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Research Paper

Enzyme-Mediated Extraction of Limonene, Linalool and Linalyl Acetate from Bergamot Peel Oil by Pervaporation

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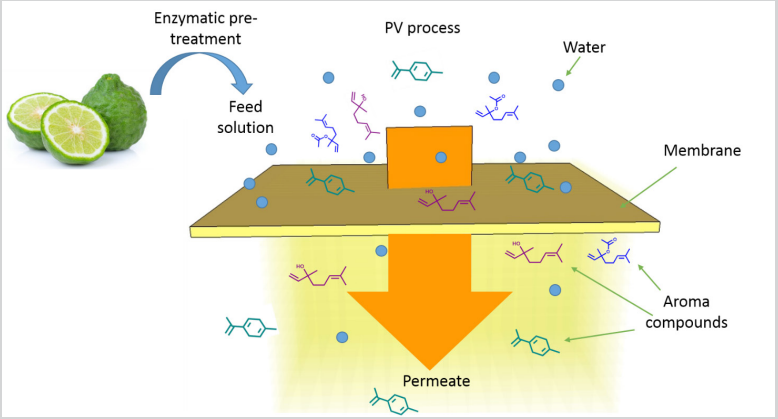
Highlights

- Enzyme-mediated extraction of limonene, linalool and linalyl acetate from bergamot
- Aroma recovery from extracted bergamot peel oil by pervaporation
- Evaluation of two commercial organophilic membrane performance in pervaporation
- Effect of temperature on flux and enrichment factor

Graphical abstract



Abstract

Bergamot peel oil is highly attractive for food and pharmaceutical industries due to its content of valuable essential oil, which is enriched with high-added valuable compounds, such as limonene, linalool and linalyl acetate. Nevertheless, there are some limitations for the separation of such compounds. In this framework, pervaporation (PV) technology was proposed as a tool for the separation of limonene, linalool, and linalyl acetate from bergamot oil by using two different commercial organophilic membranes (PDMS-1070 and POMS-PEI). The use of an enzymatic pre-treatment was also investigated in order to enhance the performance of selected membranes. All PV experiments were carried out at different temperatures (ranging from 25-40 ºC) in order to analyze the temperature dependence by the Arrhenius relationship. Experimental data indicated that both investigated membranes did not present significant differences in terms of enrichment factor, independently from the enzymatic pre-treatment (at 25 ºC). However, the enrichment factors increased significantly at 40°C when enzymes were applied. The experimental results clearly indicate that PV is a viable approach for the recovery of such aroma solutes from bergamot peel oils as it yields good separations under mild operating conditions. The efficiency of the pervaporative process is indeed enhanced if assisted by an enzymatic treatment.

1. Introduction

Aroma compounds include a wide variety of volatile organic compounds with a pleasant smell present in low concentrations in many natural sources (i.e. the concentration of individual aroma substance in common fruit juices usually ranges from less than 1 to 20 ppm). For this reason, they find a very wide application in the food, pharmaceutical and cosmetic sectors. Unfortunately, in many industrial processes, a loss of aroma compounds can occur, for instance, during the concentration step that is normally applied for juice concentration [1]. The loss of aroma causes a strong quality decrease of food, beverage and cosmetic products, influencing directly the organoleptic properties and consumer's acceptance. Therefore, aroma compounds must be recovered either from the loss stream or before the raw material is subjected to heat treatment (aroma stripping) and added back to the final product in

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order to meet its original organoleptic profile [2].

Steam distillation, solvent liquid extraction, adsorption and air stripping are among the traditional techniques used for aroma recovery. These techniques, however, present some drawbacks such as high temperature (that can cause aroma degradation), high-energy requirement and elevated cost.

Pervaporation (PV) is a valuable alternative to conventional distillation particularly attractive in the separation of azeotropic mixtures or in those cases where higher temperatures aould affect the activity of target compounds such as in the recovery of aroma compounds. This process is based on a selective transport of a target component dissolved in a liquid mixture (feed) through a dense membrane associated with an evaporation on the downstream side (permeate) [3]. This occurs thanks to driving force which lowers the permeate partial pressure creating a chemical potential gradient in the liquid phase responsible of the selective permeation of a target component through the membrane. Due to the gentle pressure and temperature applied, aroma recovery by PV allows to preserve the molecular integrity of aroma compounds, giving, at the same time, high efficiency (i.e. high selectivity) and having a small environmental impact due to the low energy consumption required [4]. The separation mechanism in PV is based on the solution-diffusion model. The chemical potential gradient is responsible of the sorption and of the subsequent permeation of the target compounds through the membrane that are finally desorbed at the downstream side in a vapor phase [5].

One of the main fields of PV applications is the aroma recovery from juices or model aqueous solutions by using hydrophobic membranes. Olsson & Tragardh [6], for instance, applied PV for the aroma recovery from an apple juice model solution using a poly-octyl-methyl-siloxane (POMS-PEI) membrane supplied by GKSS. From the obtained results, it was evidenced that aldehydes and esters presented higher selectivity than alcohols; therefore their recovery was more favoured. Sampranpiboon et al. [7] applied PV for the recovery of ethyl butanoate (ETB) and ethyl hexanoate (ETH), as characteristics aroma compounds of banana and pineapple juice, using POMS and poly dimethylsiloxane (PDMS) membranes. POMS membrane was found more selective towards the investigated aroma displaying an enrichment factor of 118-281 against an enrichment factor of 77-234 for the PDMS membrane. The permeation of the more hydrophobic compound ETH was favored in comparison to ETB which was more hydrophilic.

Karlsson et al. [8] studied the aroma recovery from muscat wine by using a GFT1060 membrane with an active layer of PDMS. The PV of the wine brought to the identification of 8 aromas, where six of them were found in the permeate. Basically, the ethyl acetate presented the highest concentration, while hexanol, isoamylic alcohol, isobutanol and methylactate had the lowest concentration.

Among the wide variety of available aroma compounds, citrus peel oils, for instance, have become of great relevance in cosmetics and perfume industries thanks to their excellent fragrance and freshness. Bergamot essential oil, in particular, presents also antiseptic and antibacterial properties making it very attractive in the pharmaceutical field. However, its essence contains some undesired compounds such as several coumarins and psoralens like bergapten. Once combined with UV radiation, melanogenesis and thickening of the stratum corneum of the skin can be promoted. In this context, organophilic PV, is known to be effective for the bergapten recovery from bergamot essential oil as demonstrated by Figoli et al. [9].

When dealing with enzymatic treatments, enzymes interact on cell walls, breaking down the structural integrity rendering the intracellular materials more exposed for extraction. Generally, the enzymes employed are of two different types: *a) Hydrolytic:* having cellulase, hemicellulase and pectinase activities, causing the disruption of the polysaccharides (mainly cellulose, hemicellulose, pectin, and lignin) composing the cell wall coats; and *b) Proteolytic (proteases):* hydrolyzing the membrane and cytoplasmic proteins. Although the use of enzymes is not a cheap technology mainly due to the elevated price of the selected biocatalyst, its cost can be justified by the relevant value of the essence sought-after by many cosmetic and pharmaceutical industries [10]. Moreover, there is a necessity of satisfying the current worldwide market demand for flavours and nutraceutical ingredients, e.g. this was estimated about €13 billion in 2006, while more recently the US market was projected around €5.5 billion in 2014 (food 36%, cosmetics and toiletries 27%, beverages 15%), and this demand is expected to increase in coming years (rise 3% per year) [10, 11].

In the present work, the extraction of three aroma compounds (linalool, limonene and linalyl-acetate) from homogenised bergamot peel aqueous solution was carried out by using two different commercial PV membranes (PDMS-1070 and POMS-PEI).

The bergamot grated peel was previously homogenized in distilled water and then subjected to an enzymatic pre-treatment, which has been proposed in order to increase the oil extraction yield. The performance of the selected membranes was investigated in terms of total permeation flux and enrichment factor for untreated and enzymatically treated samples, respectively.

2. Materials and methods

2.1. Enzymatic pre-treatment

A solution of grated bergamot peel was prepared and homogenised with distilled water before the addition of the enzyme. The enzymatic pre-treatment was performed by using a cellulase and pectinase preparation (Peclyve PE and Peclyve LI from Lyven SA, Colombelles, France) at different concentration (10, 15 and 20 wt%). The enzymatic pre-treatment was carried out in a thermostated room at 40°C. Samples enzymatically treated and control samples (not enzymatically treated) were submitted to PV tests in selected operating conditions.

2.2. Pervaporation step

PV tests were carried out by using a laboratorial set-up consisting of a permeation unit (GFT GmbH, Germany), a collection unit and a vacuum pump.

The capacity of the feed reservoir was about 600 g and the effective membrane area was 56.74 cm^2. The feed was kept at a fixed temperature and the permeate was condensed with liquid nitrogen under the steady state. The vacuum pump was set at 3 mmHg. The temperature was handled in the range of 25- 40°C. Two types of hydrophobic membranes were used in this study: PDMS-1070 (GFT, Germany) and POMS-PEI (GKSS, Germany). The schematic diagram of the PV setup is reported elsewhere [12].

All these membranes are composite. In particular, the PDMS-1070 membrane possesses a selective layer made of polydimethylsiloxane (PDMS) with incorporated silicates on a polyacrilonitrile (PAN) support. The POMS-PEI membrane is a composite asymmetric membrane with a selective layer made of polyoctylmethyl siloxane (POMS) supported in polyetherimide (PEI). The membranes used in this work were selected considering that PDMS and POMS are among the most studied membrane materials in hydrophobic PV [13]. POMS and PDMS are very well appreciated for their high chemical and thermal stability which make them ideal in various applications. Moreover, they were widely studied for the recovery of aroma compounds by means of PV [7, 14].

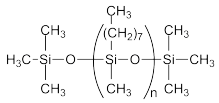
The characteristics of the investigated membranes are summarized in Table 1.

Table 1
Characteristics of selected PV membranes.

Membrane type	Skin layer	Manufacturer
PDMS-1070	PDMS[a], d = 20 µm	GFT (Germany)
POMS-PEI	POMS[b], d = 1 µm	GKSS (Germany)

[a] PDMS, polydimethylsiloxane:

[b] POMS, polyoctylmethyl siloxane:



The efficiency of the separation process was assessed in terms of two characteristic parameters: the total permeate flux (Jt) and the enrichment factor (βi). They were calculated using the following equations:

$$J_t = \frac{w}{A \cdot t} \quad (1)$$

$$\beta_i = \frac{w_{i,P}}{w_{i,F}} \quad (2)$$

where w is the weight fraction of the compounds in the permeate phase, A the effective membrane area, t the permeation time and, w_i the weight fraction of the aroma compounds in the permeate (P) and in the feed (F) phases, respectively.

To analyze the effect of temperature on total flux, an Arrhenius relationship was used:

$$J_t = J_0 \exp\left(-\frac{E_P}{RT}\right) \quad (3)$$

where J_0 is the pre-exponential factor, E_P the apparent activation energy of PV, T the absolute temperature and R the universal gas constant (8.314×10^{-3} kJ mol^{-1} K^{-1}).

The target aroma compounds collected in the feed and permeate samples have been analysed by solid phase microextraction (SPME) technique and by using a GC-MS system (Varian Saturn 2000, USA) equipped with a CP-Sil 8CB low bleed capillary column (30 cm length, 0.25 mm internal diameter, 0.25 mm film) [15].

3. Results and discussion

3.1. Effect of the enzymatic pre-treatment

Figure 1 displays the concentration of aroma extracted from the homogenized bergamot peel after the enzymatic pre-treatment at two different extraction times (2 and 8h). It is important to note that the use of the enzymatic pre-treatment enhanced the extraction of the valuable compounds. Regardless of the enzyme concentration, limonene represented the most extracted aroma due to its highest concentration (around 13-28 g/L in feed solution).

On the contrary, very low extracted concentrations of linalool and linalyl acetate were found independently of the extraction time. The enzymatic efficiency was already performing during the first two hours of treatment. Indeed, the highest limonene concentration was found using 20 wt.% of enzyme (the highest concentration) after 2h of extraction time. After this time, the extracted aromas concentrations were almost constant. This result can be related to the high specific properties of the enzymes showing a great action of degradation towards polysaccharides (e.g. cellulose, hemicellulose, pectin, lignin) at short times.

3.2. PV membrane performances

The homogenized bergamot peel aqueous solutions (with and without enzymatic pre-treatment) were, then, processed by PV. By visual observation, the difference in colour between feed (yellow-green) and permeate (transparent) denoted the retention of pigments and some other compounds contained in bergamot peel which could not permeate through the dense membranes applied. Figure 2 shows the physical difference between feed (with enzymatic pre-treatment) and permeate samples.

3.2.1. Permeation flux performances

Figure 3 displays the behavior of the total permeation fluxes for the samples with and without enzymatic pre-treatment, respectively. In both cases a linear increase of total permeation flux by increasing temperature, for both investigated membranes, can be observed. The total flux did not display any significant change independently of the enzymatic treatment. This behavior can be attributed to the high dilution of the aroma compounds making the total flux very similar to the partial water one [16]. In particular, the PDMS-1070 membrane showed, in both cases, the highest permeate fluxes in comparison to the POMS-PEI membrane.

The separation of organic compounds using hydrophobic PV membranes has been widely reported in literature [7, 17, 18] even if most of the papers are referred to organic-water binary feed mixtures [4, 19] rather than natural extracts and multicomponent and complex mixtures, like bergamot extract investigated in this study. Therefore, the trend of new researches focus on the recovery such aroma compounds from real food systems, such as beer [20], wine [21, 22], and several fruit juices [1, 23]. Both hydrophobic/organophilic membranes have displayed high enrichment factors; however; the presence of other components influences on the sorption and therefore permeation of the target compounds [18, 24]. Generally, the biggest difference between single component and multicomponent systems is the existence of a potential "coupling phenomenon" [25]. According to Raisi & Aroujalian [25], the coupling effect, if exists, will affect the calculations of multicomponent PV partial fluxes. This is the reason why are not reported in this work the partial permeate fluxes of the single components of the feed mixture. Particularly, coupling phenomenon can be divided into two parts: i) kinetic and ii) thermodynamic. The kinetic part is frequently viewed as the faster permeating component which transports a slower component through the membrane, giving a higher permeability for the slower component than if it was a single component or within a different mixture. While the thermodynamic coupling, which is defined as the change in concentration of one component in the membrane due to the presence of other components, is caused by mutual interactions between the permeating compounds in the membrane, as well as by interactions between the individual components and the membrane material. Finally, the extent of these interactions will depend on the polymer-mixed penetrant system [25].

The analysis of the temperature dependence on permeate fluxes was obtained by using the Arrhenius model. Basically, the total flux data plotted versus $1/T$ on a semi-log scale yielded straight lines (see Figure 4), indicating that the temperature dependence of J_t was well described by the Arrhenius equation ($R^2 > 0.951$). The Figure 4 confirms that there is a direct relationship between fluxes and feed temperature: the total flux tends to increase with the increase of the temperature. This behavior was observed for both samples, with/without enzymatic treatment, in PDMS-1070 and POMS-PEI membranes. Typically, the thermal motion of the polymeric chains in the amorphous region produces free volumes. In fact, at higher temperature the amplitude of the polymer chain jumping increases, resulting in an increase of free volume in the membrane. Thereby, at higher temperature the diffusion rate of individual permeating molecules increased, leading to a high permeation flux [26]. However, this thermal motion facilitates the diffusion of larger molecules through the membrane causing a decrease in the separation efficiency [27, 28].

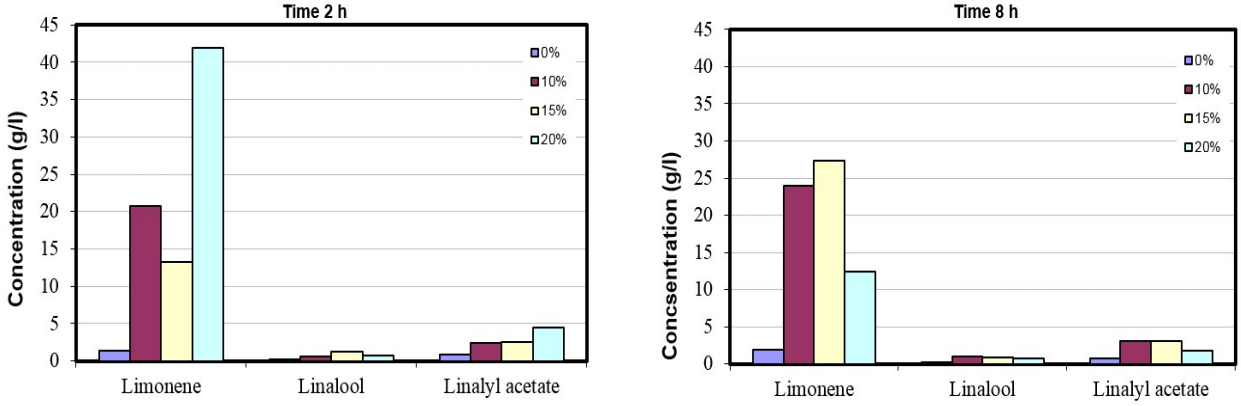


Fig. 1. Profile of the three aroma concentrations extracted from homogenised bergamot peel aqueous solution after 2 h and 8h enzymatic treatment, at different enzyme concentrations.

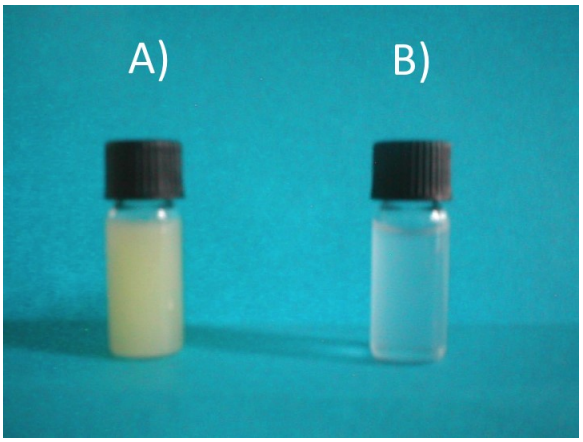


Fig. 2. Feed (homogenized bergamot peel aqueous solution) (A) and permeate (B) images.

Furthermore, the apparent activation energy (E_P), which can be calculated as the slope of the curve, and using the Eq. (3), can provide an outlook of the permeation behavior of the treated and un-treated samples with the enzymes. The two parameters, J_0 and E_P, were determined from the intercept and slope of the corresponding straight lines, giving the values listed in Table 2. The apparent activation energies ranged from approximately 29 kJ to 37 kJ mol^{-1}. Indeed, a higher value of E_p implies that a more sensitive behavior towards temperature changes in the handled range (25-40 ºC) can occur, highlighting that the applied enzymatic treatment has an effect on the permeation performance and thus in E_p values. For example, the E_p values for the PDMS-1070 membrane significantly increased by the enzymatic treatment, while in the POMS-PEI membrane slightly decreased.

Table 2
Data derived from the fitting of total flux data to Eq. (3).

Membrane	Enzyme	E_P (kJ mol^{-1})	ln J_0	R^2
PDMS-1070	none	32.54 ± 2.39	12.41 ± 0.94	0.995
PDMS-1070	PECLYVE LI	36.97 ± 0.29	14.26 ± 0.12	0.999
POMS-PEI	none	29.21 ± 6.65	8.95 ± 2.62	0.951
POMS-PEI	PECLYVE LI	28.89 ± 1.16	8.76 ± 0.46	0.998

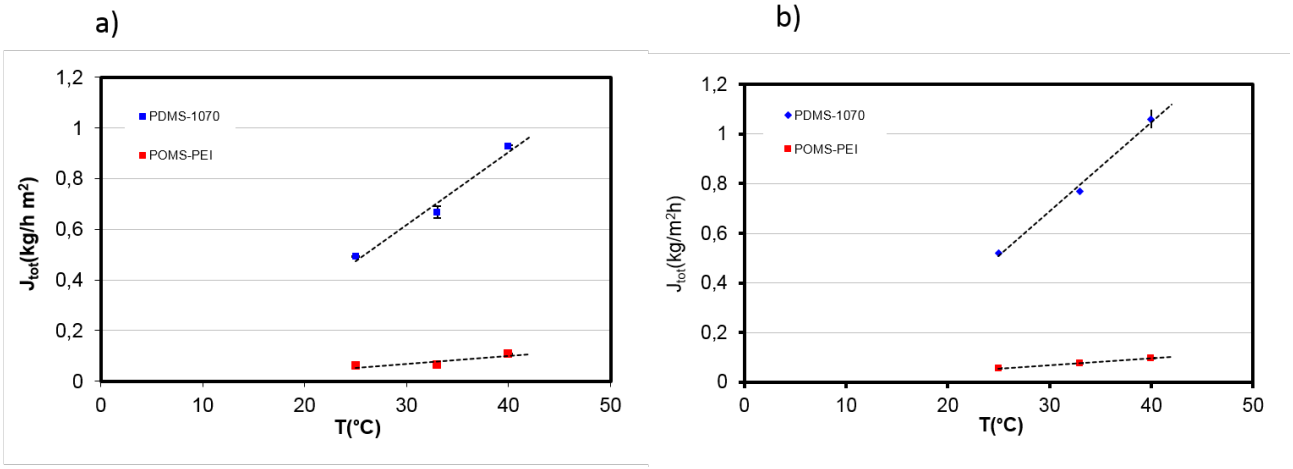


Fig. 3. Total permeation flux as a function of temperature for selected PV membranes in the treatment of: a) untreated bergamot peel aqueous solutions; b) enzymatically treated bergamot peel aqueous solutions.

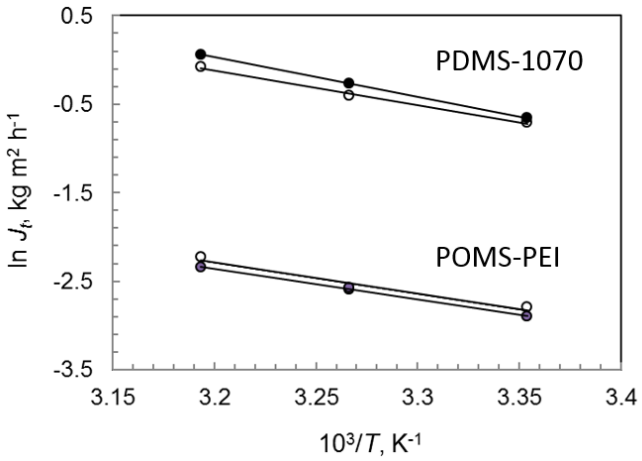


Fig. 4. Arrhenius relationship plot for the temperature dependence of permeation flux. The curves are only guides to the eye. Filled and hollow symbols represent the samples without and with enzymatic treatment, respectively.

3.2.2. Enrichment Factor (β)

The quantitative analysis of lynalool, linalyl acetate and limonene in feed and permeate samples allowed to evaluate the separation efficiency of the both membranes. Figure 5 displays a typical example of the spectrum of the aromatic compounds contained both in feed and permeate.

As previously mentioned, the limonene was highly concentrated in the feed side, while the linalool and linalyl acetate were the ones mainly contained in permeate sides. In principle, the untreated solutions processed using the PDMS-1070 membrane presented a slight decreasing of the enrichment factor as a function of the temperature for the limonene, while the inverse trend was observed for the linalyl acetate (from 12 up to 15) (Figure 6a). On the other hand, the enzymatic treatment influenced positively the enrichment factor during the PV process; as it can be seen, the concentration of the limonene tended to increase as function of the temperature (see Figure 6b). The enzyme-mediated extraction pre-treatment allowed to enhance the enrichment factor of the tested membranes, e.g. the enrichment factor of the linalyl acetate increased more than two-fold in permeate side with a value ranging from 18-48 against 11-15 when no enzyme pre-treatment was carried out. Definitely, the hydrophobic nature of the PDMS-1070 membrane mainly contributed to the permeation of this organic compound (linalyl acetate) [17]. In addition, in a previous study, it was demonstrated that the PDMS membranes are able to recover linalool and linalyl acetate from bergamot oil [9], where the membranes even showed that the temperature enhanced the β values. Particularly, linalool and linalyl acetate ratio provide mainly the characteristic essence of bergamot fruits.

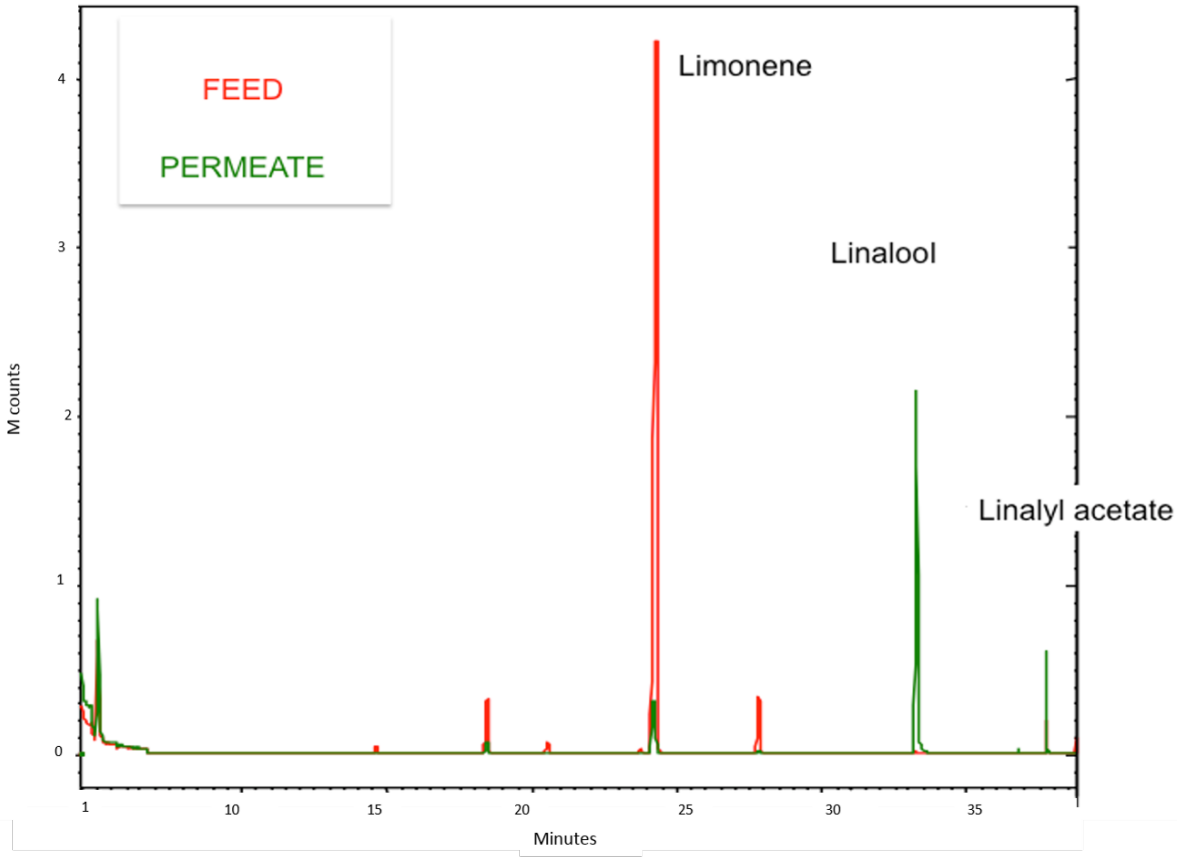


Fig. 5. Bergamot peel aromatic compounds contained in feed and in permeate samples.

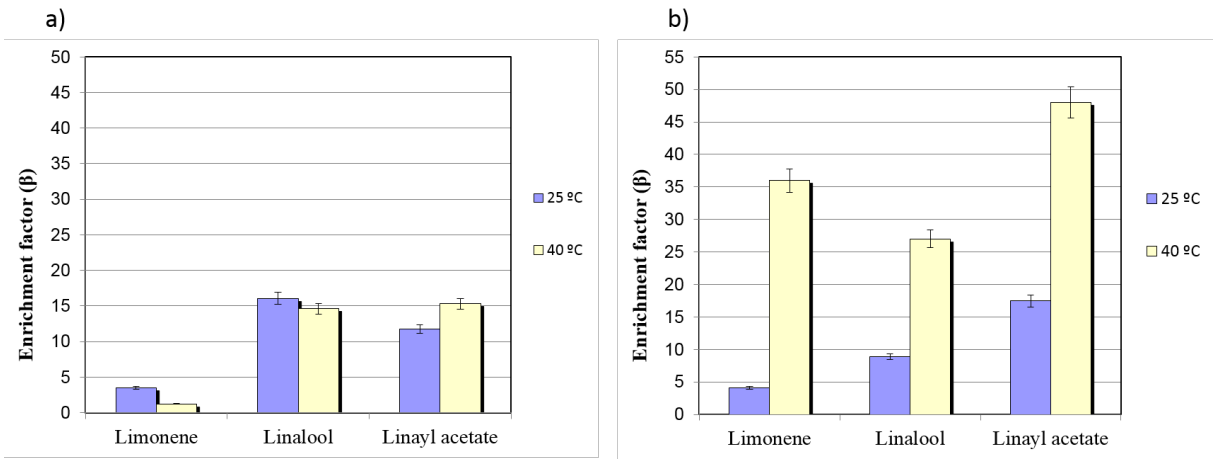


Fig. 6. Enrichment factor (β) trend of the a) untreated feed solution, and b) enzymatically treated feed solution by using the PDMS-1070 membrane at 25 and 40 ºC.

The POMS-PEI membrane, which have hydrophobic/organophilic characteristics [7], presented an almost stable enrichment factor for limonene (between 12 and 16 when enzymatic pre-treatment was used); while for both linalool and linalyl acetate an enhancement in their enrichment factors was found at the highest investigated temperature (40°C) with an enrichment factor of about 26 for linanool and 48 for linalyl acetate (Figure 7). In general, these types of POMS membranes have already demonstrated their efficiency on the recovery of some other aroma compounds from aqueous solutions [7], but it is important to note that the recovery of linalool and linalyl acetate is highly attractive due to their biological activities (e.g. anti-inflammatory) [29].

Finally, regardless the use of PDMS and POMs membranes, they have satisfactorily demonstrated their ability on recovering such aroma compounds. As it is well known, most of the organic compounds are suitable to be removed from mixtures by means of hydrophilic membranes. Basically, this is due to the fact that such solutes (limonene, linalool and linalyl acetate) present benzene nucleus [30, 31]. Their relatively low hydrophobicity could be associated to the polarity balance between the hydrophobic benzene group and the hydrophilic alcohol or aldehyde.

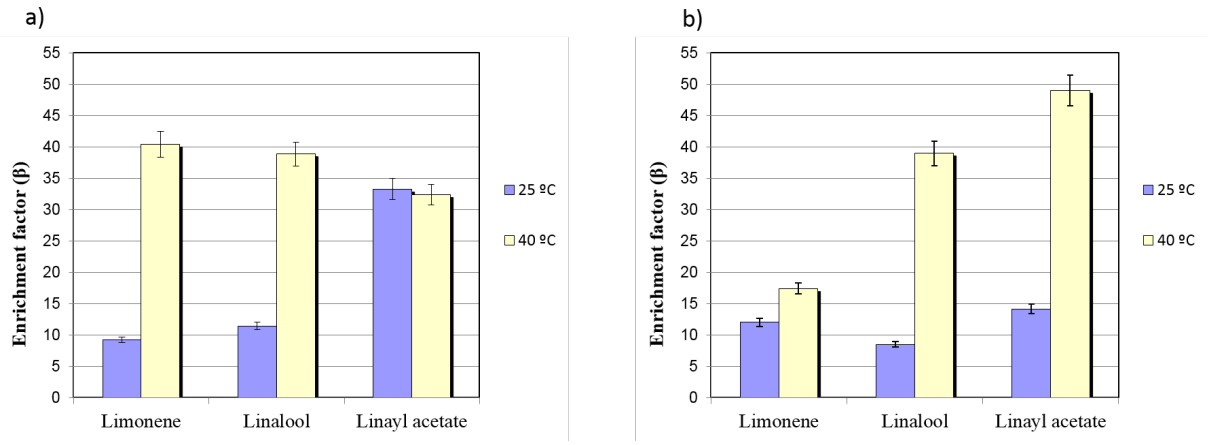


Fig. 7. Enrichment factor (β) profile of the a) untreated feed solution and b) enzymatically treated feed solution by using the POMS-PEI membrane at 25 and 40 ºC.

4. Conclusions

This work focused on the application of PV for the extraction of aroma compounds of industrial interest from bergamot peel, with and without enzymatic pre-treatment. Thereby, two commercial dense membranes (PDMS-1070 and POMS-PEI) for the recovery of limonene, lynalool and linalyl acetate from the homogenized bergamot peel aqueous solution were applied.

Particularly, at 25°C, POMS-PEI and PDMS-1070 membranes did not present significant differences in terms of enrichment factor independently from the enzymatic pre-treatment. However, the enrichment factors increased significantly at 40°C when enzymes were applied. This behaviour was due to the greater concentration of aroma in the feed solutions. Indeed the temperature optimum value for enzymatic treatment was at 40°C. Finally, we can conclude that the use of enzymes in PV technology, in particular at 40°C, caused a significant increase of permeated aromas yields. Furthermore, such commercial hydrophobic membranes implemented in PV technology have proved to be very effective for the recovery of aroma solutes.

References

[1] C.C. Pereira, C.P. Ribeiro, R. Nobrega, C.P. Borges, Pervaporative recovery of volatile aroma compounds from fruit juices, J. Memb. Sci. 274 (2006) 1–23. doi:10.1016/j.memsci.2005.10.016.

[2] B. Ali, N.A. Al-Wabel, S. Shams, A. Ahamad, S.A. Khan, F. Anwar, Essential oils used in aromatherapy: A systemic review, Asian Pac. J. Trop. Biomed. 5 (2015) 601–611. doi:10.1016/j.apjtb.2015.05.007.

[3] R. Castro-Muñoz, Ó. De La Iglesia, V. Fila, C. Téllez, J. Coronas, Pervaporation-assisted esterification reactions by means of mixed matrix membranes, Ind. Eng. Chem. Res. 10.1021/Acs.Iecr.8b01564. (2018). doi:10.1021/acs.iecr.8b01564.

[4] R.W. Baker, J.G. Wijmans, Y. Huang, Permeability, permeance and selectivity: A preferred way of reporting pervaporation performance data, J. Memb. Sci. 348 (2010) 346–352. doi:10.1016/j.memsci.2009.11.022.

[5] F. Galiano, F. Falbo, A. Figoli, Polymeric Pervaporation Membranes : Organic-Organic Separation, in: and V.O. Nazarenko, P.M. (Ed.), Nanostructured Polym. Membr., Scrivener Publishing LLC, 2016: pp. 281–304.

[6] J. Olsson, G. Trägårdh, Influence of feed flow velocity on pervaporative aroma recovery from a model solution of apple juice aroma compounds, J. Food Eng. 39 (1999) 107–115. doi:10.1016/S0260-8774(98)00154-X.

[7] P. Sampranpiboon, R. Jiraratananon, D. Uttapap, X. Feng, R.Y.M. Huang, Separation of aroma compounds from aqueous solutions by pervaporation using polyoctylmethyl siloxane (POMS) and polydimethyl siloxane (PDMS) membranes, J. Memb. Sci. 174 (2000) 55–65. doi:10.1016/S0376-7388(00)00365-3.

[8] H.O.E. Karlsson, S. Loureiro, G. Trägårdh, Aroma compound recovery with pervaporation - Temperature effects during pervaporation of a muscat wine, J. Food Eng. 26 (1995) 177–191. doi:10.1016/0260-8774(94)00050-J.

[9] A. Figoli, L. Donato, R. Carnevale, R. Tundis, G.A. Statti, F. Menichini, E. Drioli, Bergamot essential oil extraction by pervaporation, Desalination. 193 (2006) 160–165. doi:10.1016/j.desal.2005.06.060.

[10] C. Brazinha, J.G. Crespo, 12 Valorization of food processing streams for obtaining extracts enriched in biologically active compounds, (2014).

[11] R. Castro-Muñoz, C. Conidi, A. Cassano, Membrane-based technologies for meeting the recovery of biologically active compounds from foods and their by-products, Crit. Rev. Food Sci. Nutr. 0 (2018) 1–22. doi:10.1080/10408398.2018.1478796.

[12] A. Verhoef, A. Figoli, B. Leen, B. Bettens, E. Drioli, B. Van der Bruggen, Performance of a nanofiltration membrane for removal of ethanol from aqueous solutions by pervaporation, Sep. Purif. Technol. (2008). doi:10.1016/j.seppur.2007.07.044.

[13] S. Chovau, A. Dobrak, A. Figoli, F. Galiano, S.Simone, E. Drioli, S.K. Sikdar, B. Van der Bruggen, Pervaporation performance of unfilled and filled PDMS membranes and novel SBS membranes for the removal of toluene from diluted aqueous solutions, Chem. Eng. J. 159 (2010) 37–46. doi:10.1016/j.cej.2010.02.020.

[14] A. Raisi, A. Aroujalian, T. Kaghazchi, Multicomponent pervaporation process for volatile aroma compounds recovery from pomegranate juice, J. Memb. Sci. (2008). doi:10.1016/j.memsci.2008.06.001.

[15] C. Benincasa, A. De Nino, N. Lombardo, E. Perri, G. Sindona, A. Tagarelli, Assay of Aroma Active Components of Virgin Olive Oils from Southern Italian Regions by SPME-GC/Ion Trap Mass Spectrometry, J. Agric. Food Chem. 51 (2003) 733–741. doi:10.1021/jf0258095.

[16] J. Olsson, G. Trägårdh, Influence of temperature on membrane permeability during pervaporative aroma recovery, Sep. Sci. Technol. 34 (1999) 1643–1659. doi:10.1080/01496399909353762.

[17] L. Li, Z. Xiao, S. Tan, L. Pu, Z. Zhang, Composite PDMS membrane with high flux for the separation of organics from water by pervaporation, J. Memb. Sci. 243 (2004) 177–187. doi:10.1016/j.memsci.2004.06.015.

[18] T. Schäfer, A. Heintz, J.G. Crespo, Sorption of aroma compounds in poly(octylmethylsiloxane) (POMS), J. Memb. Sci. 254 (2005) 259–265. doi:10.1016/j.memsci.2004.12.047.

[19] A. Kudasheva, S. Sorribas, B. Zornoza, C. Téllez, J. Coronas, Pervaporation of water/ethanol mixtures through polyimide based mixed matrix membranes containing ZIF-8, ordered mesoporous silica and ZIF-8-silica core-shell spheres, J. Chem. Technol. Biotechnol. 90 (2015) 669–677. doi:10.1002/jctb.4352.

[20] M. Catarino, A. Mendes, Non-alcoholic beer - A new industrial process, Sep. Purif. Technol. 79 (2011) 342–351. doi:10.1016/j.seppur.2011.03.020.

[21] T. Schäfer, G. Bengtson, H. Pingel, K.W. Böddeker, J.P.S.G. Crespo, Recovery of aroma compounds from a wine-must fermentation by organophilic pervaporation, Biotechnol. Bioeng. 62 (1999) 412–421. doi:10.1002/(SICI)1097-0290(19990220)62:4<412::AID-BIT4>3.0.CO;2-R.

[22] M. Catarino, A. Mendes, Dealcoholizing wine by membrane separation processes, Innov. Food Sci. Emerg. Technol. 12 (2011) 330–337. doi:10.1016/j.ifset.2011.03.006.

[23] N. Rafia, A. Aroujalian, A. Raisi, Pervaporative aroma compounds recovery from lemon juice using poly(octyl methyl siloxane) membrane, J. Chem. Technol. Biotechnol. 86 (2011) 534–540. doi:10.1002/jctb.2547.

[24] R. Castro-Muñoz, F. Galiano, V. Fíla, E. Drioli, A. Figoli, Mixed matrix membranes (MMMs) for ethanol purification through pervaporation : current state of the art, Rev. Chem. Eng. Https//Doi.Org/10.1515/Revce-2017-0115. (2018). doi:https://doi.org/10.1515/revce-2017-0115.

[25] A. Raisi, A. Aroujalian, Aroma compound recovery by hydrophobic pervaporation: The effect of membrane thickness and coupling phenomena, Sep. Purif. Technol. 82 (2011) 53–62. doi:10.1016/j.seppur.2011.08.018.

[26] A. Figoli, A. Tagarelli, B. Cavaliere, C. Voci, G. Sindona, S.K. Sikdar, E. Drioli, Evaluation of pervaporation process of kiwifruit juice by SPME-GC/Ion Trap Mass Spectrometry, Desalination. 250 (2010) 1113–1117. doi:10.1016/j.desal.2009.09.120.

[27] S. Zereshki, A. Figoli, S.S. Madaeni, S. Simone, E. Drioli, Pervaporation Separation

of Methanol / Methyl tert -Butyl Ether with Poly (lactic acid) Membranes, J. Appl. Polym. Sci. 118 (2010) 1364–1371. doi:10.1002/app.

[28] R. Castro-Muñoz, F. Galiano, V. Fíla, E. Drioli, A. Figoli, Matrimid®5218 dense membrane for the separation of azeotropic MeOH-MTBE mixtures by pervaporation, Sep. Purif. Technol. 199 (2018) 27–36. doi:10.1016/j.seppur.2018.01.045.

[29] A.T. Peana, P.S.D. Aquila, F. Panin, G. Serra, P. Pippia, M.D.L. Moretti, Anti-inflammatory activ ity of linalool and linaly l acetate constituents of essential oils, Phytomedicine. 9 (2002) 721–726.

[30] A. Fouda, J. Bai, S.Q. Zhang, O. Kutowy, T. Matsuura, Membrane separation of low volatile organic compounds by pervaporation and vapor permeation, Desalination. 90 (1993) 209–233. doi:10.1016/0011-9164(93)80177-O.

[31] A. Baudot, M. Marin, Pervaporation of aroma compounds: Comparison of Membrane Performances with Vapour-Liquid Equilibria and Engineering Aspects of Process Improvement, Food Bioprod. Process. Trans. Inst. Chem. Eng. Part C. 75 (1997) 117–142. doi:10.1205/096030897531432.