


# Coupling crossflow microfiltration and nanofiltration for the concentration of aroma compounds in a raspberry hydroalcoholic extract

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## Abstract

This work investigated the coupling of microfiltration (MF) and nanofiltration (NF) to concentrate the volatile compounds in a raspberry hydroalcoholic extract. Enzymatic treatment increased the MF permeate flux by 30%–50%. The highest MF permeate flux was above  $50 \text{ kg}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$  at a mass reduction ratio of 5. MF allowed efficient clarification of the extract without significant retention of aroma compounds. Among the NF membranes tested using the MF permeate as feed, one membrane was clearly more effective in concentrating the extract in terms of flux ( $19 \text{ kg}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$  at 35 bar), retention of aroma compounds (average retention of 85%), phenolic compounds (61%) and dry matter (90%). Three other membranes were of interest for the fractionation of volatiles in both permeate and retentate but with a lower permeate flux. Finally, one membrane retained few aroma compounds but showed 70% dry matter retention, making it a promising method for aroma purification versus dry matter content in the permeate.

## Practical Applications

In this study, we investigated the coupling of crossflow MF and NF with a pectinolytic pretreatment, in order to concentrate the aroma compounds from a raw organic raspberry extract. The aim was to avoid aroma degradation and reduce the operating costs, compared to the conventional concentration thermal technologies. Few authors have studied aroma concentration by NF, which presents an interesting area of research for industrial applications. This work provides keys for flavor manufacturers to add value to their products at a low cost and with limited environmental impact, producing concentrated natural aroma extracts for food. Another originality of this work for industrial companies was to show that thanks to the same process, several fractionations could be achieved simply by modifying the operating conditions. Therefore, this work contributed to propose new applicable processing for the

**Abbreviations:** CR, clarification rate (Equation 4);  $C_{p,f}^+$ , chroma value of the permeate (p) or the feed (f); SM, dry matter in  $\text{g}\cdot\text{kg}^{-1}$ ; HRE, raw hydroalcoholic raspberry extract; HREP, hydroalcoholic raspberry extract with pectinase treatment;  $J_p$ , permeate flux in  $\text{kg}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ ; MRR, mass reduction ratio; TA, titratable acidity in  $\text{geq citric acid}\cdot\text{kg}^{-1}$ ; TDU, thermal desorption unit;  $TU_{f,p}$ , turbidity of feed (f) or permeate (p); TMP, transmembrane pressure in bar; TPC, total phenolic content in  $\text{geq gallic acid}\cdot\text{kg}^{-1}$ ; TSS, total soluble solids in  $\text{g}\cdot\text{kg}^{-1}$ ;  $\theta$ , Chroma retention (Equation 3);  $Y_{\text{Distortion}}$ , aroma distortion index (Equation 6);  $Y_{\text{Pressure}}$ , index of pressure dependence of aroma retention.

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production of natural flavors in a context of high consumer and market demand for organic ingredients.

#### KEYWORDS

aroma concentration, aroma fractionation, clarification, membrane separation, natural ingredient

## 1 | INTRODUCTION

Pressure-driven membranes are eco-efficient separation processes that are more and more documented for their applications in the food industry (Abdullah et al., 2023; Kumar et al., 2022). Over the last decades, applications using micro- (MF), ultra- (UF), or nanofiltration (NF) have emerged for liquid fractionation, concentration, or purification (Conidi et al., 2020; Dornier et al., 2018; Gonsalves et al., 2023; Lu et al., 2021). NF is less developed than MF/UF for the production of food extracts, because the process efficiency often involves complex phenomena that are not always well understood. Therefore, processing performances are difficult to predict without detailed and costly experimental studies (Yadav et al., 2022). However, the development of NF is gaining more and more interest because of the challenges involved in developing other low-cost, non-thermal, efficient, and sustainable food processes that result in high-quality products (Abdullah et al., 2023). NF membrane selectivity is based on size-exclusion (steric effects) but also interactions between the solutes and the membrane, especially through electrostatic effects (membrane material and surface charge), dielectric strength, or compound solubility (Nguyen et al., 2020; Van der Bruggen et al., 1999). Moreover, NF performance is also modified by the accumulation, in the vicinity of the membrane, of the compounds retained which can cause concentration polarization and fouling (Van der Bruggen et al., 2008). In recent years, NF has been used to fractionate low molecular weight organic solutes. For instance, previous studies have described NF of plant extracts, or plant by-product extracts, to concentrate low molecular weight compounds or to purify them regarding the dry matter (Acosta et al., 2017; Arend et al., 2022; Gaglianò et al., 2022; Li et al., 2021; Tamba et al., 2019; Tundis et al., 2018).

Crossflow filtration has already been employed to concentrate aroma compounds. For example, shrimp cooking juice was concentrated with minimal changes in aroma profile using a 200 Da NF membrane (Jarrault et al., 2017). The retention of the aroma compounds was above 50%. Using a polyethersulfone membrane to concentrate a tuna cooking juice, a retentate with preserved marine flavors, compared to those of the initial extract, was obtained (Walha et al., 2011). The sensory analysis of NF concentrates showed that they were less intense, but also less rancid, which was attributed to the loss of some small-sized volatile compounds. However, the flavor was evaluated without fine chemical determination. NF was also employed to concentrate aroma from the red wine Cabernet Sauvignon (Ivić et al., 2021) using a 300 Da membrane. This work concluded that NF was promising for red wine aroma concentration. The retention of volatile compounds was very close to the results obtained by reverse osmosis (RO) but using a lower transmembrane pressure, with a higher permeate flux,

resulting in lower process cost. Some low molecular weight compounds, such as ethanol, acetic acid, 4-ethylphenol, and 4-ethylguaiacol, were either partially retained or not at all by the NF membrane. However, in wine case, this can be interesting because those compounds contribute to the negative sensorial of the product.

Industry is continuously searching for new processing pathways to obtain natural extracts such as food ingredients (Carocho et al., 2014). Organic raspberry aroma is generally extracted from fresh raspberries using an organic solvent such as ethanol (Dastager, 2009). However, its fragrance is known to be degraded when processed, stored, or cooked (de Ancos et al., 2000). The main volatile compounds contributing to raspberry flavor were characterized, for example, by (Aprea et al., 2009). Of all the compounds found in the fruit headspace, 46 were identified. In ascending order of presence: terpenoids (25 compounds including 12 monoterpenes and 3 sesquiterpenes, as well as norisoprenoids,  $\alpha$ -ionone and  $\beta$ -ionone being the most abundant), other alcohols (6), aldehydes (4), esters (3), ketones (3), acids (2), furane (1), lactone (1), and hydrocarbons (1). Depending on the raspberry cultivar, the most abundant compounds in the headspace were acetate esters, alcohols, and aldehydes. Ionones are considered as essential to raspberry aroma (Hansen et al., 2016). Raspberry ketone (p-hydroxyphenyl-3-butanone) is one of the key raspberry aroma compounds but is not detectable after headspace extraction (Borejsza-Wysocki et al., 1992).

NF was studied for the concentration of aroma compounds from fresh raspberry juice after enzymatic liquefaction (Molnár et al., 2012). Enzymatic pretreatment proved to be efficient in most of cases to improve crossflow filtration performances, mainly in increasing permeate flux, without modification of the quality of the extract (Servent et al., 2020). Among all pectinolytic enzymes studied in this objective, pectinases are the most known, used and available enzyme at industrial scale (Dornier et al., 2018). In this work, MF (0.2  $\mu$ m, inorganic, 4 bar) and NF (300–500 Da, 20 bar) were coupled as a pretreatment of RO and osmotic distillation. MF was estimated as a suitable pretreatment since retention of the total polyphenol content, anthocyanins, antioxidant capacity, and TSS were close to 0%. Aroma compounds were analyzed by sensorial analysis. However, no biochemical quantification of aroma compounds was carried out. This study highlighted the potential of MF and NF coupling for raspberry volatile compound concentration. More recently, however, it has been shown that MF can also contribute to the fractionation of volatile compounds (Hammad et al., 2022). Using a 0.2- $\mu$ m ceramic membrane, the retention of aroma compounds from a citrus juice varied according to their hydrophobicity.

Conventional thermal processes like evaporation are not suitable for raspberry extract concentration due to the high heat sensitivity of the

aroma compounds (Lang et al., 2020; Roberts & Acree, 1996). Therefore, this work aimed to evaluate the feasibility of NF to concentrate aroma compounds from a raspberry hydroalcoholic extract using MF and enzymatic treatment as pretreatments. This investigation was based on an extract that was already commercialized as a flavoring ingredient, with the aim of enhancing its aroma strength by increasing its aroma concentration. The differences between the detailed aromatic profiles of the extracts produced by NF and the initial hydroalcoholic extract were characterized for each operating condition and membrane, which are very different in terms of materials and molecular cutoff, through reliable analytical aroma compound analysis.

## 2 | MATERIALS AND METHODS

### 2.1 | Hydroalcoholic raspberry extract

The raspberry hydroalcoholic extract used (100 L, 12% ethanol) was of the Cook-Herbier de France brand, supplied by Arcadie Company (Méjannes-lès-Alès, France). The extract is realized using organic raspberry (Mauguio, France) macerated at 96 h in ethanol, followed by screw pressing. This operation is carried out two times before the liquid macerate is sold in 50 mL bottles for use in commercial baking applications (Figure 1).

### 2.2 | Processing

#### 2.2.1 | Enzymatic treatment

The raspberry hydroalcoholic extract was treated by pectinase (P4716, Sigma-Aldrich, USA) at a dose of  $300 \text{ mg kg}^{-1}$ . The mixture

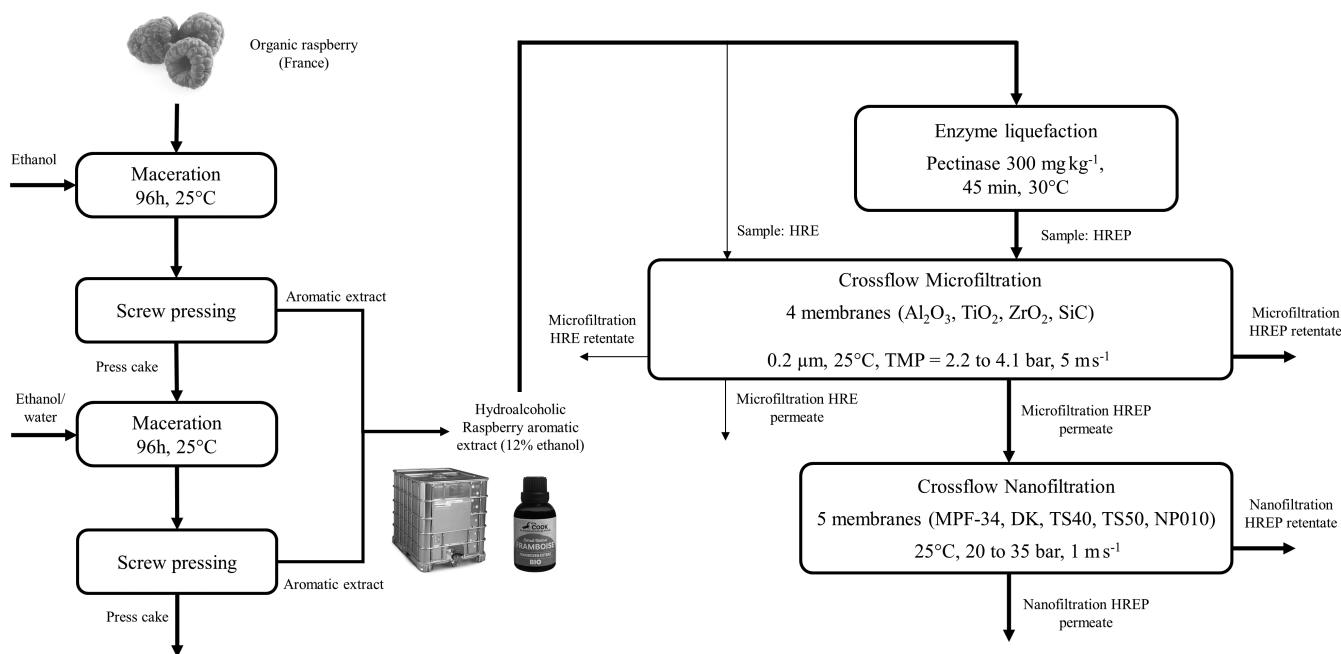
was stirred for 45 min at  $30^\circ\text{C}$  without any prior pH modification (Figure 1).

#### 2.2.2 | Crossflow MF

MF trials were carried out using the device described by Servent et al. (2020) made by TIA (Bollène, France). This laboratory scale micro-pilot (nominal volume of 3 L) held four single-channel tubular membranes and allowed four TMPs to be tested simultaneously (Figure S1). For the evaluation of MF as a pre-processing treatment to NF, four inorganic membranes with a pore size diameter of  $0.2 \mu\text{m}$  were evaluated. Membranes differed by their materials: alumina  $\text{Al}_2\text{O}_3$  ( $55 \text{ cm}^2$  area, Pall, USA), titanium dioxide  $\text{TiO}_2$  ( $55 \text{ cm}^2$  area, Tami Industries, France), zirconia  $\text{ZrO}_2$  ( $55 \text{ cm}^2$  area, Orelis, France) and silicon carbide (SiC) ( $43 \text{ cm}^2$  area, Saint-Gobain, France). Crossflow velocity was set at  $5 \text{ m s}^{-1}$  independently of TMP using a volumetric pump and the temperature was maintained at  $25 \pm 2^\circ\text{C}$ . TMP varied from 2.2 to 4.1 bar.

The membrane cleaning operations were conventional, based on alkaline ( $\text{NaOH}$  2%,  $80^\circ\text{C}$ ) and acidic cleaning ( $\text{HNO}_3$  1%,  $50^\circ\text{C}$ ). Cleaning efficiency was controlled by the verification of tap water permeability measured at 564, 876, 593, and  $1229 \text{ L h}^{-1} \text{ m}^{-2} \text{ bar}^{-1}$  for Pall, Tami, Orelis, and Saint-Gobain membranes, respectively, at  $25^\circ\text{C}$  and  $5 \text{ m s}^{-1}$ .

The mass reduction ratio (MRR) is the concentration level of the extract (Equation 1) with  $M_r$  the retentate mass and  $M_p$  the permeate mass. The retention ( $R$ ) was calculated by comparing the concentrations in the permeate ( $C_p$ ) and in the feed extract ( $C_f$ ) at a constant MRR of 1 (Equation 2). To calculate retention, the permeate was reintroduced in the retentate after every 20 mL in order to maintain  $\text{MRR} = 1$ . Process performances were estimated after 1 h of stabilization.



**FIGURE 1** Simplified chart of the process applied for the aroma compound concentration from the organic raspberry hydroalcoholic extract. HRE, hydroalcoholic raspberry extract; HREP, hydroalcoholic raspberry extract with pectinase; TMP, transmembrane pressure.

**TABLE 1** Nanofiltration membrane characteristics.

Membranes	Manufacturer	MWCO (Da)	Monovalent ion rejection	Divalent ion rejection	Membrane material	pH range
MPF34	Koch	200	0.35 NaCl (30 bar, 30°C, Feed = 3% glucose, 3% sucrose, 5% NaCl)	-	Polyethersulfone	2–10
DK	GE Osmonics	150–300	-	0.98 MgSO <sub>4</sub> (0.2% MgSO <sub>4</sub> , 8 bar, 25°C)	Polyamide-TFC	2–10
TS40	Trisep	200–300	0.4	0.98 MgSO <sub>4</sub> (0.2% MgSO <sub>4</sub> , 8 bar, 25°C, pH 8)	Poly(piperazine-amide)	2–11
TS50	Trisep	200–300	0.5	0.99 MgSO <sub>4</sub> (0.2% MgSO <sub>4</sub> , 8 bar, 25°C, pH 8)	Poly(piperazine-amide)	2–11
NP010	Microdyn-Nadir	1000	0.35–0.70 Na (40 bar, 20°C, Na <sub>2</sub> SO <sub>4</sub> )	-	Polyethersulfone	0–14

$$\text{MRR} = \frac{M_r + M_p}{M_f} = 1 + \frac{M_p}{M_f} \quad (1)$$

$$R = \left(1 - \frac{C_p}{C_f}\right) * 100. \quad (2)$$

When MF was carried out in concentration mode, the four same membranes were used, and the permeate was extracted continuously, starting with 3 L of fresh raspberry hydroalcoholic extract. The system was continuously fed with fresh extract in order to maintain the constant retentate volume. At the end of the concentration, continuous feeding was stopped leading to a progressive drop of  $M_f$  and therefore a faster increase in MRR.

### 2.2.3 | Nanofiltration

The micro-pilot used for the NF experimentation was described by Tamba et al. (2019) (Figure S1). The pilot had a nominal volume of 3 L and was based on a Sepa CF II Membrane Cell System (GE Osmonics, USA). The temperature was maintained at  $25 \pm 2^\circ\text{C}$  thanks to a water jacket around the feeding tank connected to a cryostat Julabo F12-ED (Seelbach, Germany). The membranes used for the trials were flat-sheet membranes with an effective area of 155 cm<sup>2</sup>. Crossflow velocity was fixed at 1 m·s<sup>-1</sup>. Five membranes were selected based on their intrinsic characteristics, their molecular weight cutoff (MWCO), ion rejections, or materials (Table 1). Before filtration, membranes were preconditioned with deionized water for 60 min at a TMP of 20 bar and 25°C.

As for MF, all NF membrane retentions were studied at MRR = 1. Because NF organic membrane performance is more pressure-dependent than MF inorganic ones, three TMPs were tested for 1 h for each membrane. Pressures ranged from 20 to 35 bar.

## 2.3 | Biochemical analysis

### 2.3.1 | Proximate analysis

The pH and titratable acidity (TA) were measured using an automatic TitroLine® easy titrator (SI Analytics, Germany) and expressed as

equivalent to citric acid. Dry matter was measured after drying for 16 h at 40°C and then for 48 h in a vacuum oven at 70°C and 1.5 mbar. Total soluble solids (TSS) and refractive index were measured using a PAL- $\alpha$  refractometer (Atago, Japan) with a standard deviation of  $\pm 0.5 \text{ g}\cdot\text{kg}^{-1}$  at ambient temperature. Turbidity was determined using a HI 98703 turbidimeter (HANNA instruments, USA). Color was evaluated using a Minolta CR-410 chromameter (Konica Minolta, Japan) according to the CIELAB scale in which  $a^*$  and  $b^*$  represent the red-green and blue-yellow tones, respectively, and  $L^*$  the lightness. Chroma value was calculated following Equation (3). All the analyses described were carried out in triplicate.

The clarification rate (CR) used to evaluate MF extracts was defined from the ratio between the turbidity of the initial extract ( $TU_i$ ) and permeate ( $TU_p$ ) (Equation 4), while retention of chroma ( $\Theta$ ) was used for NF extracts using chroma values (Equation 5).

$$C^* = \sqrt{a^{*2} + b^{*2}}. \quad (3)$$

$$\text{CR} = \left(1 - \frac{TU_p}{TU_i}\right) * 100. \quad (4)$$

$$\Theta = \left(1 - \frac{C_p^*}{C_f^*}\right) * 100. \quad (5)$$

### 2.3.2 | Total phenolic content

The total polyphenol content (TPC) was determined by the Folin-Ciocalteu colorimetric method (Marín-Castro et al., 2022). Briefly, hydroalcoholic extracts were directly mixed with Folin-Ciocalteu and calcium carbonate to initiate the reaction. Absorbance was measured at 765 nm with a 7205 UV/visible scanning spectrophotometer (Jenway, UK), and a calibration curve was created from 0 to 1000 mg of gallic acid·L<sup>-1</sup>. TPC was expressed as equivalent milligrams of gallic acid (mg GAE)·L<sup>-1</sup> of fresh extract. Analyses of TPC were carried out in triplicate.

### 2.3.3 | Analysis of aroma compounds

In order to obtain aroma footprints, and so to identify and semi-quantify the aroma compounds, the combination of the dynamic

headspace technique (DHS) and mass spectrometry gas chromatography (GC-MS) was employed as described by Joly et al. (2022). Aroma compound extraction was automatized through a Gerstel autosampler (Gerstel, Germany). Desorption and analysis were carried out on a GCMS Agilent 7890B GC (Agilent Technologies, Santa Clara, USA). A total of 2 g of sample was placed in a 10 mL glass vial and diluted by the exact MRR achieved after filtration to allow comparison between the samples. And 1  $\mu\text{L}$  of a 3-heptanol solution at 1  $\mu\text{L}\cdot\text{mL}^{-1}$  was added as internal standard. The vial was equilibrated to 30°C, then stirred at 500 rpm before headspace swept with a nitrogen flow at 1  $\text{mL}\cdot\text{min}^{-1}$ . The volatile compounds were collected on a Tenax TA trap and dried with an additional purge flow at 100  $\text{mL}\cdot\text{min}^{-1}$  at 50°C for 2.5 min to remove residual water. Collected volatile compounds were then desorbed using an automatic thermal desorption unit (TDU) maintained at 30°C (0.4 min) and then heated up to 300°C at 120°C $\cdot\text{min}^{-1}$ . The desorbed compounds were transferred to a CIS4 injection system, in which the compounds were first cryofocused. Then, the CIS4 temperature was raised from -10°C to 300°C at 12°C $\cdot\text{s}^{-1}$  and held for 5 min. Volatile compounds were analyzed on a DB-Wax column (60 m  $\times$  250  $\mu\text{m}$   $\times$  0.25  $\mu\text{m}$ ). Mass spectra were recorded in EI<sup>+</sup> mode at 70 eV within a range of 40 to 350 Da with a solvent delay time of 2 min and a scan speed of 4.52  $\text{m}\cdot\text{s}^{-1}$ . Analyzer and source temperatures were 150°C and 250°C, respectively. Mass spectrometry data were analyzed using MassHunter software version B.08.00. Volatile compounds were identified by comparing their mass spectra to the NIST 08 library (Wiley, New Jersey, USA). Analyses of aroma compounds were carried out in triplicates. Results were expressed either in relative percent of total aroma compounds, considering the area of one compound over the total area of all compounds, or by semi-quantification in  $\mu\text{g eq 3-heptanol}\cdot\text{L}^{-1}$  used as internal standard.

The variations of the aroma compound profile during processing are complex. The aroma compound contents decreased differently depending on operating conditions during NF. To integrate the variation of contents for all compounds and appreciate the aroma distortion through the process, the indicator “aroma distortion index”  $Y_{\text{Distortion}}$  was defined (Equation 6). This indicator helped to understand the aroma profile variation, however without giving more information on the direction of which compound was impacted. The more different the retention between aroma compounds, the higher the distortion.

$$Y_{\text{Distortion}} = \frac{\sigma_{\text{retention}}}{\bar{R}_{\text{et}}} * 100. \quad (6)$$

With  $Y_{\text{Distortion}}$  is the aroma distortion index,  $\sigma_{\text{retention}}$  is the standard deviation of retentions, and  $\bar{R}_{\text{et}}$  is the mean of retention of all the aroma compounds.

## 2.4 | Statistical analysis

Statistical analyses were carried out using XLSTAT v.2019 (Addinsoft, Paris, France). An analysis of variance using Tukey's range test was

conducted at  $p < 0.05$  ( $n = 3$ ). The results are presented as means with standard deviations in brackets.

## 3 | RESULTS AND DISCUSSION

### 3.1 | Clarification of the hydroalcoholic raspberry extract by MF

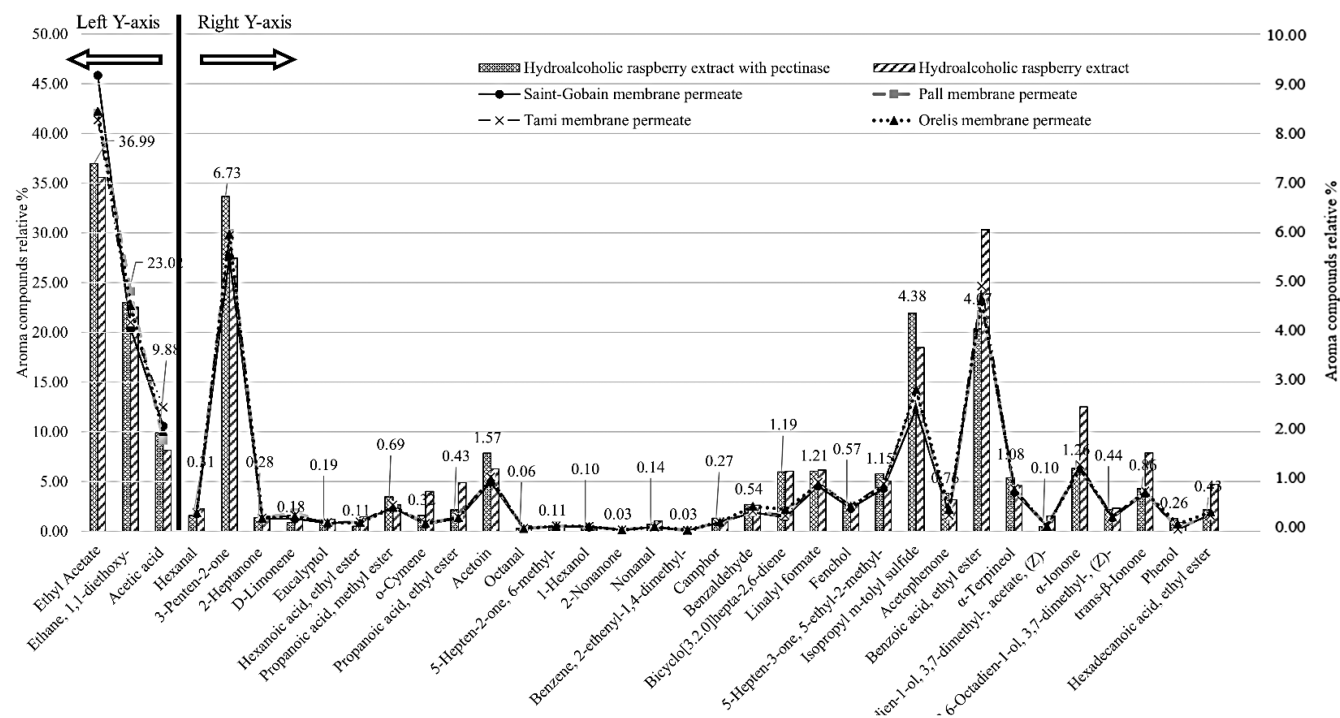
The raw raspberry hydroalcoholic extract (HRE) and the raspberry hydroalcoholic extract after enzymatic liquefaction (HREP) compositions are reported in Table 2. Overall, the enzymatic treatment did not show any significant impact on almost all the tracked quality markers, except for turbidity and TPC. Indeed, pectinase addition affects pectin structures, and therefore the particles, product viscosity, and consistency, without affecting other intrinsic changes (Patel et al., 2022). The HREP extract presented a 7% loss of turbidity compared to HRE resulting in a slightly less cloudy extract. The TPC increased by 27% after enzymatic liquefaction. This augmentation could be caused by the TPC extraction from the remaining raspberry residue during enzymatic liquefaction of the raw extract (Versari et al., 1997). The difference in refractive index, which is representative of TSS and ethanol content, was also non-significant between HRE and HREP samples.

The enzymatic liquefaction step did not have an impact either on the aroma profile as shown in Figure 2, which reports the relative contents of the main aroma compounds for HRE and HREP. This representation was realized without considering ethanol. Indeed, results showed that enzymatic treatment had no significant impact on ethanol content and the high abundance of ethanol in the headspace disturbed the representation of other volatile compounds in relative percent. Thirty-five main raspberry volatile compounds were

**TABLE 2** Proximate analysis of the raspberry extract without and with enzyme treatment (HRE and HREP, respectively) used as raw materials for the crossflow filtration.

	Hydroalcoholic raspberry extract (HRE)	Hydroalcoholic raspberry extract with pectinase (HREP)
Brightness L	21.0 (1.2) <sup>a</sup>	21.2 (2.3) <sup>a</sup>
Chroma C	49.3 (2.8) <sup>a</sup>	45.8 (5.4) <sup>a</sup>
Turbidity (NTU)	53.1 (1.2) <sup>a</sup>	49.3 (2.1) <sup>b</sup>
Refractive index	1.3551 (0.0002) <sup>a</sup>	1.3547 (0.0002) <sup>a</sup>
Dry matter (DM) (g $\text{kg}^{-1}$ )	72 (2) <sup>a</sup>	74 (2) <sup>a</sup>
Titratable acidity (TA) (g eq citric acid $\text{kg}^{-1}$ )	15 (1) <sup>a</sup>	15 (1) <sup>a</sup>
pH	3.43 <sup>a</sup>	3.34 <sup>a</sup>
Total phenolic compounds (TPC) (mg eq galic acid $\text{L}^{-1}$ )	73.2 (5.0) <sup>b</sup>	93.5 (4.2) <sup>a</sup>

Note: Mean values calculated using three repetitions. Different letters in line expressed the significant difference between values group by means of ANOVA-Tukey test ( $p < 0.05$ ).



**FIGURE 2** Fingerprint of the main aroma compounds (expressed in relative percent of total aroma compounds without ethanol) in the raspberry extracts with and without enzyme treatment and in the microfiltration permeates (MRR = 1, pooled permeates for all TMP). Aroma compounds were classified by order of retention time. MRR, mass reduction ratio; TMP, transmembrane pressure.

considered among the 60 detected by DHS-GC-MS. All the volatile compounds with a relative abundance below 0.03%, excluding ethanol for the calculation, were not integrated into the analysis. These results were in agreement with Aprea et al. (2009) which identified similar aroma compounds in three raspberry cultivars. Furthermore, raspberry ketone was absent from the elution probably due to its low volatility and content which make it difficult to analyze with headspace methodology (Borejsza-Wysocki et al., 1992).

Values of brightness ( $L^*$ ), chroma ( $C^*$ ), TPC, refractive index, and DM of MF permeates were similar for all the membranes. There were no significant differences in these results between all permeates (Table 3). DM of HRE and HREP permeates essentially consist of simple sugars and organic acids which were not retained by MF, and this measurement is linked to refractive index (Hammad et al., 2021). The same is true for TPC and color caused by anthocyanins present in raspberry (Bobinaite et al., 2012; Cisse et al., 2011). The TA was also non-retained by the membranes. The mean TA for all permeates, considering all membranes (36 values for each extract), were 15.1 (0.4) and 16.0 (1) g eq citric acid·kg<sup>-1</sup> for the HRE and HREP extracts, respectively, identical to the initial feeding value. On the contrary, the CR was more affected by the membrane/pressure combination. The HRE permeates seemed to be fully clarified by MF with CR up to 96%, while the HREP permeates were slightly less clarified with CR between 88% and 92%. In Figure 2, the aroma compound profiles (means of all TMPs) are shown to be quite similar for all MF permeates.

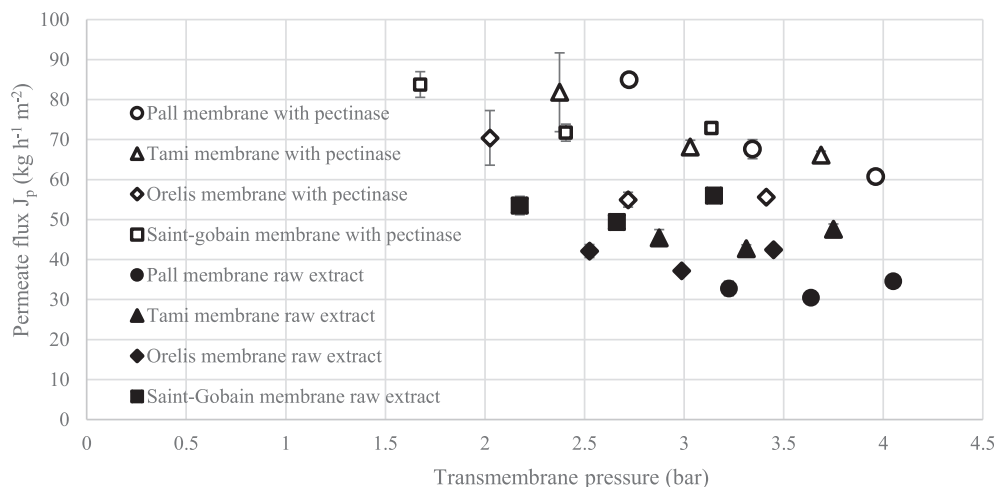
The MF assays at MRR = 1 carried out with the four inorganic membranes revealed that, whatever the membrane, the enzymatic treatment allowed the permeate flux to be improved by between 30% and 50% (Figure 3). This increase in flux confirmed the positive action of pectinases, reducing the viscosity and membrane long-term fouling, and enhancing MF performance. For HREP extract, all the fluxes were above 50 kg·h<sup>-1</sup>·m<sup>-2</sup> which represents the critical limit generally admitted for industrial applications (Abdullah et al., 2023). Among all the membranes, Saint-Gobain (SiC) obtained a better permeate flux ( $J_p$ ) at a lower TMP. Using this membrane, the  $J_p$  with HREP extract was 84 kg·h<sup>-1</sup>·m<sup>-2</sup> at a TMP of 1.6 bar.  $J_p$  with HRE extract was 35% lower. Since the filtration operating cost is directly linked to the TMP, the lower the TMP the cheaper the process. Therefore, among the studied membranes, the SiC membrane was the most appropriate for clarification before NF.

To conclude this MF membrane selection section, the membrane performances, between all tested inorganic 0.2 μm membranes, were similar and systematically enhanced by the enzymatic liquefaction. However, the Saint-Gobain 0.2 μm membrane presented better  $J_p$  at low TMP. So, this membrane, associated with an enzymatic liquefaction, was chosen for the concentration step (increasing MRR). Figure 4 shows the evolution of the  $J_p$  versus MRR up to 5 using the Saint-Gobain SiC membrane (172 cm<sup>2</sup>) at an average TMP of 2.4 bar. This TMP was superior to 1.6 bar because in this case it was the mean of the TMP of 4 same membranes equipped in the pilot used. As usually observed, the  $J_p$  dropped off at the beginning of filtration from 111 to 73 kg·h<sup>-1</sup>·m<sup>-2</sup> at

**TABLE 3** Proximate analysis of the permeates obtained by microfiltration of the raspberry extracts with and without enzyme treatment, at a mass reduction ratio (MRR) = 1 for the different membranes and transmembrane pressures (TMPs).

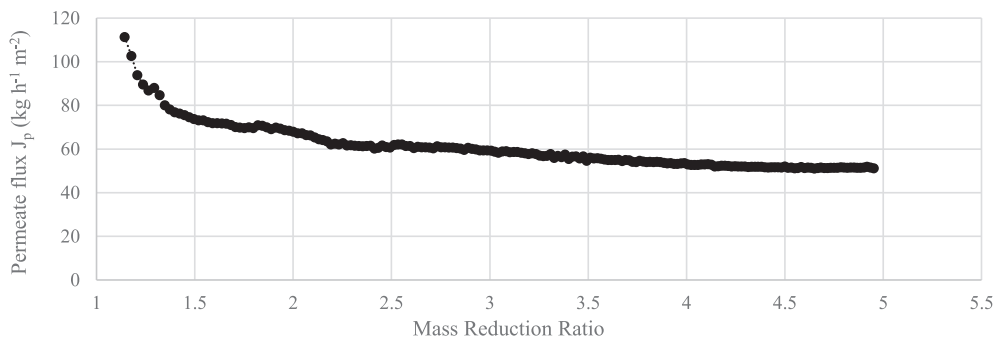
	Membrane	TMP (bar)	$L^*$	$C^*$	Total phenolic content (mg galic acid·L <sup>-1</sup> )	Refractive index ± 0.0007	Dry matter (g·kg <sup>-1</sup> )	Clarification rate (CR) (%)
Raw raspberry hydroalcoholic extract (HRE)	Pall (Al <sub>2</sub> O <sub>3</sub> )	3.2	21.9 (3.0) <sup>a</sup>	50.0 (4.9) <sup>a</sup>	67.5 (6.6) <sup>a</sup>	1.3544 <sup>a</sup>	70 (2) <sup>a</sup>	98.2 (1.0) <sup>a</sup>
	Pall (Al <sub>2</sub> O <sub>3</sub> )	3.6	22.5 (0.6) <sup>a</sup>	52.1 (1.7) <sup>a</sup>	69.4 (4.9) <sup>a</sup>	1.3544 <sup>a</sup>	72 (2) <sup>a</sup>	98.7 (0.6) <sup>a</sup>
	Pall (Al <sub>2</sub> O <sub>3</sub> )	4.1	21.2 (2.9) <sup>a</sup>	48.2 (7.7) <sup>a</sup>	70.5 (4.1) <sup>a</sup>	1.3546 <sup>a</sup>	72 (1) <sup>a</sup>	98.4 (0.3) <sup>a</sup>
	Tami (TiO <sub>2</sub> )	2.9	22.3 (1.0) <sup>a</sup>	53.5 (2.0) <sup>a</sup>	68.0 (6.5) <sup>a</sup>	1.3540 <sup>a</sup>	73 (2) <sup>a</sup>	97.9 (0.5) <sup>a</sup>
	Tami (TiO <sub>2</sub> )	3.3	19.8 (2.2) <sup>a</sup>	47.8 (2.7) <sup>a</sup>	67.2 (6.8) <sup>a</sup>	1.3544 <sup>a</sup>	71 (2) <sup>a</sup>	98.2 (0.3) <sup>a</sup>
	Tami (TiO <sub>2</sub> )	3.7	21.7 (0.1) <sup>a</sup>	50.4 (1.2) <sup>a</sup>	69.9 (6.6) <sup>a</sup>	1.3546 <sup>a</sup>	73 (2) <sup>a</sup>	97.7 (0.7) <sup>a</sup>
	Orelis (ZrO <sub>2</sub> )	2.5	20.7 (2.7) <sup>a</sup>	47.4 (4.7) <sup>a</sup>	71.2 (3.9) <sup>a</sup>	1.3541 <sup>a</sup>	73 (2) <sup>a</sup>	97.5 (0.7) <sup>a</sup>
	Orelis (ZrO <sub>2</sub> )	3.0	19.7 (1.8) <sup>a</sup>	48.8 (4.7) <sup>a</sup>	67.1 (5.6) <sup>a</sup>	1.3544 <sup>a</sup>	73 (2) <sup>a</sup>	97.7 (1.3) <sup>a</sup>
	Orelis (ZrO <sub>2</sub> )	3.4	20.2 (1.2) <sup>a</sup>	49.7 (3.9) <sup>a</sup>	71.7 (5.2) <sup>a</sup>	1.3546 <sup>a</sup>	73 (2) <sup>a</sup>	98.3 (0.7) <sup>a</sup>
	Saint-Gobain (SiC)	2.2	22.9 (1.9) <sup>a</sup>	52.5 (4.9) <sup>a</sup>	72.6 (6.2) <sup>a</sup>	1.3544 <sup>a</sup>	72 (2) <sup>a</sup>	97.6 (0.9) <sup>a</sup>
	Saint-Gobain (SiC)	2.7	19.0 (1.4) <sup>a</sup>	48.2 (3.0) <sup>a</sup>	67.6 (6.0) <sup>a</sup>	1.3544 <sup>a</sup>	73 (2) <sup>a</sup>	98.6 (0.6) <sup>a</sup>
	Saint-Gobain (SiC)	3.1	20.0 (2.8) <sup>a</sup>	47.5 (3.8) <sup>a</sup>	66.8 (5.9) <sup>a</sup>	1.3546 <sup>a</sup>	71 (2) <sup>a</sup>	97.4 (0.8) <sup>a</sup>
Raspberry hydroalcoholic extract with pectinase (HREP)	Pall (Al <sub>2</sub> O <sub>3</sub> )	2.7	22.7 (1.2) <sup>a</sup>	53.2 (2.3) <sup>a</sup>	91.2 (6.8) <sup>a</sup>	1.3547 <sup>a</sup>	75 (2) <sup>a</sup>	89.1 (4.1) <sup>a</sup>
	Pall (Al <sub>2</sub> O <sub>3</sub> )	3.3	23.2 (0.3) <sup>a</sup>	53.4 (0.5) <sup>a</sup>	89.6 (4.4) <sup>a</sup>	1.3547 <sup>a</sup>	74 (1) <sup>a</sup>	91.6 (4.9) <sup>a</sup>
	Pall (Al <sub>2</sub> O <sub>3</sub> )	4.0	22.4 (1.9) <sup>a</sup>	50.6 (5.1) <sup>a</sup>	94.6 (3.8) <sup>a</sup>	1.3543 <sup>a</sup>	74 (1) <sup>a</sup>	91.5 (4.4) <sup>a</sup>
	Tami (TiO <sub>2</sub> )	2.4	23.2 (0.1) <sup>a</sup>	53.7 (0.3) <sup>a</sup>	93.1 (4.7) <sup>a</sup>	1.3546 <sup>a</sup>	75 (4) <sup>a</sup>	88.6 (4.8) <sup>a</sup>
	Tami (TiO <sub>2</sub> )	3.0	22.8 (0.7) <sup>a</sup>	50.4 (1.6) <sup>a</sup>	94.6 (6.1) <sup>a</sup>	1.3546 <sup>a</sup>	76 (4) <sup>a</sup>	90.4 (2.8) <sup>a</sup>
	Tami (TiO <sub>2</sub> )	3.7	22.2 (1.6) <sup>a</sup>	51.8 (2.7) <sup>a</sup>	95.2 (3.9) <sup>a</sup>	1.3547 <sup>a</sup>	75 (2) <sup>a</sup>	88.3 (3.5) <sup>a</sup>
	Orelis (ZrO <sub>2</sub> )	2.0	24.2 (1.1) <sup>a</sup>	55.5 (3.3) <sup>a</sup>	94.5 (1.7) <sup>a</sup>	1.3543 <sup>a</sup>	76 (2) <sup>a</sup>	91.3 (3.8) <sup>a</sup>
	Orelis (ZrO <sub>2</sub> )	2.7	22.4 (1.1) <sup>a</sup>	50.7 (2.3) <sup>a</sup>	101.8 (7.3) <sup>a</sup>	1.3547 <sup>a</sup>	76 (4) <sup>a</sup>	88.2 (2.2) <sup>a</sup>
	Orelis (ZrO <sub>2</sub> )	3.4	22.8 (1.5) <sup>a</sup>	52.8 (2.9) <sup>a</sup>	95.8 (4.0) <sup>a</sup>	1.3547 <sup>a</sup>	75 (3) <sup>a</sup>	88.8 (4.7) <sup>a</sup>
	Saint-Gobain (SiC)	1.7	21.7 (1.9) <sup>a</sup>	50.7 (1.6) <sup>a</sup>	96.6 (6.9) <sup>a</sup>	1.3547 <sup>a</sup>	74 (4) <sup>a</sup>	88.6 (4.9) <sup>a</sup>
	Saint-Gobain (SiC)	2.4	23.4 (0.8) <sup>a</sup>	53.5 (1.5) <sup>a</sup>	101.4 (7.5) <sup>a</sup>	1.3549 <sup>a</sup>	73 (3) <sup>a</sup>	90.5 (1.6) <sup>a</sup>
	Saint-Gobain (SiC)	3.1	22.5 (1.2) <sup>a</sup>	50.2 (0.8) <sup>a</sup>	96.8 (5.9) <sup>a</sup>	1.3546 <sup>a</sup>	76 (2) <sup>a</sup>	90.1 (4.9) <sup>a</sup>

Note: Means calculated using three repetitions. Same letters in column, specifically for each pretreatment, expressed non-significant difference between the value group by means of ANOVA–Tukey test ( $p < 0.05$ ).

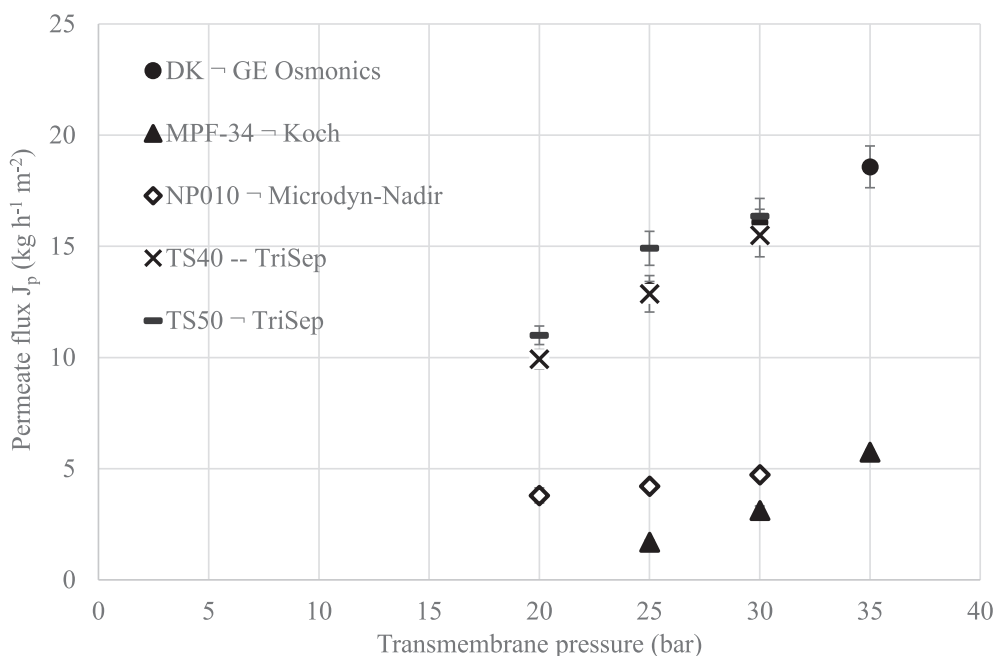
**FIGURE 3** Microfiltration permeate flux ( $J_p$ ) for each membrane at different TMPs using raspberry extracts with and without enzyme at MRR = 1. MRR, mass reduction ratio; TMP, transmembrane pressure.

MRR = 1.5 and then the curve flattened. The  $J_p$  stabilized at  $52 \text{ kg h}^{-1} \text{ m}^{-2}$  at MRR = 5 (28% less) which stayed above the critical value regarding industrial application. This performance stability

(retention and permeate flux) provides the possibility of clarifying up to MRR = 5 without  $J_p$  decrease, and so to plan continuous processing where the MF permeate is used as feed for NF processing.



**FIGURE 4** Microfiltration permeate flux ( $J_p$ ) evolution versus the mass reduction ratio MRR using the raspberry extract with enzyme liquefaction (HREP) and the Saint-Gobain membrane (SiC) at a transmembrane pressure of 2.4 bar, 25°C, and a crossflow velocity of 5 m s<sup>-1</sup>. HREP, hydroalcoholic raspberry extract with pectinase; MRR, mass reduction ratio.



**FIGURE 5** Nanofiltration permeate flux ( $J_p$ ) for each membrane (DK, MPF-34, NP010, TS40, and TS50) versus transmembrane pressure at MRR = 1 using the raspberry extract with enzyme liquefaction (HREP) clarified by microfiltration 0.2 μm using Saint-Gobain membrane at an average transmembrane pressure of 2.4 bar, 25°C, and a crossflow velocity of 5 m s<sup>-1</sup>. HREP, hydroalcoholic raspberry extract with pectinase; MRR, mass reduction ratio.

### 3.2 | Concentration of raspberry aroma compounds by NF

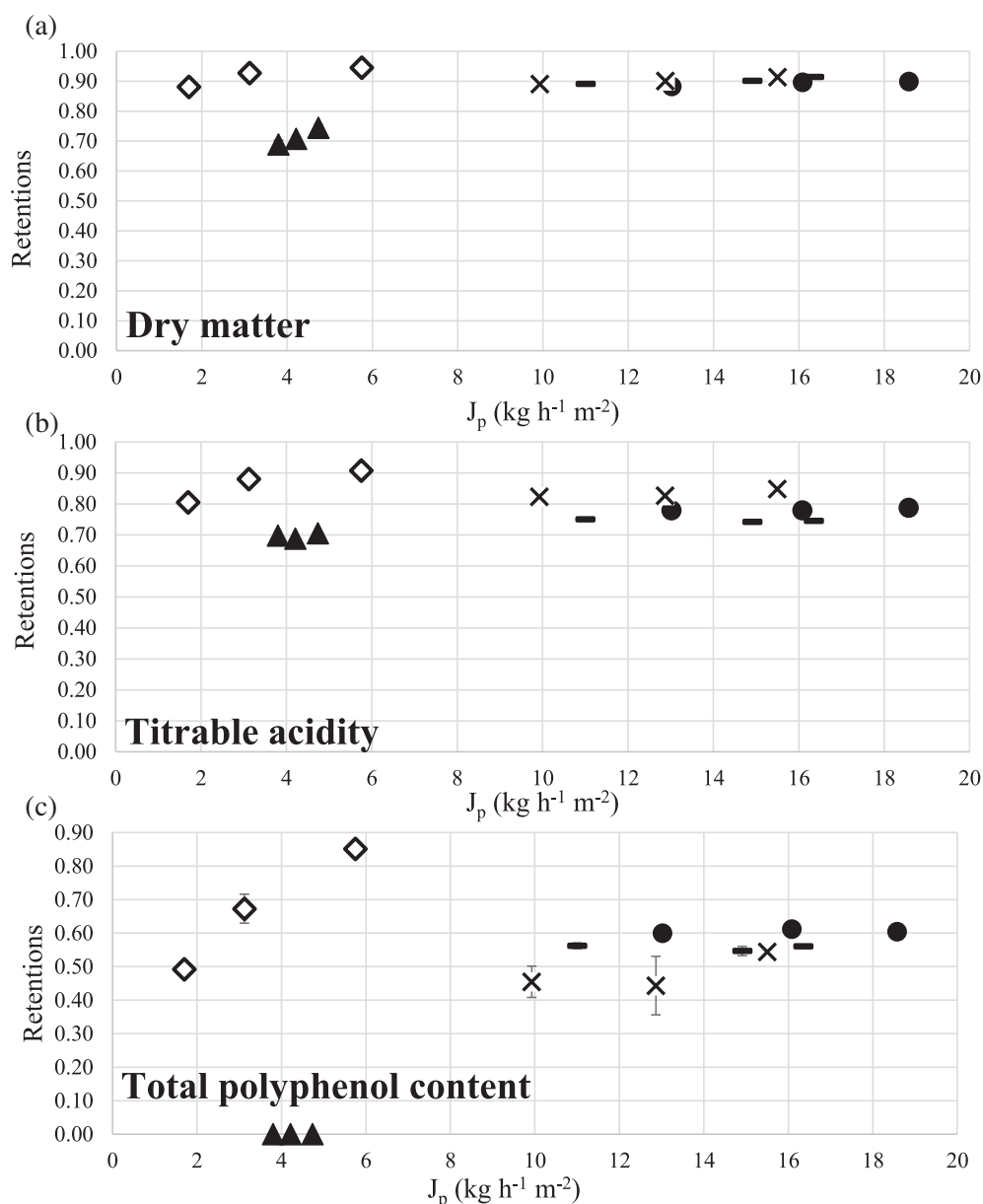
The relation between the  $J_p$  and TMP applied during NF is described in Figure 5 for all membranes. Two groups of membranes could be discriminated by their permeate flux. On one hand, the TS50, TS40, and DK membranes showed permeate flux close to 10 kg h<sup>-1</sup> m<sup>-2</sup> at 20 bar. On the other hand, the NP010 and MPF-34 membranes led to  $J_p$  of between 2 and 5.5 kg h<sup>-1</sup> m<sup>-2</sup>. The NF performance depends on multiple factors that are difficult to predict (Schäfer & Fane, 2021), the main ones being the physical membrane properties and fouling during the process, but also solute interactions with the membrane (Van der Bruggen et al., 2002; Van der Bruggen et al., 2008).

The group of membranes with the highest permeate flux (DK, TS40, and TS50), also presented stable retentions of the DM, TA, and TPC at TMP between 20 and 35 bar (Figure 6). However, the retentions of the DM, TA, and TPC associated with low  $J_p$  membranes (MPF-34 and NP010) depended on TMP. This behavior was

consistent because the usual relation between retention and permeate flux during NF is that, generally, they both increase together until reaching a level after which the retention is maximal (Cisse et al., 2011; Tamba et al., 2019). Overall, the DM was retained for more than 90% except for the NP010 membrane which allowed DM to be retained at about 70% (Figure 6a). In the permeate, the refractive index values were in a range of 50%–75% of the refractive index of the feed depending on the membrane. The DK membrane allowed the lowest presence of sugar in permeate with about 58% of the refractive index measured in the feed. The compounds analyzed with a strong impact on refractive index measurement were mainly sugars and ethanol. Since the sugars are also related to DM content (and therefore to high retention), the differences in the refractive index values were attributed to ethanol retention. The ethanol retentions were evaluated with DHS-GC-MS. They were, on average, 71 (30)%, 76 (2)%, 65 (20)%, and 56 (8)% for the MPF-34, TS50, TS40, and NP010 membranes, respectively. The DK membrane presented the highest ethanol retention value with 91 (27)%. The standard deviation



**FIGURE 6** Retention of (a) dry matter, (b) titratable acidity, and (c) total polyphenol content versus permeate flux ( $J_p$ ) with ● for the DK membrane, ◇ for MPF-34, ▲ for NP010, × for TS40, and ▬ for TS50 at MRR = 1 using the raspberry extract with enzyme (HREP) prefiltered by microfiltration 0.2  $\mu\text{m}$  using Saint-Gobain membrane at an average transmembrane pressure of 2.4 bar, 25°C and a crossflow velocity of 5  $\text{m}\cdot\text{s}^{-1}$ . HREP, hydroalcoholic raspberry extract with pectinase; MRR, mass reduction ratio.



of ethanol retention showed that it depended on the TMP for the MPF-34, TS40, and DK membranes. The alcohol interactions with the NF membrane are a phenomenon that has already been referenced. The modification of the ethanol content of the extract during NF can modify the relation between  $J_p$  and TMP as well as the selectivity of the membrane by modulating compound solubility (Braeken et al., 2004; Nguyen et al., 2020). In a propolis extract, for instance, the presence of ethanol greatly influenced the retentions during filtration by the compound solubilization and precipitation, and by the membrane pore dilatation (Mello et al., 2010). In this example, retentions of flavonoids were 84% when the solvent was water which decreased to 54% when the solvent was ethanol 80%. Therefore, a membrane with a high dependency of ethanol retention to TMP can result in a process that is difficult to control during concentration, due to a change in membrane selectivity.

Concerning polyphenols, the retention of the DK, TS40, and TS50 membranes ranged between 44% and 62%, and from 49% to 85% for the MPF-34 membrane depending on permeate flux. The NP010 membrane did not retain TPC (Figure 6c). This result for the NP010 membrane was coherent with its MWCO and was close to 1000 Da, often resulting in a low TPC rejection rate (Cassano et al., 2021; Conidi et al., 2012). The means of chroma retentions were 89%, 88%, 79%, and 63%, respectively, for TS50, DK, TS40, and NP010 membranes. Since anthocyanins are the main pigment of raspberry extract, this chroma evolution could be linked to anthocyanin retention. The DK, TS40, and TS50 membranes retained more chroma intensity than the NP010 membrane, which was consistent with TPC retention. For these membranes, the retentate color was an intense red, while the permeate was slightly pink. Therefore, the TS50, TS40, and DK membranes led to the concentration of anthocyanins in the

**TABLE 4** Average, standard deviation, and aroma distortion index ( $Y_{\text{Distortion}}$ ) of nanofiltration retention aggregated for the 34 main aroma compounds, the three transmembrane pressures (TMPs), and the five membranes studied.

	Average retention	Standard deviation	Global $Y_{\text{Distortion}}$ (%)	$Y_{\text{Distortion}}$ (%)			
				TMP = 20 bar	TMP = 25 bar	TMP = 30 bar	TMP = 35 bar
DK $\rightarrow$ GE Osmonics	0.85	0.09	11.0	n.p.	13.4	11.4	11.0
MPF-34 $\rightarrow$ Koch	0.72	0.30	42.2	n.p.	48.1	44.4	30.0
NP010 $\rightarrow$ Microdyn	0.51	0.31	60.1	64.4	62.2	58.3	n.p.
TS40 $\rightarrow$ TriSep	0.58	0.31	53.9	59.1	55.1	49.1	n.p.
TS50 $\rightarrow$ TriSep	0.66	0.27	41.7	n.p.	43.9	44.3	39.4

retentate. However, the NP010 permeate color was more intense in red tones than the DK, TS50, and TS40 permeates, but less than the initial extract. This could be attributed to a decrease of co-pigmentation phenomenon in the permeate (Enaru et al., 2021). The MPF-34 chroma retention increased with TMP, as did the TPC retention. At 25 bar, the TPC retention was less than 50% and the chroma retention was 48%. At 35 bar, the retention of chroma increased to 80%, linked to the highest TPC retention compared to all the other membranes (85%). The MPF-34 membrane concentrated anthocyanins up to 35 bar with 25% TPC more than the other membranes. The TA retentions were between 70% and 80% for TS50, NP010, and DK, and above 80% for TS40 and MPF-34 (Figure 6b). Finally, the turbidity was fully retained for all membranes. Overall, among the three membranes that presented high  $J_p$  (DK, TS40, and TS50), the DK membrane seemed at first sight to be more accurate for an industrial application aiming to purify aroma compounds relating to the TPC, TA, or DM with an incertitude about the ethanol retention effect on the selectivity during MRR increase.

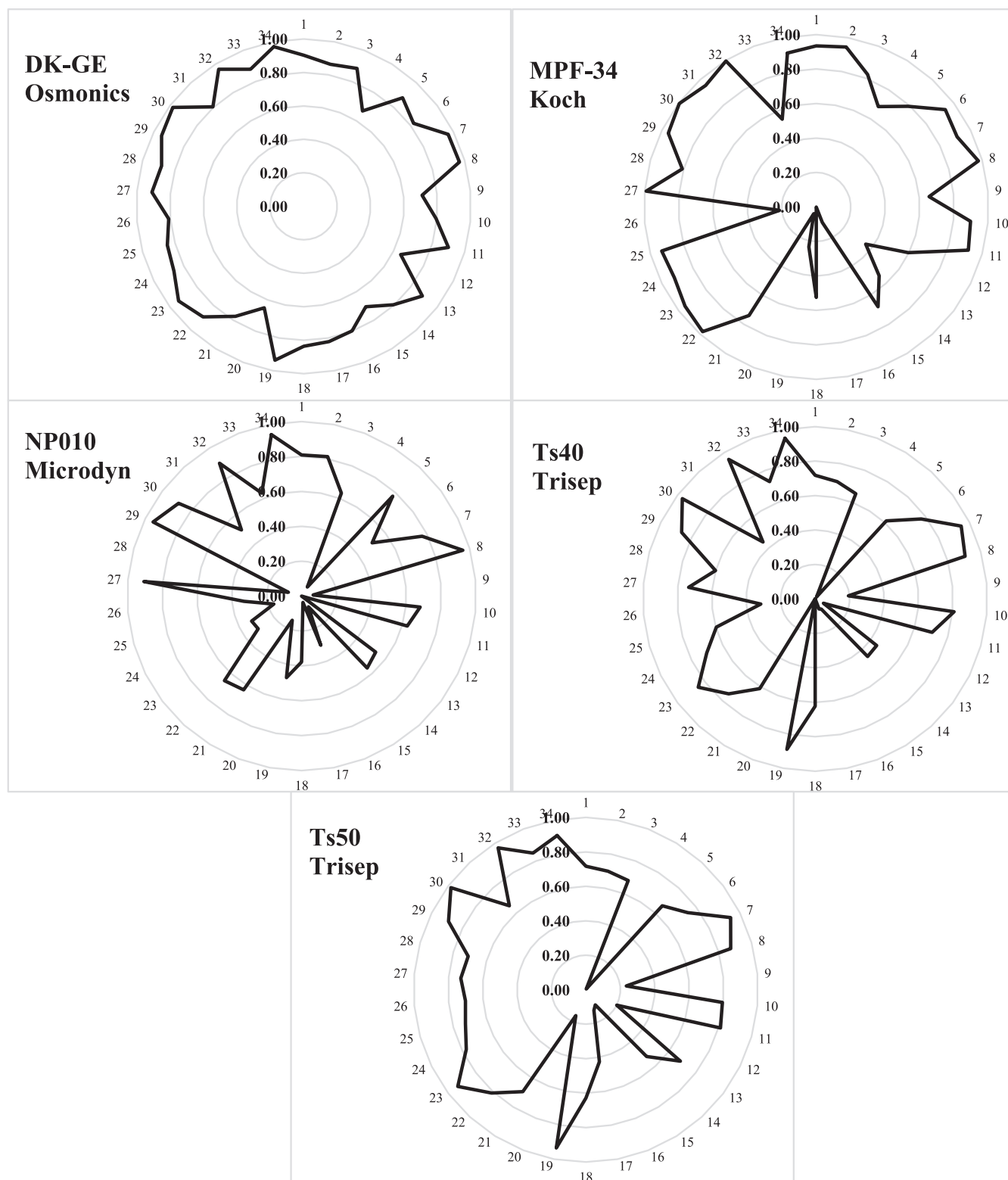
The aroma compound analysis identified the retentions of the 34 main compounds for each TMP. The average retentions of the 34 compounds for all the membranes are reported in Table 4. The mean  $Y_{\text{Distortion}}$  value (Equation 6), which quantified the distortion of the aromatic profile, allowed the classification of the membranes from the one that led to the highest impact on the aromatic profile to the one that led to its preservation. The DK membrane presented the highest retention of aromatic compounds with only an 11% aroma distortion index. This value indicated that DK retentate was very close in terms of volatile composition to the initial extract. This high retention was correlated with the TPC, DM, TA, and ethanol retentions mentioned before. The MPF-34 and TS50 membranes made a second group of  $Y_{\text{Distortion}}$ , with an average retention of around 70%, which denoted a significant impact of NF on the retentate aroma composition. Finally, the NP010 and TS40 membranes exhibited the lowest average retention, with the highest  $Y_{\text{Distortion}}$  of 60% and 54%, respectively.

The average retentions of each compound are illustrated in Figure 7 with radars for the different membranes. The volatile compound retentions for the DK membrane were graphically close to the edges, with retentions mostly above 0.80 for all compounds. The MPF-34 membrane had an interesting profile with elevated retentions for most of the compounds except acetophenone, and a

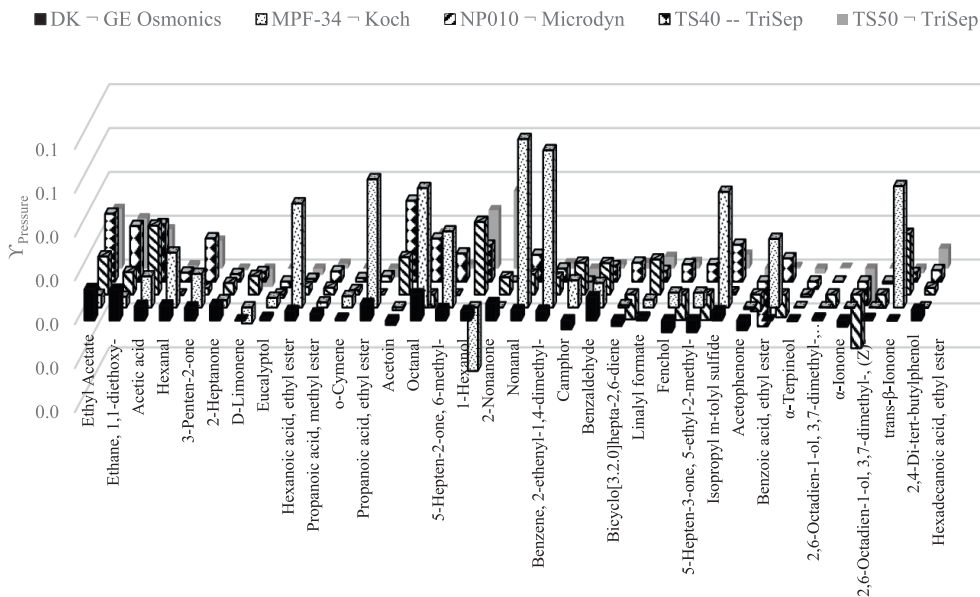
selective high rejection of all compounds numbered between 12 and 20 (acetoin, octanal, 5-hepten-2-one-6-methyl-, 1-hexanol, 2-nonanone, nonanal, benzene- 2-ethenyl-1-4-dimethyl-, camphor, and benzaldehyde). The compounds were represented by their order of elution, and therefore mainly by their order of volatility. The TS50 membrane presented a low retention of a few compounds. Among the less retained were 3-penten-2-one (no retention), 2-heptanone (66%), propanoic acid-methyl ester (24%), acetoin (22%), 1-hexanol (52%), 2-nonanone (10%), nonanal (43%), and benzaldehyde (16%). Interestingly, the same aroma compounds were concerned by a low retention on the TS40 and NP010 membranes. The NP010 membrane showed a low retention for almost all volatile compounds compared to the other membranes. Therefore, this membrane can be an interesting option to recover raspberry aroma in permeate.

The influence of the TMP on each volatile compound retention can be evaluated in Figure 8. The pressure dependence index  $Y_{\text{pressure}}$  which is the slope of retention versus TMP, is proposed in order to evaluate the effect of pressure, and therefore  $J_p$ , on retention. The DK  $Y_{\text{pressure}}$  was constant and close to 0 for all aroma compounds (Figure 8). Therefore, the DK membrane allowed all the aroma compounds in the retentate to be preserved, on the range of the TMP studied, without being influenced by the TMP. This interesting result was linked to an elevated retention above 80% (Table 4). DK  $Y_{\text{Distortion}}$  ranged from 13.4 to 11.0 depending on TMP. These results showed that there was a low dispersion of retention and a light aroma profile distortion in retentate compared to the NF initial feeding throughout the range of the TMPs studied. Therefore, retentate from the TS50 and TS40 membranes presented a change in aroma profile compared to the NF feeding extract, with a slight variation in retention during TMP increase compared to the MPF-34 and NP010 membranes (Figure 8). This could also be observed by the evolution of their  $Y_{\text{Distortion}}$  (Table 4). If the TS40 retentate aroma profile seemed similar to the TS50 one (Figure 7), its global  $Y_{\text{Distortion}}$  was slightly higher than the TS50 (53.9% for the TS40 and 41.7% for the TS50) and also varied more according to TMP from 59.1 to 49.1% (Table 4). The  $Y_{\text{Distortion}}$  of the TS50 membrane decreased from 43.9% to 39.4% with the TMP increase.

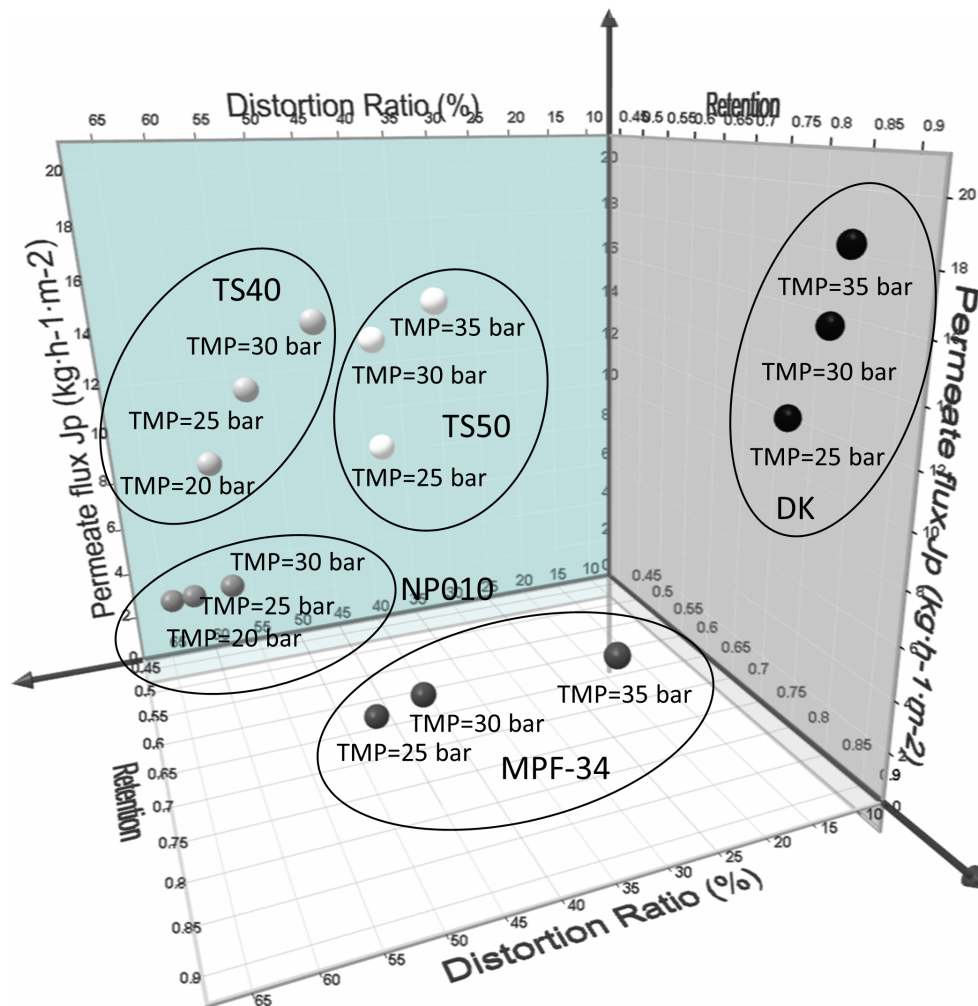
The selectivity of MPF-34 and NP010 membranes for each compound seemed more variable with the TMP increase (Figure 8). The retention of the NP010 membrane increased with TMP mainly for ethyl acetate, ethane 1-1-diethoxy, hexanal, 2-heptanone, d-limonene, acetoin,



**FIGURE 7** Retention pattern of the main aroma compounds of raspberry extract (means for all transmembrane pressures) for the DK, MPF-34, NP010, TS40, and TS50 membranes after nanofiltration at MRR = 1 using HREP, clarified by microfiltration. Compounds are presented by order of elution. Results are mean values for all transmembrane pressures. Correspondence of compounds; (1) Ethyl acetate, (2) Ethane, 1,1-diethoxy-, (3) Hexanal, (4) 3-penten-2-one, (5) 2-heptanone, (6) D-limonene, (7) Eucalyptol, (8) Hexanoic acid, ethyl ester, (9) Propanoic acid, methyl ester, (10) O-cymene, (11) Propanoic acid, ethyl ester, (12) Acetoin, (13) Octanal, (14) 5-hepten-2-one, 6-methyl-, (15) 1-hexanol, (16) 2-nonanone, (17) Nonanal, (18) Benzene, 2-ethenyl-1,4-dimethyl-, (19) Camphor, (20) Benzaldehyde, (21) Bicyclo[3.2.0]hepta-2,6-diene, (22) Linalyl formate, (23) Fenchol, (24) 5-hepten-3-one, 5-ethyl-2-methyl-, (25) Isopropyl m-tolyl sulfide, (26) Acetophenone, (27) Benzoic acid, ethyl ester, (28)  $\alpha$ -terpineol, (29) 2,6-octadien-1-ol, 3,7-dimethyl-, acetate, (Z)-, (30)  $\alpha$ -ionone, (31) 2,6-octadien-1-ol, 3,7-dimethyl-, (Z)-, (32)  $\beta$ -ionone, (33) 2,4-di-tert-butylphenol, and (34) Hexadecanoic acid, ethyl ester. HREP, hydroalcoholic raspberry extract with pectinase; MRR, mass reduction ratio.



**FIGURE 8** Slope of the curve retention versus TMP for the aroma compounds, called the pressure dependence index  $\gamma_{\text{Pressure}}$ , for each nanofiltration membrane (DK, MPF-34, NP010, TS40, and TS50) and for the set of 34 aroma compounds. All retentions were calculated at MRR = 1 using the raspberry extract with enzyme (HREP) prefiltered by microfiltration. HREP, hydroalcoholic raspberry extract with pectinase; MRR, mass reduction ratio; TMP, transmembrane pressure.



**FIGURE 9** 3D plot of the mean retentions, permeate flux ( $J_p$ ), and aromatic profile distortion index ( $\gamma_{\text{distortion}}$ ) for each membrane (DK, MPF-34, NP010, TS40, and TS50) calculated at MRR = 1 using the raspberry extract with enzyme (HREP) prefiltered by microfiltration for all TMPs. HREP, hydroalcoholic raspberry extract with pectinase; MRR, mass reduction ratio; TMP, transmembrane pressure.

1-hexanol, 2-nonanone, nonanal, camphor, benzaldehyde, linalyl formate, and trans- $\beta$ -ionone, while the retentions of benzaldehyde, fenchol, acetophenone, benzoic acid methyl ester, and  $\alpha$ -ionone decreased when the

TMP increased. Among compounds with a high dependence of retention on TMP, for the MPF-34 membrane, there were hexanal, 3-penten-2-one, hexanoic acid methyl ester, propanoic acid ethyl ester, octanal,

1-hexanone, nonanal, trans- $\beta$ -ionone, and 1-hexanol. The MPF-34 membrane showed the highest retention of the aromatic profile after the DK membrane (Table 4). However, its  $Y_{\text{Distortion}}$  was greatly influenced by the TMP augmentation (with a loss of 18.1% between 25 and 35 bar). Moreover, its selectivity was particular with a profile of “all or nothing” retention (Figure 7). This behavior may be of interest to fractionate the aroma compounds, but a change in retention when the TMP increases will make difficult the prediction of the aroma in retentate. The NP010 membrane had the highest  $Y_{\text{Distortion}}$  of all the membranes (60.1%), and so resulted in the retentate with the least similar aroma profile compared to the initial extract. This  $Y_{\text{Distortion}}$  was higher at TMP = 20 bar than at 30 bar. Thus, the permeate of the NP010 membrane had the higher content of aroma, with the  $Y_{\text{Distortion}}$  of the permeate of 35.6%, resulting in the lowest  $Y_{\text{Distortion}}$  after the DK retentate. The MPF-34 and NP010 membranes were the least accurate regarding the objective to concentrate the extract with minimal aromatic change. However, they presented interesting behavior in purifying or fractionating volatile compounds.

It is worth noting that for all the membranes,  $Y_{\text{Distortion}}$  decreased when the TMP increased. So, the more the TMP increased, the less the profiles were modified and the more similar the aromatic profiles to the initial extract were. This is in accordance with the previous statement showing that the retentions increased with TMP tending toward a plateau.

No correlation was found between the aroma compound retentions and their intrinsic characteristics, such as molar weight, boiling point, LogP, density, or solubility in water (Table S1). Ivić et al. (2021) stated during red wine filtration that this kind of generic behavior could not be established (i.e., regarding hydrophobicity, polarity, electrostatic repulsion of membrane). Along the same lines, Van der Bruggen and Vandecasteele (2002) studied, among others, the interactions between the organic compounds and NF membranes. They concluded that the influence of parameters such as the dipole moment, the octanol–water partition coefficient, the molecular size, and so on, had a significant influence on the NF membrane adsorption and fouling. However, forecasting this behavior is complex, even in a model extract. So, to better understand aroma compound retention, further study should be carried out.

A three-dimensional plot (Figure 9) was designed as a tool for the membrane selection. This representation clearly confirmed that the DK membrane stood out from the other membranes by its high retention factor linked to an elevated  $J_p$  and a low aroma distortion profile. Moreover, this membrane was also associated with a higher TPC, DM, TA, and color retention. Therefore, among all membranes assessed in this study, the DK membrane at TMP = 35 bar, would be the best option for concentration with minimal modification of the raw extract.

The MPF-34, TS40, and TS50 membranes showed an interesting range of retention, specific from one compound to another. Their positions in the representation were intermediate between the DK and NP010 performance. Their performance made them interesting for specific applications such as aroma or TPC fractionation. However, they should be avoided for the concentration or purification of raspberry aroma compounds.

NP010 performance was opposed to the DK one. The NP010 membrane presented a low  $J_p$ , a low retention of aromas, and a high distortion ratio. TPC was not retained by the membrane. Moreover, the retention of DM and TA was high (>70%). This membrane is not a good choice for HREP aroma concentration in the retentate. Nevertheless, the permeate is of interest for the purification of aroma compounds versus DM content.

## 4 | CONCLUSION

Each NF membrane presented specific performances (i.e., selectivity and permeate flux) according to its intrinsic characteristics during the filtration of a raspberry hydroalcoholic extract. It allowed different fractionation schemes to be defined under appropriate operating conditions: concentration of the aroma compounds, purification of the aroma compounds, and separation of the aroma compounds. Moreover, crossflow filtration has a low energy consumption and does not generate thermal degradation compared to concentration by conventional thermal evaporation. Among the NF membranes tested, the use of the DK one at 35 bar was the best option for aroma concentration with a high permeate flux. The use of the NP010 at 30 bar resulted in the production of a permeate with low aroma distortion, purified versus DM content. The MPF-34, TS40, and TS50 membranes were not more efficient in terms of aroma concentration in retentate but were of interest for aroma fractionation.

However, understanding the retention phenomena during the treatment of an extract with a complex composition is important to enhance the genericity toward NF applications. Moreover, if the aroma profile of the DK retentate changed slightly, it remained uncertain whether the human sensory evaluation would also change. Therefore, sensory analysis should be carried out to understand if the aroma distortions observed in this study have an impact on aroma perception. Finally, a further in-depth study should evaluate the process at higher MRR, to allow the scaling-up to an industrial level and the verification of its economic viability.

## AUTHOR CONTRIBUTIONS

**Adrien Servent:** Conceptualization; data curation; formal analysis; funding acquisition; investigation; methodology; project administration; software; supervision; validation; visualization; roles/writing—original draft; and writing—review and editing. **Lumley Hector:** Formal analysis; investigation; methodology. **Guillaume Jobard:** Resources; supervision; visualization; project administration; formal analysis. **Manuel Dornier:** Conceptualization; data curation; funding acquisition; investigation; methodology; project administration; software; supervision; validation; visualization; roles/writing—original draft; and writing—review and editing.

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## CONFLICT OF INTEREST STATEMENT

The authors declare no conflicts of interest.

## DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available on request from the corresponding author.

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