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Ionic Liquid Membrane Process for Removal of Volatile Organic Compounds from Lab to Industrial Scale

Hybrid processes have received more attention in pollutant removal due to the combination of advantages of each process. A membrane combined with absorption was developed and studied for the removal of volatile organic compounds (VOCs) from lab to industrial scale. The ionic liquid membrane containing 1-butyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)imide ([Bmim][NTf₂]) showed competitive absorption on toluene. An industrial-length ionic liquid membrane was investigated under optimized conditions based on lab-scale results for a long time. The arrangement of the membrane modules was also evaluated, including connection in series and parallel. As a result, the proposed ionic liquid membrane is highly promising for industrial applications.

Keywords: Absorption, Hybrid processes, Ionic liquid membranes, Volatile organic compounds

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1 Introduction

Ionic liquids (ILs) are organic molten salts with many excellent properties such as negligible vapor pressure and non-flammability, making them safer and environmentally friendly [1–3]. Recently, ILs, as an alternative for conventional organic solvents, showed great potential in separation processes. However, many scientists have questioned the widespread use of ILs because of the unknown toxicity [4–6] which will increase the difficulty to meet the given process requirements with reduction of their hazard potential.

Gas separative membranes are attractive due to low energy consumption and mild operating conditions [7–9]. ILs combined with membrane processes have been becoming a promising approach in separation fields in recent years, promoting solvent properties of ILs and enhancing membrane separation performances [10].

Here, a new hybrid process, i.e., a combination of advantages of membranes (modularity and compactness) and absorption relying on ILs, is developed for separation of gases (volatile organic compounds, VOCs) from lab scale to industrial scale. This process can be applied industrially while ensuring an efficient absorption separation efficiency. Therefore, the cost of the separation process and membrane has not been given much discussion at this stage. However, ILs are cheaper in production and more environmentally friendly in separation processes. More importantly, the ILs can be recycled, and the absorption performance still keeps relatively high.

2 Materials and Methods

2.1 Ionic Liquid Membrane

As illustrated in Fig. 1, the support of ionic liquid membranes (ILMs) is a multichannel tubular ceramic membrane (Alsys Society, Salindres, France). For lab scale, the ceramic multichannel membrane was divided into four parts of 25 cm, and each of them was sealed with the solution normally used to seal the inlet/outlet. For the industrial scale, the industrial length of the ceramic membrane (1.178 m) is used directly. The coating is a fluoropolymer that is conventionally employed for the ends of micro-ultra-nanofiltration membranes. In this study, a molecular weight cutoff (MWCO) of 1 kDa ceramic membrane was used (1 Da = 1 g L⁻¹) decided according to the viscosity of the selected IL (function of the VOC removal). Some channels

¹Dr. Xueru Yan, Prof. Philippe Moulin
philippe.moulin@univ-amu.fr

Aix-Marseille Université, CNRS, Cent Marseille, M2P2, Equipe Procédés Membranaires (EPM), Europole de l'arbois, Bat. Laennec, Hall C, BP 80, 13545 Aix-en-Provence Cedex, France.

²Dr. Stéphane Anguille,
IUT Aix-Marseille, Département Chimie, 142 Traverse C. Susini, 13013 Marseille France.

³Dr. Marc Bendahan
Aix-Marseille Université, Université de Toulon, CNRS, IM2NP, Av. Escadrille Normandie Niémen, 13397 Marseille Cedex 20, France.

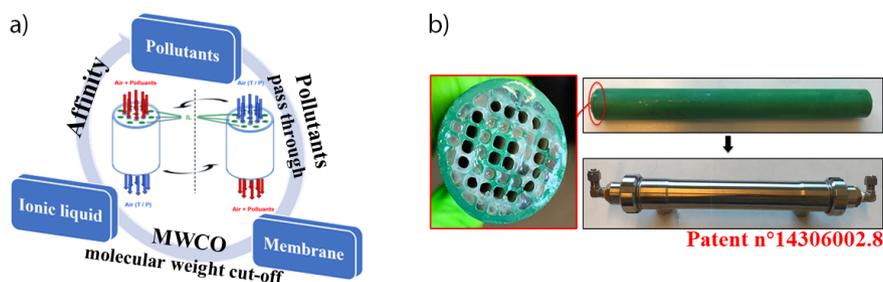


Figure 1. (a) Concept of ILM, (b) photos of ILM with/without carter [11].

of the ceramic membrane are filled with ILs and some channels are empty as gas or liquid access.

The methodology described is optimized after different tests. The channels containing ILs are closed by glue on each extremity to keep the ILs inside. Before preparing the ILM, the dissolved gases into the selected IL are removed by evaporation and heating [11]. The specific stainless-steel carter is taken to stabilize and connect the ILM. The sealing between inlet/outlet and permeate is ensured by a thoracic seal at the inlet and outlet. The porous hydrophobic ceramic membrane acts as a fixed interface between the gas or liquid phase and the IL phase without dispersing one phase into another. The membrane offers a flexible modular energy-efficient device with high specific surface area. The absorption process can offer a very high selectivity and a remarkable driving force for mass transfer even at very low concentration.

It should be noticed that the choice of the testing pressure range is explained by the pressure at the gas effluent as a function of the IL surface tension, and high pressure can move the IL outside of the channel. However, it is important to note that the MWCO is small, and the pore diameter is lower than 2.0 nm to reduce this risk. The critical entry pressure of the membrane can be calculated by the Young-Laplace equation [12,13]. The pressure to push the IL into the small pore is higher than 55.0 atm. The pressure ranges were lower than 55.0 atm for the ILM to investigate the effect of the driving force resulting into target gas through the channel walls and reaching to IL channels.

$$\Delta P = -(4\gamma L \cos \theta) / \sigma \quad (1)$$

where $\Delta P^{(1)}$ represents the critical entry pressure (breakthrough pressure), γ_L , θ , and σ denote the surface tension of the liquid, the contact angle between the liquid phase and the membrane, and the membrane pore diameter, respectively.

2.2 VOCs Removing Process

The gas generation-dilution system is purchased from Omicron technologies (Eybens, France). The VOCs sensor (Ametek Mocon) is a photoionization detector (PID sensor) with $\pm 10\%$ of accuracy. In this system, the desorption process is carried out with continuous dry air flow with absorption operating

conditions. Desorption was completed in all cases, i.e., most of the toluene absorbed was desorbed at the absorption temperature without heating or vacuum.

2.2.1 Lab-Scale Process

Before testing the separation performances of ILMs, it is necessary to check each device of the process to exclude their influences and to ensure that only the selected IL can absorb VOCs. The removal process of gases is illustrated in Fig. 2a. Each gas and mixture flow is controlled in terms of mass flow, pressure, and initial concentration. The absorption-desorption curves were obtained by a PID sensor placed at the outlet of the ILM.

2.2.2 Industrial-Scale Process

With the sizeable industrial membrane (length = 1.178 m), it could not register into this thermostatically controlled chamber. In this specific case, the industrial membrane experiment was conducted at room temperature, as Fig. 2b indicates. Other parts, such as gas dilution system, pressure regulator, and a gas sensor, are the same as in the lab-scale process.

3 Results

The room-temperature IL 1-butyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)imide ([Bmim][NTf₂]) is selected as a physical absorbent. A ceramic tubular membrane acts as a hydrophobic support and has no impact on mass transfer.

3.1 Effects of Different Operating Conditions on Lab Scale

The absorption performance of toluene by the ILM containing [Bmim][NTf₂] was investigated by studying the influences of operating conditions, including concentration, flow rate, pressure, and temperature. Based on lab-scale experimental results, high concentration, flow rate, and pressure have a positive effect on toluene removal, while high temperature has a negative influence on toluene removal by the ILM. Effects of different operating conditions on toluene by the ILM were tested and discussed comprehensively in our previous study [14]. This work mainly focuses on extending the ILM process to industrial scale based on results obtained from lab scale.

The optimized operating conditions, i.e., concentration inlet 70 ppm, flow rate 0.10 L min⁻¹, pressure 1.17 atm, temperature 20 °C, are proposed for toluene removal by the ILM. The lab-scale ILM (length 0.25 m) was tested for a long time until its saturation under optimized conditions [14]. When the concentration at the outlet equals that at the inlet, the ILM is considered saturated. Results (Fig. 3) indicate that the ILM needed

1) List of symbols at the end of the paper.

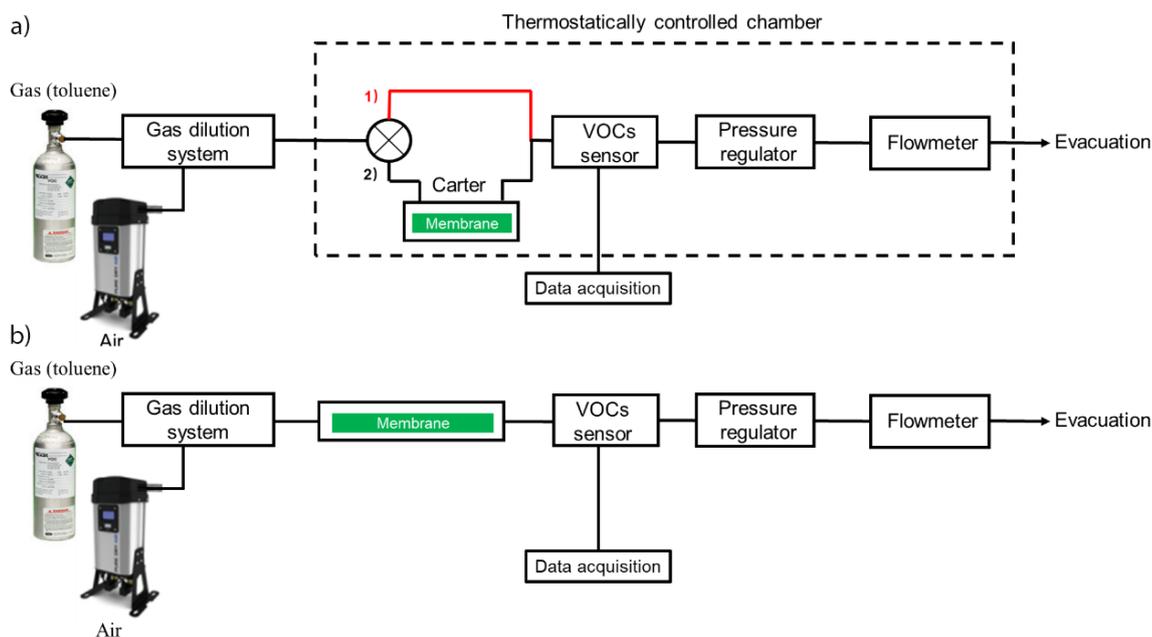


Figure 2. Toluene removal process on (a) lab scale and (b) industrial scale.

32 h to reach saturation because the mass of toluene absorbed was not increasing. The saturation concentration is $0.22 \text{ g toluene g IL}^{-1}$ which agrees with the state-of-the-art result, i.e., $1 \text{ g of [Bmim][NTf}_2\text{] absorbs } 0.21 \text{ g of toluene at } 1.00 \text{ atm and } 20^\circ\text{C}$ [15]).

3.2 Toluene Removal by Industrial-Scale ILM

From lab to industrial scale, the length of the ILM increases from 0.25 to 1.178 m . This test is operated at 1.00 atm and room temperature. Fig. 4b indicates that around 20 h the outlet concentration became fluctuated regularly up and down due to the diurnal temperature variation of the day (high temperature) and night (low temperature), which is in agreement with the effect of temperature discussed before [6]. It is well-known that the surface area, the quantity of ILMs and gas residence time will be higher with the length of membrane increasing from 0.25 m to 1.178 m , resulting in higher absorption.

At the beginning of absorption, the toluene concentration in the IL phase is zero or very low, resulting in a big concentration gradient which corresponds to a fast absorption rate. With testing time going on, the concentration of toluene in the IL increases, therefore, the concentration difference between gas flow and IL phase decreased resulting in a lower absorption rate. The industrial-length ILM could operate more than 150 h continuously. More importantly, there is no IL leaking observed during the whole process.

About 70 ppm of toluene passes through three industrial-length ILM modules continuously more than 150 h . This duration is the maximum value of the stabilized outlet concentration. Each module contains only one and the same ILM. As a result, Fig. 4a demonstrates that 70 ppm of toluene is reduced to 12 ppm . For industrial application, membrane modules connected in series could treat high concentrations of pollutants. Furthermore, different modules containing various ILMs could achieve stepwise the removal of different gases. Membrane modules connected in parallel could treat large flow rates of

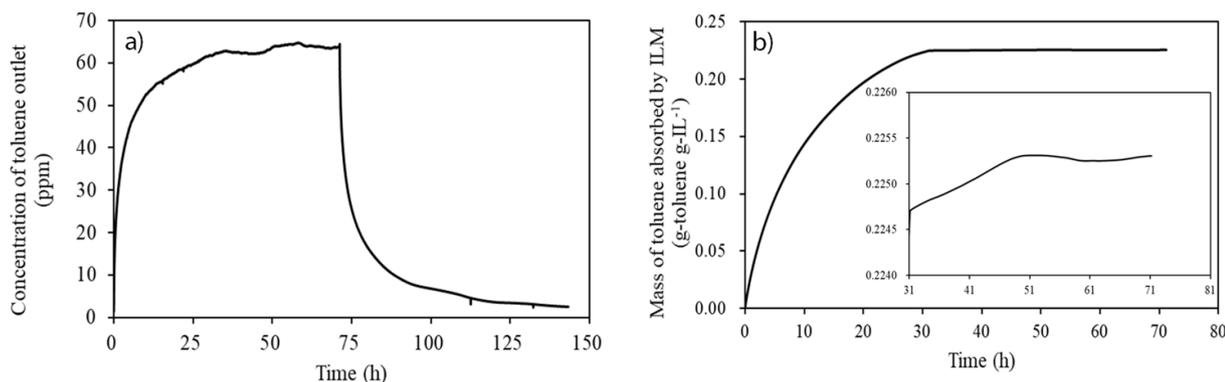


Figure 3. (a) Concentration of toluene outlet as a function of time, (b) quantity of toluene absorbed by the ILM [14].

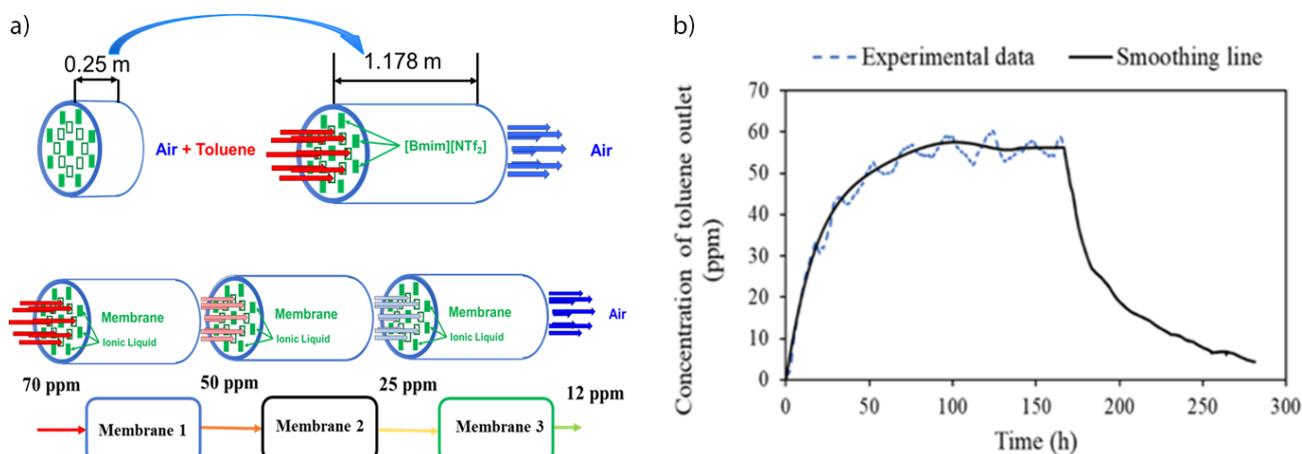


Figure 4. (a) Scheme of membrane modules connected in series, (b) toluene removal on industrial scale under proposed conditions.

pollutants because the residence time of pollutants increased and the removal efficiency enhanced.

4 Conclusion

A new hybrid process, i.e., the ionic liquid membrane (ILM), is developed for gas treatment from lab scale to industrial scale. For lab scale, effects of operating conditions on toluene removal are studied. Results indicate that high concentrations, flow rates, and pressures are beneficial for gas removal. However, a high temperature is positive for gas removal by ILMs. Optimized conditions are applied to measure the absorption capacity.

The absorption capacity is 0.224 g toluene per g [Bmim][NTf₂] under the proposed conditions, i.e., concentration inlet 70 ppm, flow rate 0.10 L min⁻¹, pressure 1.17 atm, temperature 20 °C [14]. For industrial scale, the length of each ILM is increased to 1.178 m.

The arrangement of industrial membrane modules was also tested at room temperature and atmospheric pressure. The concentration decreased from 70 to 12 ppm when three industrial membrane modules were connected in series. For long-time operation and several absorption-desorption cycles, the ILM still keeps high separation performance and stability. When ILM modules were connected in parallel, high flow rates of pollutants could be treated effectively. This result gives an indication of the industrial applicability of ILMs.

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The authors have declared no conflict of interest.

Symbols used

ΔP	[Pa]	critical entry pressure
γ_L	[N m ⁻¹]	surface tension of the liquid
θ	[°]	contact angle between liquid phase and membrane
σ	[m]	membrane pore diameter

Abbreviations

[Bmim][NTf ₂]	1-butyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)imide
IL	ionic liquid
ILM	ionic liquid membrane
PID	photoionization sensor
VOC	volatile organic compound

References

- [1] N. V. Plechkova, K. R. Seddon, *Chem. Soc. Rev.* **2008**, *37*, 123–150. DOI: <https://doi.org/10.1039/B006677J>
- [2] S. Zhang, J. Zhang, Y. Zhang, Y. Deng, *Chem. Rev.* **2017**, *117* (10), 6755–6833. DOI: 10.1021/acs.chemrev.6b00509
- [3] S. Zeng, X. Zhang, L. Bai, X. Zhang, H. Wang, J. Wang, D. Bao, M. Li, X. Liu, S. Zhang, *Chem. Rev.* **2017**, *117* (14), 9625–9673. DOI: <https://doi.org/10.1021/acs.chemrev.7b00072>
- [4] T. P. Thuy Pham, C.-W. Cho, Y.-S. Yun, *Water Res.* **2010**, *44*, 352–372. DOI: <https://doi.org/10.1016/j.watres.2009.09.030>
- [5] C. W. Cho, T. P. T. Pham, T. Zhao, S. Stolte, Y. S. Yun, *Sci. Total Environ.* **2021**, *786*, 147309. DOI: <https://doi.org/10.1016/j.scitotenv.2021.147309>
- [6] C. Verma, S. H. Alrefae, M. A. Quraishi, E. E. Ebenso, C. M. Hussain, *J. Mol. Liq.* **2021**, *321*, 114484. DOI: <https://doi.org/10.1016/j.molliq.2020.114484>
- [7] K. Bélafi-Bakó, N. Nemestóthy, P. Bakonyi, in *Ionic Liquids in Separation Technology* (Eds: A. Pérez De Los Ríos, F. J. Hernández Fernández), Elsevier, Amsterdam **2014**, Ch. 8,

- 261–273. DOI: <https://doi.org/10.1016/B978-0-444-63257-9.00008-0>
- [8] Q. Qian, P. A. Asinger, M. J. Lee, G. Han, K. M. Rodriguez, S. Lin, F. M. Benedetti, A. X. Wu, W. S. Chi, Z. P. Smith, *Chem. Rev.* **2020**, *120* (16), 8161–8266. DOI: <https://doi.org/10.1021/acs.chemrev.0c00119>
- [9] R. S. K. Valappil, N. Ghasem, M. Al-Marzouqi, *J. Ind. Eng. Chem.* **2021**, *98*, 103–129. DOI: <https://doi.org/10.1016/j.jiec.2021.03.030>
- [10] X. Yan, S. Anguille, M. Bendahan, P. Moulin, *Sep. Purif. Technol.* **2019**, *222*, 230–253. DOI: <https://doi.org/10.1016/j.seppur.2019.03.103>
- [11] X. Yan, A. Favard, S. Anguille, M. Bendahan, P. Moulin, *Membranes* **2019**, *9*, 65. DOI: <https://doi.org/10.3390/membranes9050065>
- [12] A. Jelea, *J. Nucl. Mater.* **2018**, *505*, 127–133. DOI: <https://doi.org/10.1016/j.jnucmat.2018.03.051>
- [13] H. Gharedaghi, A. Dousti, J. Eshraghi, P. Hanafizadeh, M. Ashjaee, *Chem. Eng. Sci.* **2017**, *173*, 37–48. DOI: <https://doi.org/10.1016/j.ces.2017.07.018>
- [14] X. Yan, S. Anguille, M. Bendahan, P. Moulin, *Chem. Eng. J.* **2021**, *404*, 127109. DOI: <https://doi.org/10.1016/j.cej.2020.127109>
- [15] J. Bedia, E. Ruiz, J. de Riva, V. R. Ferro, J. Palomar, J. J. Rodriguez, *AIChE J.* **2013**, *59*, 1648–1656. DOI: <https://doi.org/10.1002/aic.13926>