Development of asymmetric membranes modified with ionic liquids for the recovery of aromas and fragrances from model agricultural residues to be used in pervaporation processes

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Abstract This study focuses on the development of asymmetric multilayer membranes modified with ionic liquids for the recovery of aromas and fragrances (AF) from model agricultural waste streams through pervaporation. The membranes were prepared using hydrophobic polymers PEBA and POMS combined with two ionic liquids: [Bmim][Tf_2N] and [P1444][Tf_2N], stabilized through gelation with 12-hydroxystearic acid. The research evaluated membrane preparation, extraction capacity, transmembrane flux, selectivity, and mass transfer resistance.

Results showed that the membrane PEBA/[Bmim][Tf_2N]/PEBA exhibited the highest extraction rates and lowest mass transfer resistance for key aroma compounds such as hexanal and linalool. The choice of ionic liquid significantly influenced the membrane's affinity towards different compounds: [Bmim][Tf_2N] favored polar compounds, while [P_{1444}][Tf_2N] enhanced transport of hydrophobic ones. Membranes containing ionic liquids showed improved selectivity toward aroma compounds over water, outperforming single-layer membranes.

These findings confirm that the integration of ionic liquids into polymeric membranes enhances the efficiency of pervaporation for aroma recovery. This approach offers a sustainable and high-value solution for the valorization of agro-industrial residues, with promising applications in the cosmetics industry. The study supports the development of environmentally friendly separation processes aligned with circular economy principles.

Keywords: Ionic liquid-modified membranes, Pervaporation, Aroma and fragrance recovery, Agricultural waste valorization, Circular economy

1. **Introduction:** The valorization of agro-industrial residues has become a central focus in the transition toward more sustainable production systems, in line with the principles of the circular economy. One notable example is the blueberry industry, which generates large volumes of liquid waste during post-harvest washing processes (FAO, 2023). These effluents contain valuable volatile compounds such as alcohols, aldehydes, and esters that possess high potential for reuse in the cosmetics and food industries due to their aromatic, antioxidants, and antimicrobial properties.

Recovering these compounds efficiently requires advanced separation technologies capable of operating under mild conditions to preserve their functional characteristics. In this context, pervaporation membranes have emerged as a promising alternative, offering selective separation of volatile organic compounds from aqueous mixtures without the use of organic solvents or high temperatures (Souchon et al., 2002).

To further enhance the selectivity and stability of these membranes, the incorporation of ionic liquids (ILs) into the membrane matrix has gained increasing attention. Ionic liquids exhibit tunable physicochemical properties, high thermal stability, and low volatility, making them ideal for improving membrane affinity toward specific target compounds (Merlet et al., 2023). This study explores the design of IL-modified asymmetric membranes for the recovery of aroma and fragrance compounds from model blueberry washwaters, contributing to sustainable waste management and high-value product generation.

2. **Methodology:** this study focused on the preparation, characterization, and performance evaluation of asymmetric membranes modified with ionic liquids for the recovery of aroma compounds from model blueberry wastewaters using pervaporation. The membranes were designed in a trilayer configuration, consisting of a polymeric support (PEBA or POMS), a gelified ionic liquid phase ([Bmim][Tf_2N] or [P_{1444}][Tf_2N]), and an external polymeric layer to ensure mechanical stability.

The preparation process involved the casting of polymer solutions and the incorporation of the ionic liquids through gelation using 0.5 wt% 12-hydroxystearic acid, which was optimized to balance structural stability and permeability. Membranes were characterized in terms of their extraction capacity, transmembrane flux, and selectivity toward target compounds (Ethanol, Hexanol, Linalool, Benzyl alcohol, Hexanal, Z-3-hexen-1-ol, and E-2-hexen-1-ol). Experimental pervaporation (Figure 1) tests were conducted under controlled flow rates (100, 500 and 1.000 mL/min) and temperatures using model aqueous solutions containing volatile aroma compounds. The concentration of these compounds in the feed and permeate was measured using analytical techniques to calculate flux and selectivity values. Additionally, mass transfer resistance was analyzed to assess the compatibility between the membrane matrix and the transported compounds. This methodological approach enabled the identification of the most effective membrane-IL combinations for selective aroma recovery from aqueous waste streams.

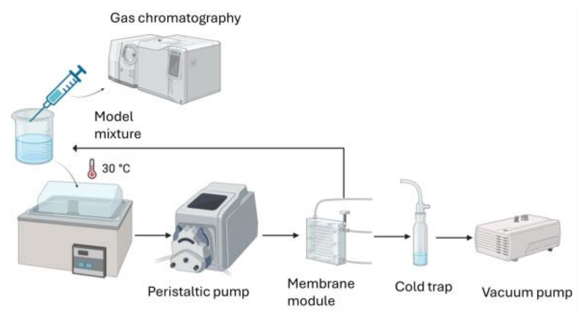

Figure 1. Outline of the experimental setup used for pervaporation of the solutes from AF solutions.

3. Results and Discussions:

The analysis of the PEBA/[Bmim][Tf_2N]/PEBA membrane (Figure 2) indicates a strong affinity for linalool and hexanal. Linalool is initially extracted more rapidly due to its higher solubility in the PEBA matrix, but its interaction with the ionic liquid gradually reduces its mobility. In contrast, hexanal, with greater diffusivity, eventually surpasses linalool during the process. Hexanol shows decreasing extraction with increasing flow, while E-2-hexen-1-ol and Z-3-hexen-1-ol increase their extraction, likely due to lower ionic liquid interaction and higher mobility. Overall, hexanal and linalool are the most efficiently extracted compounds, combining volatility with moderate affinity for the ionic liquid phase.

Hexanol demonstrates greater affinity for [P1444][Tf_2N] at high flow rates (Figure 3), whereas its extraction drops when using [Bmim][Tf_2N], suggesting its transport is favored in hydrophobic environments and limited by saturation effects in more polar systems. The highest transmembrane flux densities were observed for hexanal and linalool in PEBA/[Bmim][Tf_2N]/PEBA membranes. Hexanol performed better in POMS/[Bmim][Tf_2N]/POMS due to polymer flexibility and hydrophobicity. Benzyl alcohol and ethanol showed the lowest permeability, constrained by their polarity and limited solubility in ionic liquids. E-2- and Z-3-hexen-1-ol diffused more efficiently in [Bmim][Tf_2N], especially in PEBA membranes, supported by favorable hydrogen bonding. Membrane performance is highly influenced by the compatibility between the polymer–ionic liquid system and the target compound's properties.

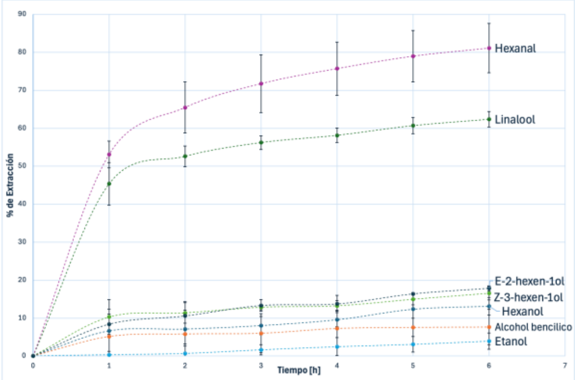

Figure 2. Extraction percentage of the compounds in the PEBA/[Bmim][Tf_2N]/PEBA membrane at a flow rate of 1.000 [mL/min].

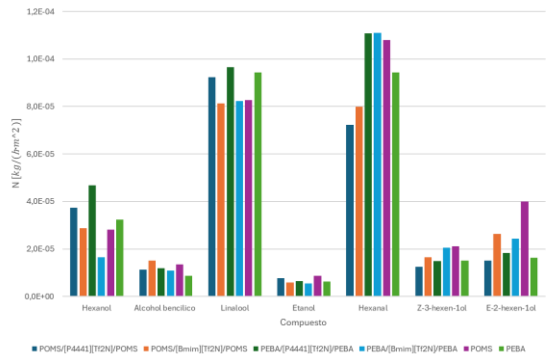

Figure 3. Transmembrane flux density of the compounds in diferent membranes at 1000 [mL/min

Conclusions:

This study demonstrated that ionic liquid-modified asymmetric membranes are a promising solution for the selective recovery of aroma and fragrance compounds from agricultural residues using pervaporation. The trilayer membranes, particularly those containing [Bmim][Tf_2N], showed enhanced transmembrane flux and selectivity for key volatile compounds. Membrane performance was influenced by the type of polymer, ionic liquid, and target compound polarity. These findings support the development of sustainable separation technologies aligned with circular economy principles, enabling the valorization of agro-industrial waste into high-value products for cosmetic and food applications, while reducing environmental impact and promoting resource efficiency.

References

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Acknowledgments

The financial support of FONDECYT INICIACIÓN Project Nº. 11230415