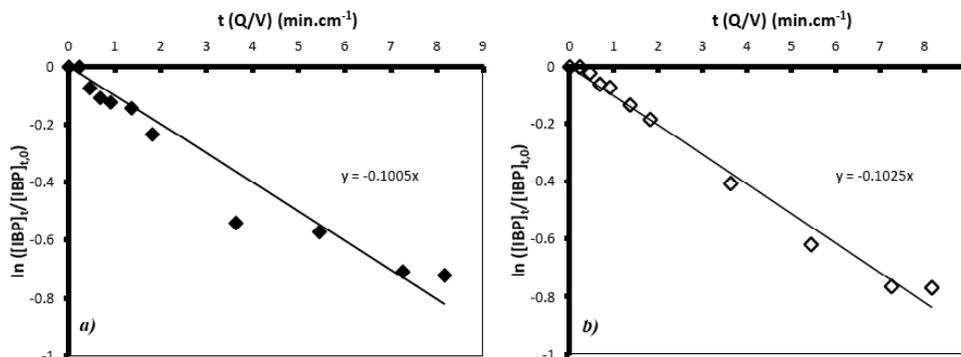
Figure 5: ln ([IBP]$_t$ / [IBP]$_{t,0}$) variation as a function of t(Q/V) during the IBP transfer through the SLM. Feed phase: [IBP] = 50 mg.L^{-1} dissolved in solution at pH 2. Stripping phase: a) Phosphate buffer at pH 7, b) Carbonate buffer at pH 7 SLM: hydrophobic polyvinylidene difluoride support (PVDF) impregnated with TOA 1% w/V dissolved in dodecane. Stirring rate for both cells: 1000 rpm.

constant. Table **1** shows the Permeability as well as the Molar Flux obtained after 3 hours of contact between the SLM and the phases

The P and J values are quite similar for all the conditions. But if Figure **6** is analyzed, it is possible to observe some differences between the [IBP]$_t$/[IBP]$_o$ curves as a function of time. When the stirring rate is 1000 rpm into the feed phase, the IBP transfer is slightly faster than the other stirring rates. Other difference is that the point where the [IBP] in the feed phase crosses the line of the [IBP] in the stripping phase is close to 0.5 for the [IBP]$_t$/[IBP]$_o$ rate. This means that the IBP does not accumulate on the SLM and all the ibuprofen is transferred to the stripping phase.

Effect of TOA Concentration on SLM Efficiency

The influence of TOA concentration in the mass transfer process of IBP through the SLM was evaluated for 1% w/V and 2% w/V of TOA, after 10 hours of transfer time. The results obtained are shown in Figure **7**, from which the Permeability value was deduced.
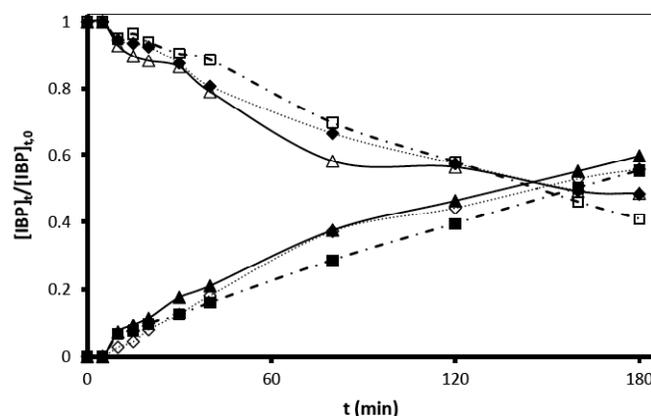

Figure 6: IBP transfer by SLM. Stir rate: □ Feed 500rpm, ■ Strip 1000 rpm; ◆ Feed 800 rpm, Strip1000 rpm ◇ ;△ Feed 1000 rpm, ▲ Strip 1000 rpm. Feed: [IBP] = 50 mg.L^{-1} dissolved in solution at pH 2, Strip: phosphate buffer at pH 7, SLM: hydrophobic polyvinylidene difluoride support (PVDF) impregnated with TOA 1% w/V dissolved in dodecane.

For a TOA concentration of 1% w/V a permeability value of 0.085 cm.min^{-1} was obtained and 0.1197 cm.min^{-1} for 2% w/V of TOA. That is, the SLM impregnated with 2% w/V of TOA allows a more IBP transfer through it with a flux molar value of 3.1 x 10^{-8} mol.cm^{-2}.mol^{-1}.

Table 1:   Permeability and Molar Flux of IBP. Feed Phase: [IBP] = 50 mg.L^{-1} Dissolved in Solution at pH 2, Stripping Phase: Phosphate Buffer at pH 7, SLM: Hydrophobic Polyvinylidene Difluoride Support (PVDF) Impregnated with 1% w/V TOA + Dodecane

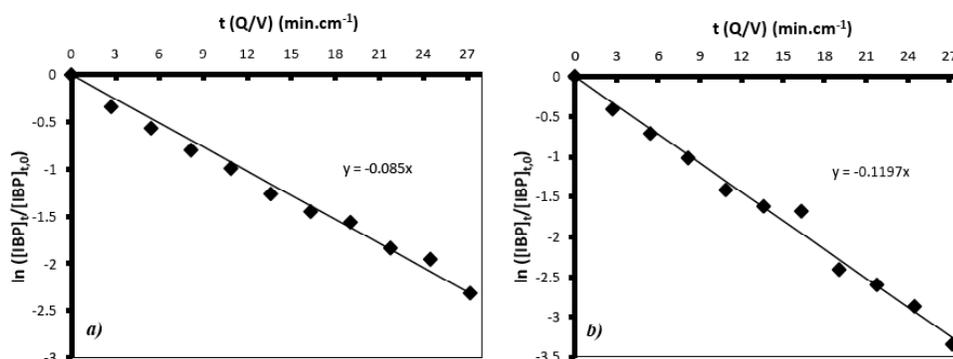| Feed Phase v (rpm)	Stripping Phase v (rpm)	Transfer Time (hr)	P (cm.min^{-1})	J (mol.cm^{-2}.min^{-1})
500	1000	3	0.1044	2.5 x 10^{-8}
800	1000	3	0.0963	2.3 x 10^{-8}
1000	1000	3	0.1005	2.4 x 10^{-8}

Figure 7: ln ([IBP]$_t$ / [IBP]$_{t,0}$) variation during the IBP transfer by SLM. TOA concentration: a) 1 % w/V; b) 2 % w/V. Feed phase: [IBP] = 50 mg.L^{-1} dissolved in solution at pH 2, Stripping phase: phosphate buffer at pH 7. SLM: hydrophobic polyvinylidene difluoride support (PVDF) impregnated with TOA dissolved in dodecane. Transfer time: 10 hr, stirring rate: 1000 rpm for both phases.

However, this increase of TOA concentration in the SLM provokes that IBP stays in more quantity on the membrane because of the complex formed (IBP-TOA) is more stable at higher TOA concentrations. Figure **8** reveals this phenomenon; a higher Permeability is obtained when a bigger concentration of TOA is used, but some IBP mass remains into the SLM.

It is important to remark that the 98% of IBP was transferred to stripping phase after 10 hours, and that the SLM was stable during all the experiment. No droplets of organic phase were observed in any of the phases. On the other hand, the PVDF is a polymer that allows re-using the membrane many times.
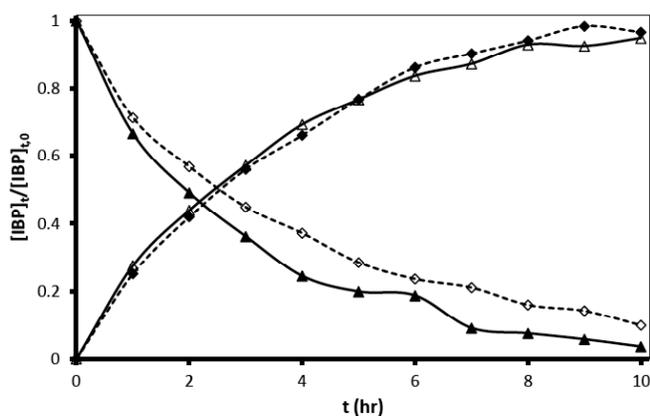

Figure 8: IBP transfer trough the SLM. TOA concentration: 1 % w/V ◇ Feed, ◆ Strip; 2 % w/V Feed ▲ Strip △ Feed: [IBP] = 50 mg.L^{-1} dissolved in solution at pH 2, Strip: phosphate buffer at pH 7, SLM: hydrophobic polyvinylidene difluoride support (PVDF) impregnated with TOA dissolved in dodecane. Stirring rate 1000 rpm in the both cells.

Surfactant Effect on SLM Efficiency

In order to improve the IBP flux through the supported liquid membrane, a surfactant, Abil EM 90, was added to organic phase with which the membrane was impregnated. The surfactant is able to decrease the interfacial tension, between the impregnated phase and the aqueous phase and allowing a better wetting of the membrane; hence a greater solute flux [29, 31].

Table **2** shows the SLM efficiency with respect the IBP recovery through the Permeability and Molar Flux at different surfactant concentrations.

The Permeability and Molar Flux values increase when the surfactant concentration increases. According to these values, the membrane impregnated with 1% w/V Abil EM 90 + 1% TOA + Parleam 4 has a permeability of 0.1939 cm.min^{-1}; then, is more permeable to ibuprofen. For this reason, it is possible to say that the increase of surfactant concentration favors the recovery percentages of IBP.

When the TOA concentration was varied, the IBP transfer increases according to the TOA concentration. Permeability and Molar Flux values (see Table **2**) are 0.1939 cm.min^{-1} and 4.8 x 10^{-8} mol.cm^{-2}.min^{-1} respectively with a SLM with 1% w/V TOA + 1% w/V Abil EM 90 + Parleam 4, that represents the best performance vis-à-vis the IBP transfer.

On the other hand, it is possible to observe that the Permeability and the Molar Flux values are higher for a stirring rate of 2000 rpm and 2000 rpm for feed and stripping phases, respectively. Figure **9** shows the IBP transfer at 2000 rpm as stirring rate for the both phases. It can see that the IBP can be recovered in about 90% after 10 hours of transfer time, and also the 50% of IBP transferred is reached very fast, comparing it with the other conditions studied. Then the IBP transfer from the feed phase to the SLM and from the

Table 2:　Permeability and Molar Flux of IBP for Several Values of TOA and Surfactant (Abil EM 90) Concentrations, at Different Stirring Rates. Feed: [IBP] = 50 mg.L^{-1} Dissolved in Solution at pH 2, Strip: Phosphate Buffer at pH 7, SLM: Hydrophobic Polyvinylidene Difluoride Support (PVDF) Impregnated with TOA + Abil EM 90 + Parleam 4. Transfer Time: 5 hr

[Abil EM 90] (% w/V)	[TOA] (% w/V)	Feed Phase v (rpm)	Stripping Phase v (rpm)	P (cm.min^{-1})	J (mol.cm^{-2}.min^{-1})
0.5	1	2000	2000	0.1139	2.9×10^{-8}
1	1	2000	2000	0.1939	4.8×10^{-8}
1	0.5	2000	2000	0.1851	4.6×10^{-8}
1	0.1	2000	2000	0.1600	3.9×10^{-8}
1	1	1000	2000	0.1422	2.1×10^{-8}
1	1	2000	1000	0.1797	4.6×10^{-8}
1	1	2000	2000	0.1939	4.1×10^{-8}

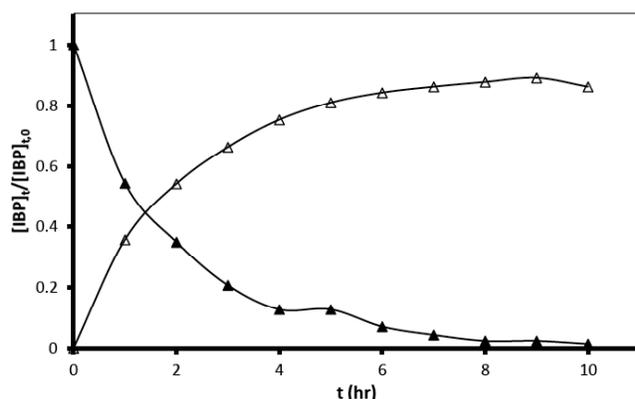SLM to the stripping phase is almost complete at these conditions.

Figure 9: IBP transfer through SLM. Feed: [IBP] = 50 mg.L^{-1} dissolved in solution at pH 2, Strip: phosphate buffer at pH 7. Stirring rate: Feed 2000 rpm, Strip 2000 rpm SLM: hydrophobic polyvinylidene difluoride support (PVDF) impregnated with 1% w/V TOA + 1% w/V Abil EM 90 + Parleam 4.

Reactions involved in the mass transfer of IBP through the SLM

Taking into account that the extraction process was carried out at acidic pH (~ 2), the molecules of TOA can solvate the non-charged form of ibuprofen, HIBP (pka 4.9) [44, 45] (see Figure **10**), allowing the extraction of this one to the organic phase by a solvation extraction mechanism.

Figure 10: IBP predominance diagram as a function of pH.

With respect to the stripping mechanism, the ibuprofen-amine complex is broken by the OH$^-$ ions contained into the stripping phase, hence transferred to the stripping phase. Both reactions are represented as follows:

Extraction: $\overline{TOA} + HIBP \quad \rightarrow \quad \overline{TOA:HIBP}$

Stripping: $\overline{TOA:HIBP} + OH^- \quad \rightarrow \quad IBP^- + \overline{TOA} + H_2O$

Where, the species with the overbar represent those into the organic phase (SLM phase).

CONCLUSIONS

The recovery of IBP from acidic aqueous solutions has been performed with a SLM composed by Parleam 4 (or dodecane) as diluent, tri-octylamine (TOA) like carrier and Abil EM 90 as surfactant. In the case of SLM without surfactant, the nature of stripping phase was evaluated, being the phosphate buffer slightly more efficient for the IBP mass transfer from feed phase to membrane and from this one to stripping phase at less time and able to regulate the pH value at 7, which it is favorable for the IBP recovery. An efficient IBP transfer was reached without accumulation of drug on the SLM, when the stirring rate is higher of 1000 rpm for the both phases. An IBP transfer almost complete (98 %) to stripping phase was reached after 10 hours, and the SLM was stable during all this time. In the case of the SLM with surfactant, it was observed that for a 1% w/Vof Abil EM 90, the SLM had a good performance, with a Permeability of 0.1939 cm.min^{-1}.

The SLM needs very low quantities of solvent and extractant to recover almost the 98% of ibuprofen. This method is friendly with the environment and it can be

useful as secondary process during the wastewater treatment.

ACKNOWLEDGEMENTS

REFERENCES

[1] Kosjek T, Heath E, Krbavcic A. Determination of non-steroidal anti-inflammatory drug (NSAIDs) residues in water samples. Environ Int. 2005; 31: 679-85.
http://dx.doi.org/10.1016/j.envint.2004.12.001

[2] Pal A, Gin KY-H, Lin AY-C, Reinhard M. Impacts of emerging organic contaminantes on freshwater resources: Review of recent occurrences, sources, fate and effects. Sci Total Environ. 2010; 408: 6062-9.
http://dx.doi.org/10.1016/j.scitotenv.2010.09.026

[3] Ziylan A, Ince NH. The occurrence and fate of anti-inflammatory and analgesic pharmaceuticals in sewage and fresh water: treatability by conventional and non-conventional processes. J Hazard Mater. 2011; 187: 24-36.
http://dx.doi.org/10.1016/j.jhazmat.2011.01.057

[4] Stuart M, Lapworth D, Crane E, Hart A. Review of risk from potential emerging contaminants in UK groundwater. Sci Total Environ. 2012; 416: 1-21.
http://dx.doi.org/10.1016/j.scitotenv.2011.11.072

[5] Meffe R, Bustamante Id. Emerging organic contaminants in surface water and groundwater: a first overview of the situation in Italy. Sci Total Environ. 2014; 481: 280 - 95.
http://dx.doi.org/10.1016/j.scitotenv.2014.02.053

[6] Li WC. Occurence, sources, and fate fo pharmaceuticals in aquatic environment and soil. Environ Pollut. 2014; 187: 193 - 201.
http://dx.doi.org/10.1016/j.envpol.2014.01.015

[7] Sires I, Brillas E. Remediation of water pollution caused by pharmaceutical residues based on electrochemical separation and degradation technologies: a review. Environ Int. 2012; 40: 212-29.
http://dx.doi.org/10.1016/j.envint.2011.07.012

[8] Owa FD. Water pollution: sources, effects, control and management. Mediterr J Soc Sci. 2013; 4(8): 65-8.
http://dx.doi.org/10.5901/mjss.2013.v4n8p65

[9] Comeau F, Surette C, Brun GL, Losier R. The occurrence of acidic drugs and caffeine in sewage effluents and receiving waters from three coastal watersheds in Atlantic Canada. Sci Total Environ. 2008; 396: 132-46.
http://dx.doi.org/10.1016/j.scitotenv.2008.02.031

[10] Razo-Lazcano TA, Stambouli M, González-Mu-oz MdP, Pareau D, Ávila-Rodríguez M. Emulsion liquid membranes for recovery of ibuprofen from aqueous solutions. J Chem Technol Biotechnol. 2014; 89: 890-8.
http://dx.doi.org/10.1002/jctb.4329

[11] Daughton CG. Emerging pollutants, and communicating the science of environmental chemistry and mass spectrometry: pharmaceuticals in the environment. J Am Soc Mass Spectrom. 2001; 12: 1067-76.
http://dx.doi.org/10.1016/S1044-0305(01)00287-2

[12] Buser H-R, Poiger T, Muller M. Occurrence and environmental behavior of the chiral pharmaceutical drug ibuprofen in surface waters and in wastewater. Environ Sci Technol. 1999; 33: 2529-35.
http://dx.doi.org/10.1021/es981014w

[13] Andreozzi R, Raffaele M, Nicklas P. Pharmaceuticals in STP effluents and their solar photodegradation in aquatic environment. Chemosphere. 2003; 50(10): 1319-30.
http://dx.doi.org/10.1016/S0045-6535(02)00769-5

[14] Stumpf M, Ternes TA, Wilken R-D, Silvana Vianna R, Baumann W. Polar drug residues in sewage and natural waters in the state of Rio de Janeiro, Brazil. Sci Total Environ. 1999; 225(1–2): 135-41.
http://dx.doi.org/10.1016/S0048-9697(98)00339-8

[15] Blaise C, Gagné F, Eullaffroy P, Férard J. Ecotoxicity of selected pharmaceuticals of urban origin discharged to the Saint-Lawrence river (Québec, Canada): a review. Braz J Aquat Sci Technol. 2006; 10(2): 29-51.
http://dx.doi.org/10.14210/bjast.v10n2.p29-51

[16] Ashton D, Hilton M, Thomas KV. Investigating the environmental transport of human pharmaceuticals to streams in the United Kingdom. Sci Total Environ. 2004; 333: 167-84.
http://dx.doi.org/10.1016/j.scitotenv.2004.04.062

[17] Boyd GR, Palmeri JM, Zhang S, Grimm DA. Pharmaceuticals and personal care products (PPCPs) and endocrine disrupting chemicals (EDCs) in stormwater canals and Bayou St. John in New Orleans, Louisiana, USA. Sci Total Environ. 2004; 333: 137-48.
http://dx.doi.org/10.1016/j.scitotenv.2004.03.018

[18] Heckmann L-H, Callaghan A, Hooper H, Connon R, Hutchinson T, Maund S, et al. Chronic toxicity of ibuprofen to Daphnia magna: effects on life history traits and population dymanics. Toxicol Lett. 2007; 172: 137-45.
http://dx.doi.org/10.1016/j.toxlet.2007.06.001

[19] Daughton CG, Ternes TA. Pharmaceuticals and personal care products in the environment: agents of subtle change? Environ Health Perspect. 1999; 107(6): 907-38.
http://dx.doi.org/10.1289/ehp.99107s6907

[20] Hernando MD, Mezcua M, Fernández-Alba AR, Barceló D. Environmental risk assessment of pharmaceutical residues in wastewater effluents, surface waters and sediments. Talanta. 2006; 69: 334-42.
http://dx.doi.org/10.1016/j.talanta.2005.09.037

[21] Méndez-Arriaga F, Torres-Palma RA, Pétrier C, Esplugas S, Giménez J, Pulgarin C. Ultrasonic treatment of water contaminated with ibuprofen. Water Res. 2008; 42: 4243-8.
http://dx.doi.org/10.1016/j.watres.2008.05.033

[22] Méndez-Arriaga F, Esplugas S, Giménez J. Degradation of emerging contaminant ibuprofen in water by photo-Fenton. Water Res. 2010; 44: 589-95.
http://dx.doi.org/10.1016/j.watres.2009.07.009

[23] 23. Szabó RK, Megyeri C, Illés E, Gajda-Schrantz K, Mazellier P, Dombi A. Phototransformation of ibuprofen and ketoprofen in aqueous solutions. Chemosphere. 2011; 84: 1658-63.
http://dx.doi.org/10.1016/j.chemosphere.2011.05.012

[24] Ghauch A, Tuqan AM, Kibbi N. Ibuprofen remova by heated persulfate in aqueous solution: a kinetics study. Chem Eng J. 2012; 197: 483-92.
http://dx.doi.org/10.1016/j.cej.2012.05.051

[25] Mestre AS, Bexiga AS, Proenca M, Andrade M, Pinto ML, Matos I, et al. Activated carbons from sisal waste by chemical activation with K2CO3: kinetics of paracetamol and ibuprofen removal from aqueous solution. Bioresour Technol. 2011; 102: 8253-60.
http://dx.doi.org/10.1016/j.biortech.2011.06.024

[26] De-Gyves J. Metal ion separations by supported liquid membranes. Ind Eng Chem Res. 1999; 38: 2182-202.

http://dx.doi.org/10.1021/ie980374p

[27] Parhi P. Supported liquid membrane principle and its practices: a short review. J Chem 2013: 1-11.
http://dx.doi.org/10.1155/2013/618236

[28] Kocherginsky NM, Yang Q, Seelam L. Recent advances in supported liquid membrane technology. Sep Purif Technol. 2007; 53: 171-7.
http://dx.doi.org/10.1016/j.seppur.2006.06.022

[29] Voorde IVd, Pinoy L, Ketelaere RFd. Recovery of nickel by supported liquid membrane (SLM) extraction. J Memb Sci. 2004; 234: 11-21.
http://dx.doi.org/10.1016/j.memsci.2004.01.002

[30] Yang Z-F, Guha AK, Sirkar KK. Novel membrane-based synergistic metal extraction and recovery processes. Ind Eng Chem Res 1996; 35(4): 1383-94.
http://dx.doi.org/10.1021/ie950313g

[31] Kakoi T, Goto M, Nakashio F. Separation of platinum and palladium by liquid surfactant membranes utilizing a novel bi-functional surfactant. J Memb Sci. 1996; 120: 77-88.
http://dx.doi.org/10.1016/0376-7388(96)00137-8

[32] Perez MEM, Reyes-Aguilera JA, Saucedo TI, Gonzalez MP, Navarro R, Avila-Rodriguez M. Study of As (V) transfer through a supported liquid membrane impregnated with trioctylphosphine oxide (Cyanex 921). J Membr Sci. 2007; 302: 119-26.
http://dx.doi.org/10.1016/j.memsci.2007.06.037

[33] Reyes-Aguilera JA, Gonzalez MP, Navarro R, Saucedo TI, Avila-Rodriguez M. Supported liquid membranes (SLM) for recovery of bismuth from aqueous solutions. J Memb Sci. 2008; 310: 13-9.
http://dx.doi.org/10.1016/j.memsci.2007.10.020

[34] Santiago-Santiago LA, Reyes-Aguilera JA, Gonzalez MP, Cholico-Gonzalez D, Avila-Rodríguez M. Separation of Bi (III) and Sb (III) from Cu (II) HCl/H2SO4 mixed media by supported liquid membranes using Cyanex 921 as carrier. Ind Eng Chem Res. 2012; 51: 15184-92.
http://dx.doi.org/10.1021/ie301447x

[35] Juang R-S, Chen L-J. Analysis of the transport rates of citric acid through a supported liquid membrane containing Tri-n-octylamine. Ind Eng Chem Res. 1996; 35: 1673-9.
http://dx.doi.org/10.1021/ie950468o

[36] Vilt ME, Ho WSW. Supported liquid membranes with strip dispersion for the recovery of cephalexin. J Memb Sci. 2009; 342: 80-7.
http://dx.doi.org/10.1016/j.memsci.2009.06.026

[37] Msagati TAM, Nindi MM. The use of supported liquid membranes in the extraction of macrolides in biomatrices. Microchim Acta. 2004; 148: 199-214.
http://dx.doi.org/10.1007/s00604-004-0262-y

[38] Kouki N, Tayeb R, Dhahbi M. Recovery of acetaminophen from aqueous solutions using a supported liquid membrane based on a quaternary ammonium salt as ionophone. Chemical Papers. 2014; 68(4): 457-64.
http://dx.doi.org/10.2478/s11696-013-0479-5

[39] Pedersen-Bjergaard S, Rasmussen KE. Extraction across supported liquid membranes by use of electrical fields. Anal Bioanal Chem. 2007; 388: 521-3.
http://dx.doi.org/10.1007/s00216-007-1142-1

[40] Krull F, Fritzmann C, Melin T. Liquid membranes for gas/vapor separations. Journal of Membrane Science. 2008; 325: 509-19.
http://dx.doi.org/10.1016/j.memsci.2008.09.018

[41] Danesi PR. Separation of metal species by supported liquid membranes. Sep Sci Technol. 1984; 19(11-12): 857-94.
http://dx.doi.org/10.1080/01496398408068598

[42] Lee S. Extraction of succinic acid from simulated media by emulsion liquid membranes. J Membr Sci. 2011; 381: 237-43.
http://dx.doi.org/10.1016/j.memsci.2011.07.039

[43] Schöller C, Chaudhuri J, Pyle D. Emulsion liquid membrane extraction of lactic acid from aqueous solutions and fermentation broth. Biotechnol Bioeng. 1993; 42: 50-8.
http://dx.doi.org/10.1002/bit.260420108

[44] Eyal RCA. pH dependence of carboxylic and mineral acid extraction by amine-based extractants: effects of pKa, amine basicity and diluents properties. Ind Eng Chem Res. 1995; 34: 1789-98.
http://dx.doi.org/10.1021/ie00044a030

[45] Huber M, Göbel A, Joss A, Hermann N, Löffler D, Mcardell C, et al. Oxidation of Pharmaceuticals during ozonation of municipal wastewater effluents: a pilot study. Environ Sci Technol. 2005; 39: 4290-9.
http://dx.doi.org/10.1021/es048396s