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Integrated Membrane Filtration for the Recovery of Antioxidants from Lavender Spent Plant Material

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Abstract

The present study explores the possibility of combining membrane concentration, spray drying, and low-temperature precipitation into a single process for the valorization of spent lavender biomass as a source of ingredients rich in antioxidants. Lavender spent plant material was subjected to solid–liquid extraction, and the obtained hydroalcoholic extracts were further concentrated using a dead-end membrane filtration cell (METcell) with a polyamide–urea thin-film composite X201 membrane. The feed and the obtained retentate were subsequently spray dried using a Nano Spray Dryer B-90 (BÜCHI) under different temperature conditions (120 °C and 85 °C). Low-temperature precipitation was further applied for the retentate. An eight-fold concentration of the extracts was achieved, with membrane rejection coefficients of 100% for antioxidant activity and 98.5% for dry solids content. The permeate flux ranged from 2.25 to 0.201 $L \cdot m^{-2} \cdot h^{-1}$. Spray drying at a lower inlet temperature resulted in minimal losses for antioxidant activity (below 6%). The low-temperature storage of the membrane concentrate led to clear phase separation, allowing for the recovery of a precipitated fraction. The obtained results demonstrate that the integrated approach may support the sustainable and scalable valorization of lavender by-products.

Keywords: spent lavender; membrane filtration; antioxidant activity; spray drying; precipitation

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1. Introduction

Lavender (*Lavandula* spp.) is widely grown around the world as an essential oil crop. While it is often associated with rose oil production, Bulgaria has emerged as a major producer and exporter of lavender oil since 2015, overtaking France in export value [1]. In 2021, there was a record of 18,000 hectares of lavender, from which roughly 82,000 tons of the plant were obtained, according to the Ministry of Agriculture, Food, and Forestry [2]. Studies have shown that the waste biomass from steam distillation still contains significant amounts of non-volatile phenolic compounds such as rosmarinic acid, as well as flavonoids like luteolin [3,4]. The notable total phenolic content and radical scavenging capacity of the by-products [5] are in direct connection with their antioxidant and antimicrobial activities [6–8], highlighting the importance of reusing these materials rather than discarding them and contributing to environmental issues [9].

To recover and concentrate bioactive compounds effectively, the applied methods must preserve their activity and also be suitable for industrial-scale production. Membrane-based separation has become a viable, energy-efficient, and thus economical alternative to the conventional thermal separation processes [10,11]. Techniques such as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis can selectively remove solutes based on size and charge [12]. Membrane technologies have been successfully applied in water purification, wastewater treatment, and recovering polyphenols from food and agricultural residues [13,14]. Research on food and agro-industrial by-products also shows that the use of membrane systems can concentrate polyphenols without causing thermal degradation [15].

After concentration, lavender extracts need to be stabilized so they can preserve their phenolic compounds and thus their biological activity. Spray drying is a technique that has been used in converting plant extracts into powders with improved handling, solubility, and shelf life [16]. Publications regarding the pharmaceutical applications of microparticles produced via spray drying often show that these particles have a large surface area, which can improve dissolution rates and potentially enhance the bioavailability of active compounds. This is particularly beneficial for substances that do not dissolve easily in water [17].

In addition to drying, precipitation is often used to isolate and enrich phenolic compounds from lavender extracts. Due to their partially amphiphilic characteristics, bioactive compounds such as rosmarinic acid, luteolin, and quercetin can be selectively recovered, thereby increasing the antioxidant and antimicrobial activities of the analyzed fractions [18,19].

The present study aims to investigate the possibility and conditions to combine membrane concentration, spray drying, and precipitation as an integrated approach to turn lavender by-products into valuable ingredients for various industries.

The membrane pre-concentration of the spent lavender biologically active extract prior to spray drying or precipitation has not been reported in the literature. Despite the potential of membrane concentration of the hydroalcoholic extract being illustrated in previously reported research [5], in the present study, for the first time, we achieved a practically viable eight-fold degree of concentration.

2. Materials and Methods

2.1. Materials

Spent lavender biomass used in this study was supplied by Galen N Ltd. (Zelenikovo, Bulgaria). The plant material originated from *Lavandula angustifolia* grown in the Chirpan region (Bulgaria). It was collected directly after the industrial steam distillation for essential oil production at the Galen N Ltd. facility. The residual biomass consisted of stems, flowers, and leaves. Drying was performed under ambient conditions in a ventilated environment sheltered from direct sunlight. Subsequently, the dried material was milled, homogenized, and stored in airtight containers in the dark until further use.

All reagents were of analytical grade. Absolute ethanol (99%) was purchased from Valerus Ltd. (Sofia, Bulgaria) and 2,2-diphenyl-1-picrylhydrazyl (DPPH•) from Sigma–Aldrich (Darmstadt, Germany). High-purity solvents and reference standards for HPLC analysis were acquired as follows: anhydrous methanol and acetonitrile (ChromaAR HPLC Super Gradient, Macron Fine Chemicals, Phillipsburg, NJ, USA), deionized water (ChromaAR HPLC, Macron Fine Chemicals, Phillipsburg, NJ, USA), rosmarinic acid (>97%, Sigma Aldrich, Darmstadt, Germany), and luteolin (97%, Alfa Aesar, Ward Hill, MA, USA).

The membrane used was a reverse osmosis polyamide–urea thin film composite (PA-Urea-TFC, NaCl rejection 99.5%) X201 membrane provided by Trisep (Goleta, CA,

USA), as well as cellulose acetate microfiltration discs with a pore size of 0.45 µm and diameter of 90 mm (Chemplus Scientific Ltd., Danyang, China), supplied by Biotechlab (Sofia, Bulgaria).

2.2. Methods

2.2.1. Solid–Liquid Extraction of Spent Lavender Biomass

The extraction was conducted according to previously reported methodology by Chilev et al. [3]. The experimental setup is shown in Figure 1.

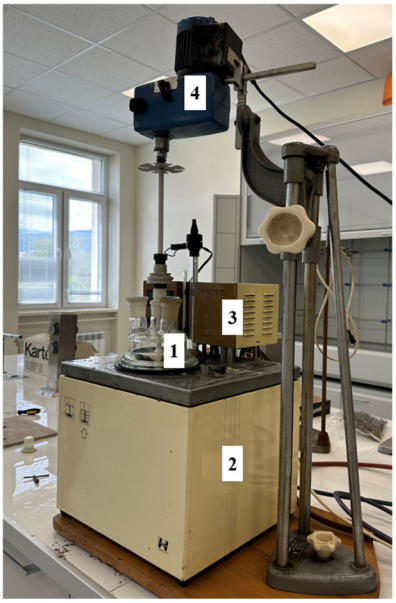

Figure 1. Extraction setup: 1—extraction flask; 2—thermostatic water bath with stirring; 3—temperature controller; 4—mechanical stirrer.

2.2.2. Membrane Filtration

Batch membrane filtration was conducted using the dead-end membrane filtration cell METcell (Evonik Membrane Extraction Technology, London, UK). The cell is designed to operate with round polymeric flat sheet membranes (effective area 54 cm^2) at a working pressure of up to 69 bar and with a maximum feed volume of 250 mL. The laboratory setup is shown in a previous publication [5].

To minimize the concentration polarization, the stirring rate was maintained at 350 rpm. The experiment was carried out at an ambient temperature (20 ± 2 °C) and an operating pressure of 20 bar, supplied by high-purity (99.996%) compressed nitrogen cylinder. Prior to nanofiltration, the feed solution was microfiltrated through cellulose acetate membranes with pore sizes of 0.45 µm. Each experiment was performed with a new membrane in order to preclude the so-called "memory" effect on membrane properties. According to a number of studies [20–22], reverse osmosis membranes require pretreatment through solvent permeation until a steady flux is attained. In this work, the membranes were conditioned by permeation of 40% v/v ethanol at 20-bar transmembrane pressure until a stable permeate flux was reached and at least 160 mL of permeate had been collected. This procedure was intended to minimize the compaction effects in later stages of the experiment and to remove the conditioning agent applied to preserve the membrane structure.

For all batch experiments, 170 mL of the extract of spent lavender (V_F) was fed into the METcell. The permeate was continuously collected in a graduated cylinder during the process, while the collection time for 148.75 mL of permeate was determined with a stopwatch. Upon completion of the membrane filtration, 21.25 mL of retentate (V_R)

remained in the dead-end cell. The degree of feed volume reduction, expressed as V_F/V_R, was therefore 8 in all membrane filtration experiments. Finally, samples of the feed and its membrane-filtered fractions were collected for determination of antioxidant capacity and content of key biologically active compounds (KBAC).

The evaluation of membrane selectivity was carried out using rejection coefficients (R), determined through two distinct approaches. The first was based on the antioxidant activity and uses the deviation in the absorbance per milliliter (AU/mL) undiluted sample (see Section 2.2.5), as calculated by Equations (1)–(3). The second relied on the absolute concentrations of individual key components, measured by HPLC analysis in accordance with Equations (5)–(7):

$$R_1 = \left(1 - \frac{\frac{\Delta Abs_P}{mL_P}}{\frac{\Delta Abs_F}{mL_F}}\right)100, [\%] \quad (1)$$

$$R_2 = \left(1 - \frac{\Delta Abs_P/mL_P}{\Delta Abs_R/mL_R}\right)100, [\%] \quad (2)$$

$$R_3 = \left(1 - \frac{lg\left(\frac{\Delta Abs_R/mL_R}{\Delta Abs_F/mL_F}\right)}{lg(V_F/V_R)}\right)100, [\%] \quad (3)$$

$$Err = \frac{V_F\Delta Abs_F/mL_F - [V_P\Delta Abs_P/mL_P + V_R\Delta Abs_R/mL_R]}{V_F\Delta Abs_F/mL_F}100, [\%] \quad (4)$$

$$R_{4,i} = \left(1 - \frac{C_{P,i}}{C_{F,i}}\right)100, [\%] \quad (5)$$

$$R_{5,i} = \left(1 - \frac{C_{P,i}}{C_{R,i}}\right)100, [\%] \quad (6)$$

$$R_{6,i} = \left(1 - \frac{lg(C_{R,i}/C_{F,i})}{lg(V_{F,i}/V_{R,i})}\right)100, [\%] \quad (7)$$

$$Err = \frac{V_{F,i}C_{F,i} - [V_{P,i}C_{P,i} + V_{R,i}C_{R,i}]}{V_{F,i}C_{F,i}}100, [\%] \quad (8)$$

where $\Delta Abs_F/mL_F$, $\Delta Abs_P/mL_P$, and $\Delta Abs_R/mL_R$ correspond to the absorbance deviation per milliliter (AU/mL) for the undiluted feed, permeate, and retentate, respectively. The symbols $V_{F,i}$, $V_{P,i}$, and $V_{R,i}$ denote the volumes of the corresponding fractions, whereas $C_{F,i}$, $C_{P,i}$, and $C_{R,i}$ represent, respectively, the concentrations of the KBAC or the DS content in the feed, permeate, and retentate. Thus, the subscript i refers to the measured parameter, where $i = KBAC$ or $i = DS$.

Equations (4) and (8) were used to compute the deviation from the material balance when employing the two approaches for assessing membrane selectivity discussed above.

2.2.3. Spray Drying

Spray drying experiments were performed using the Nano Spray Dryer B-90 (BÜCHI Labortechnik AG, Flawil, Switzerland), with the experimental setup depicted in Figure 2.

Nitrogen was used as the drying gas, supplied by an aspirator equipped with a filter to ensure a constant flow. The gas was heated by an electric coil and directed downward through the apparatus, passing through the spray head, where the suspension was atomized via a peristaltic pump. The spray head contained a piezoelectric actuator that vibrated a stainless-steel membrane with conically shaped openings. For this study, a membrane with 7 μm openings was selected to minimize particle agglomeration.

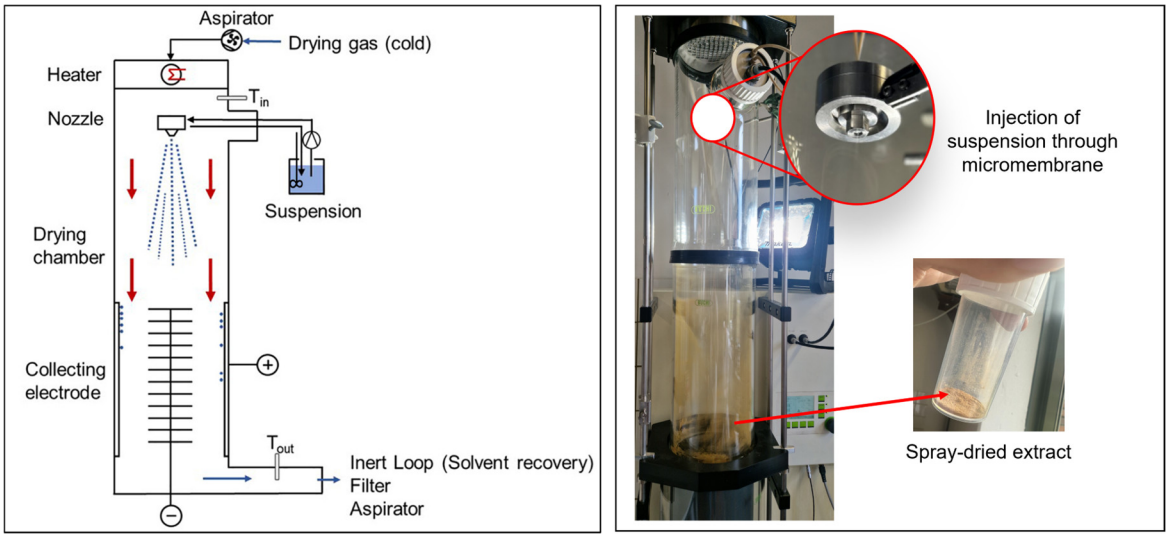

Figure 2. Scheme of the operation principle of the Nano Spray Dryer B-90 (Büchi Labortechnik AG, Flawil, Switzerland) (**a**); laboratory setup for spray drying process (**b**).

Within the drying section, the atomized droplets were exposed to a heated gas stream, causing rapid evaporation of the liquid. The resulting particles were separated from the gas flow by a high-voltage electric field and collected on a deposition electrode for subsequent retrieval. The filtered nitrogen gas exited the dryer, entered an inert loop for cooling, and underwent condensation to recover the evaporated liquid before being recycled back to the aspirator.

Two sets of operating parameters were examined, utilizing inlet gas temperatures of 120 °C and 85 °C. Gas volume flow rates were set to 130 L/h. The extract obtained from lavender waste plant material (27.05 g, 29.15 mL) was spray dried at 120 °C for 4.5 h. The retentate (20.58 g, 22 mL) was dried at 85 °C for 3 h. The spray rate was kept constant during both drying experiments.

To ensure uniform particle distribution, the suspension was continuously stirred. Pure ethanol was initially sprayed to test system functionality. Following successful ethanol evaporation and stable process conditions, the suspension was introduced, and the drying process commenced. Process parameters were recorded at 15 min intervals.

Once the suspension had been completely sprayed, the system was flushed with pure solvent to remove residual material from the spray head and tubing. The nitrogen supply was then discontinued, and the spray dryer and aspirator were powered down. After the system had cooled, the apparatus was disassembled, and the particles were collected from the deposition electrode.

2.2.4. Precipitation of Membrane-Concentrated Extract from Spent Lavender Biomass

Low-temperature precipitation of membrane-concentrated extract from lavender spent biomass was conducted. The retentate (concentrate) was stored in a cooling unit at 4 °C for 24 days. After completion of the experiment, the formation of two distinct phases—the supernatant and the precipitate—was clearly observed. The supernatant was then carefully decanted, and the wet precipitate was subsequently dried at room temperature 20 ± 2 °C.

The progress of drying of the precipitate was assessed by periodical measurement of its mass. The process continued for a total of 24 days. The samples were weighed every fourth day. Complete drying was assumed when no significant change in weight was observed between three consecutive measurements. The mass deviation between the last three consecutive measurements was less than 0.54%.

For analytical purposes, the resinous precipitate was diluted in 40% v/v ethanol in a ratio corresponding to the volume of the retentate from which it was derived. The resulting solution was used for determination of KBAC, as well as for antioxidant analyses.

2.2.5. Antioxidant Activity

The antioxidant activity of the extract obtained from spent lavender biomass was determined through the interaction between the DPPH (2,2-diphenyl-1-picrylhydrazyl) free radical and the antioxidant compounds present in the sample. Determination of antioxidant capacity was carried out spectrophotometrically. In ethanolic solution, DPPH• exhibits a strong absorption band with a maximum at 517 nm, while its reduced form shows negligible absorbance, allowing for quantitative colorimetric determination [5,23].

The experimental setup involved preparing a 0.1 mM DPPH solution in absolute ethanol (99.9%), which exhibited an absorbance in the range of 0.8–0.9 AU. The assay was conducted in disposable polystyrene cuvettes (3 mL volume, 10 mm path length) using a T70 UV/Vis spectrophotometer (PG Instruments Ltd., Lutterworth, UK). The reaction mixture consisted of 1.50 mL of the DPPH solution and 0.05 mL of the sample at the respective degree of dilution. A control containing 1.50 mL of DPPH solution and 0.05 mL of absolute ethanol was prepared, while the blank for all tested samples consisted of 1.55 mL of absolute ethanol. Each sample was analyzed in quintuplicate. Absorbance was recorded at 15 min intervals over a period of 1 h (measurements at 0, 15, 30, 45, and 60 min).

The scavenging efficiency of the tested samples against the DPPH radical was calculated according to Equation (9):

$$\Delta Abs = A_c - A_s \quad (9)$$

where A_c and A_s correspond to the absorbance of the control and the tested sample, respectively. The change in the absorbance per milliliter of the undiluted sample was calculated as follows:

$$\Delta \frac{Abs}{mL} = \frac{\Delta Abs \times (timesdilution)}{0.05} \quad (10)$$

According to Equation (10), the value of the $\Delta Abs/mL$ was independent of the degree of sample dilution and of the absorbance of the control during the analyses. Consequently, the value of this parameter at 60 min of reaction was used for quantitative assessment of the absolute antioxidant capacity of the samples.

2.2.6. HPLC Analysis

Quantification of KBAC in the 40% v/v ethanol extract of spent lavender biomass was performed by high-performance liquid chromatography (HPLC). HPLC is widely applied for the analysis of natural extracts rich in phenolic acids (rosmarinic acid [24,25]) and flavonoids (luteolin [26,27]) because of its high reliability and precision in compound identification and quantification [28–30]. The analytical procedure applied in this work was adapted from previously reported protocols and had already been validated in earlier investigations by our research group [3,5,31].

The chromatographic analyses were carried out on a Hewlett Packard (HP) Series II 1090 liquid chromatography system equipped with a UV/Vis diode array detector (Hewlett Packard, Palo Alto, CA, USA). Separation was performed on an Agilent C18 column (150 mm × 4.6 mm, 5 µm particle size). The operating conditions were as follows: column temperature 30 °C, flow rate 0.7 mL/min, and injection volume 5 µL. The mobile phase consisted of solvent A (75 mL acetonitrile + 420 mL water + 4.25 mL acetic acid) and solvent B (methanol). A 105 min gradient program was developed to achieve optimal separation under the following conditions: (1) 0–90 min, B: 0–100%; (2) 90–103 min, B: 100%; (3) 103–104 min, B: 100–0%; and (4) 104–105 min, B: 0%. Detection was set at two

wavelengths: 330 nm for rosmarinic acid and 360 nm for luteolin. Identification of analytes was based on the comparison of retention times with those of authentic standards.

Calibration was performed using at least five concentration levels in the range of 0–2 g/L for each compound. The linear correlation coefficients (R^2) for all calibration curves were higher than 0.996.

In our previous publication, the ethanol content of the solvent was determined by gas chromatography (GC) to confirm that the membrane separation did not alter the solvent composition [5].

2.2.7. Dry Solids Determination

The determination of dry solids (DS) in liquid samples of waste fractions from essential oil production was carried out using a laboratory oven (BD 23, Binder GmbH, Tuttlingen, Germany). The samples were evenly distributed in pre-heated glass Petri dishes to ensure homogeneous and effective drying. The applied sample volumes were as follows: feed—7 mL, permeate—20 mL, and retentate—3 mL. For the determination of DS in the supernatant obtained after precipitation of lavender retentate, 1 mL aliquots were prepared. All analyses were performed in triplicate. The prepared samples were dried at 50 °C and atmospheric pressure for 24 h. After complete drying, the residues were weighed, and the DS content was expressed as grams of DS per liter of initial solution.

3. Results and Discussion

3.1. Flux Determination

The cumulative volume collected per unit membrane area as a function of time can be fitted by a second-order polynomial (Equation (11)):

$$\frac{V}{A} = at + bt^2 \tag{11}$$

Differentiation of this expression provides the instantaneous flux J:

$$J = \frac{dV}{Adt} = a + 2bt \tag{12}$$

In the case of solvent flux (J_s) during the conditioning stage, the initial transient decrease is primarily due to membrane compaction and the removal of the conditioning agent. Once conditioning is complete, a steady-state J_s is established, which is considered representative of the intrinsic membrane permeability and serves as a reference for subsequent experiments. Therefore, description of the solvent flux evolution with time during membrane conditioning was out of the scope. In the present study, the steady-state solvent flux (J_s) was determined as 8.39 L m^{-2} h^{-1}, which is reasonable when compared to previously reported data for the same membrane and operating conditions (11.7 L·m^{-2}·h^{-1}) [5]. The permeate flux (J_p) during the filtration of real feed solutions decreased with time, reflecting the combined effects of concentration polarization and membrane fouling. In this study, the nonlinear regression performed in MATLAB R2025a was applied to the experimental data for the permeate flux, yielding coefficients of a = 2.2498 and b = −0.0465 with a correlation coefficient (R^2 = 0.9945). The experimental results for the cumulative permeate volume are shown in Figure 3.

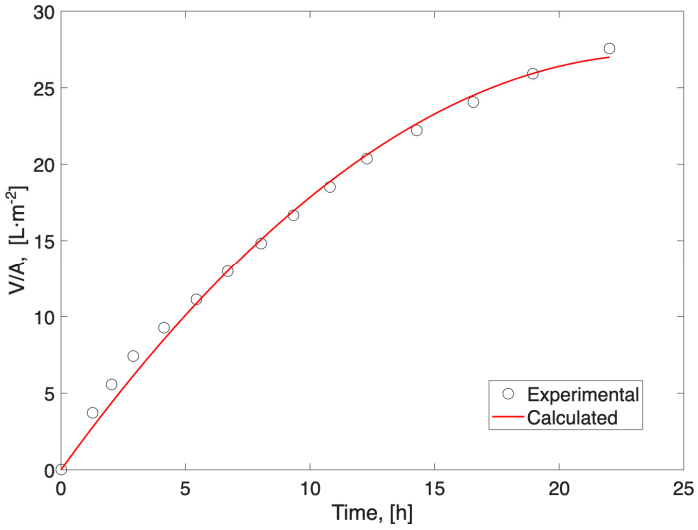

Figure 3. Cumulative permeate volume per unit membrane surface area as a function of collection time. Points—experimental data; curve—calculated via Equation (11).

Permeate flux variation with time during membrane filtration of extract of spent lavender biomass using the X201 membrane, as described by Equation (12), is illustrated in Figure 4.

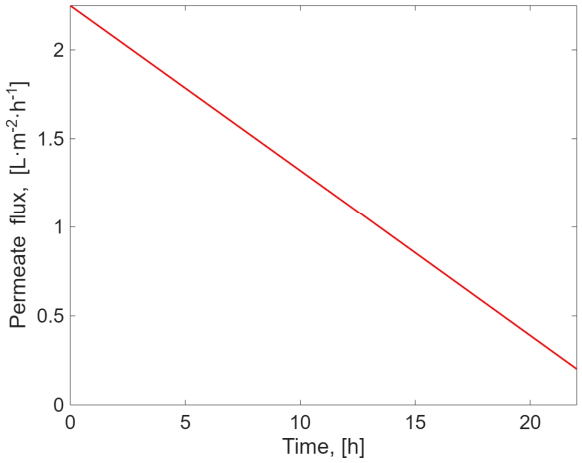

Figure 4. Permeate flux ($L \cdot m^{-2} \cdot h^{-1}$) as a function of time (hours) during batch membrane filtration of spent lavender extract at a transmembrane pressure of 20 bar using the X201 membrane, in accordance with Equation (12).

In Figure 4, one can see that immediately after contact of the membrane with the liquid extract, the permeate flux drops approximately four times from the steady-state solvent flux of 8.39 $L \cdot m^{-2} \cdot h^{-1}$ to somewhat above 2 $L \cdot m^{-2} \cdot h^{-1}$. A plausible explanation for this multiple simultaneous permeate flux decline can be the interaction of the extract components with the membrane functional groups, which increases the intrinsic membrane resistance to the filtration process. This adversely impacts the economic viability and is often a major challenge to the implementation of the membrane filtration technology in the processing of biologically active extracts from aromatic plants. An inside view into the nature of this interaction and its more precise quantification can be gained experimentally via cross-flow membrane filtration in steady-state mode, using the same membrane–extract system. During the dead-end batch concentration in the present work, the permeate flux declined linearly versus process time and proportionally to the DFVR. This indicates that

during the process, only the build-up of osmotic pressure and concentration polarization (mass transfer) resistances affect the productivity (Section 3.3).

3.2. Membrane Selectivity Against Total Antioxidant Activity and Key Biologically Active Constituents

The radical scavenging behavior of the spent lavender extract and its membrane separation fractions was investigated to assess the selectivity of the X201 membrane. The purpose of the experiment was to define a standardized reaction time that would allow for consistent evaluation of the absolute antioxidant capacities of the tested materials. Figure 5 illustrates that all three samples exhibited a rapid reaction with the DPPH• radical during the first 30 min, after which the reaction reached a plateau, indicating equilibrium. Accordingly, a standardized reaction time of 60 min was adopted.

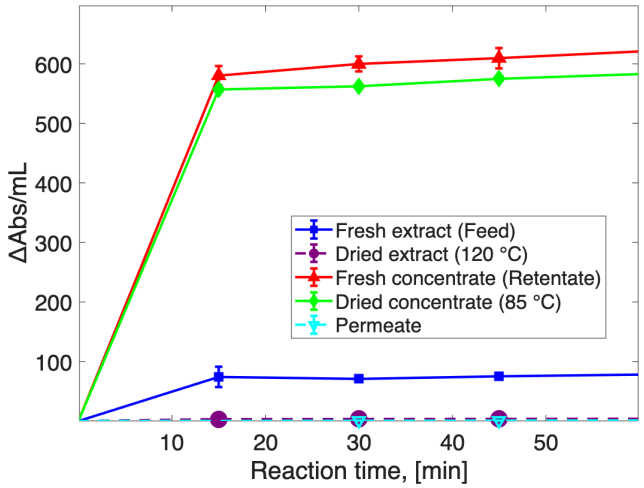

Figure 5. Kinetics of DPPH• radical scavenging using fresh and dried (120 °C) lavender extracts, membrane-filtered fractions—lavender retentate (fresh and dried at 85 °C)—and permeate.

The results in Figure 5 show that the retentate possessed nearly eight times higher antioxidant potential compared to the feed, whereas the permeate exhibited negligible activity. These observations indicate an almost complete retention of antioxidant compounds in the solutions, leading to their effective concentration in the retentate.

Membrane rejection coefficients were used to quantitatively assess the selective retention of antioxidant constituents from the spent lavender extract by the X201 membrane. Using Equations (1)–(3), the coefficients were determined as R_1 = 98.7%, R_2 = 99.8%, and R_3 = 100%, respectively. The deviation from the material balance during batch membrane concentration of the lavender waste extract in 40% v/v ethanol was calculated according to Equation (4) and was found to be 0.096%.

Table 1 summarizes the calculated membrane rejection coefficients with respect to the key biologically active compounds, as well as the deviations from the material balance obtained using Equation (8). HPLC analysis confirmed the presence of rosmarinic acid and luteolin in the 40% v/v ethanolic extract of spent lavender biomass.

The membrane filtration results demonstrate high selectivity and efficiency in concentrating rosmarinic acid. The retention coefficients for rosmarinic acid ($R_{4,KBAC}$ = 70.4%, $R_{5,KBAC}$ = 95.2%, and $R_{6,KBAC}$ = 86.4%) confirm the good selectivity of the X201 membrane.

Luteolin was detected in all fractions, yet its apparent retention was lower than that of rosmarinic acid. This behavior can be described with its smaller molecule size resulting in higher membrane permeability.

Table 1. Experimental data on membrane filtration of lavender spent biomass extract and its fractions using the X201 membrane at 20 bar.

Component	Fraction	Concentration, [mg/L]	Membrane Rejection, [%]			Material Balance Deviation, [%]
			$R_{4,KBAC}$	$R_{5,KBAC}$	$R_{6,KBAC}$	
Rosmarinic acid	Feed	71.0	70.4	95.2	86.4	1.85
	Permeate	21.0				
	Retentate	437				
Luteolin	Feed	97.0	40.9	85.1	65.9	3.03
	Permeate	57.3				
	Retentate	386				

$R_{6,KBAC}$ was used as the objective indicator for evaluating the membrane retention capability, as it was derived from the material balance of the batch membrane concentration under the assumption of constant rejection (independent of the concentration of the filtered solution). It is therefore plausible as long as the deviation from the material balance is sufficiently low, which was justified in the present study. The difference between $R_{4,KBAC}$ and $R_{5,KBAC}$ is not unexpected, given that by definition they are dependent on the chosen DFVR, which, in the present work, was relatively high.

The higher rejection coefficient measured for total antioxidant activity compared to the one for both rosmarinic acid and luteolin indicates that there are also higher-molecular-weight antioxidant constituents of the extracts (e.g., flavonoid glycosides), which were not identified chromatographically, but they are completely rejected by the membrane.

3.3. Process Resistance Due to Osmotic Pressure and Concentration Polarization

The relationship between process resistance and retentate concentration during batch membrane filtration has been investigated in several previous studies. Peev et al. [32] were the first to demonstrate this dependence for hydroalcoholic extracts of lemon balm, and it was later confirmed for 40 vol% ethanolic extracts of spent lavender biomass [5]. In both cases, the combined resistance, arising from osmotic pressure and concentration polarization, followed a power-law relationship with respect to the retentate concentration.

In the present study, no signs of membrane fouling or formation of a surface cake layer were observed during the filtration of the spent lavender extract. Therefore, the additional resistances—beyond the intrinsic membrane resistance—resulting from the osmotic pressure difference across the membrane R_O and concentration polarization in the retentate R_P were calculated as time-dependent functions according to Equation (13) [33]:

$$(R_O + R_P)_t = \Delta P\left(\frac{1}{J_P} - \frac{1}{J_S}\right) \quad (13)$$

In the classical resistance-in-series model [34], the resistance unit is m^{-1}; however, in this study, all resistance values were multiplied by the viscosity of the solutions, which changed the unit to $kg \cdot m^{-2} \cdot h^{-1}$. The viscosities of the solvent, extract, and its fractions were assumed constant, as the ethanol concentration did not change during filtration and the extracts represented relatively dilute hydroalcoholic systems. Under these conditions, the application of the modified resistance model was considered both theoretically and experimentally justified.

Due to the high rejection of the membrane, the permeate concentration was assumed negligible, and the instantaneous retentate concentration $C_R(t)$ was calculated according to Equation (14) [5].

$$C_R(t) = C_F \frac{V_F}{V_F - A\left(at + bt^2\right)} \quad (14)$$

Figure 6 presents the combined process resistance ($R_O + R_P$) as a function of the current retentate concentration, calculated using Equations (13) and (14). The resulting straight line in double-logarithmic coordinates showed a power-law dependence described by Equation (15):

$$R_O + R_P = kC_R^n \quad (15)$$

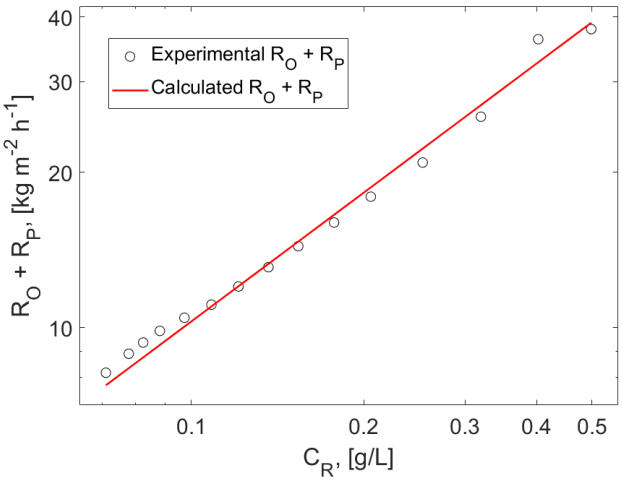

Figure 6. Additional resistance induced by osmotic pressure and concentration polarization versus retentate concentration, with experimental data (points) and model predictions (solid line).

The obtained straight line in the double-logarithmic plot yielded parameter values of k = 69.55 and n = 0.8305, with a regression coefficient of 0.9845, confirming the good agreement between the model and the experimental data. The value of n falls within the characteristic range of 0.8–1.2 previously reported for hydroalcoholic systems enriched in rosmarinic acid [5,32]. This agreement suggests that the same concentration–resistance dependence is valid for the spent lavender extract investigated here. As demonstrated in earlier work, once the slope n is established for a given extract, it can be used to estimate the process resistance at other solute concentrations. After determining the intercept k through an initial measurement, resistance values at different concentrations can be predicted by extrapolating the line defined by the known slope.

3.4. Assessment of Spray Drying Efficiency in Relation to Antioxidant Activity

Figure 5 illustrates the reaction kinetics between the DPPH• free radical and the antioxidant constituents in the different samples: fresh extract, dried extract (120 °C), fresh retentate, and dried retentate (85 °C).

As shown in Figure 5, all analyzed samples exhibited a rapid reaction with the DPPH• radical, with the process being essentially completed within the first 20 min. Subsequently, the reaction curves reached a stable plateau that was maintained until the completion of the 60 min measurement period. High-temperature drying (120 °C) led to a pronounced reduction in the antioxidant activity of the fresh extract, resulting in an approximate 95% loss of its initial activity (from $\Delta Abs/mL$ = 78.05 to $\Delta Abs/mL$ = 3.86). These findings indicate that exposure to a 120 °C operating temperature leads to thermal degradation of the bioactive compounds.

The fresh retentate exhibited high antioxidant activity ($\Delta Abs/mL$ = 620.6). Drying at a lower temperature (85 °C) caused only a minor loss of activity—about 6%—resulting in a final value of $\Delta Abs/mL$ = 582.8. These results emphasize the pronounced influence of drying temperature on antioxidant activity. Whereas high-temperature drying (120 °C) leads to thermal degradation of bioactive constituents, drying at a lower temperature (85 °C) effectively preserves the active compounds.

3.5. Evaluation of the Effect of Precipitation on the Antioxidant Activity

The effect of precipitation on the antioxidant activity was evaluated by examining the kinetics of the DPPH• radical scavenging reaction. The retentate, as well as the precipitate and the supernatant generated during the precipitation process, were subjected to analysis. The precipitate was re-dissolved in 40% v/v ethanol–water solvent in a volume equivalent to that of the retentate from which it was obtained (0.4802 g in 20 mL) in order to assess its antioxidant capacity. The results are presented in Figure 7.

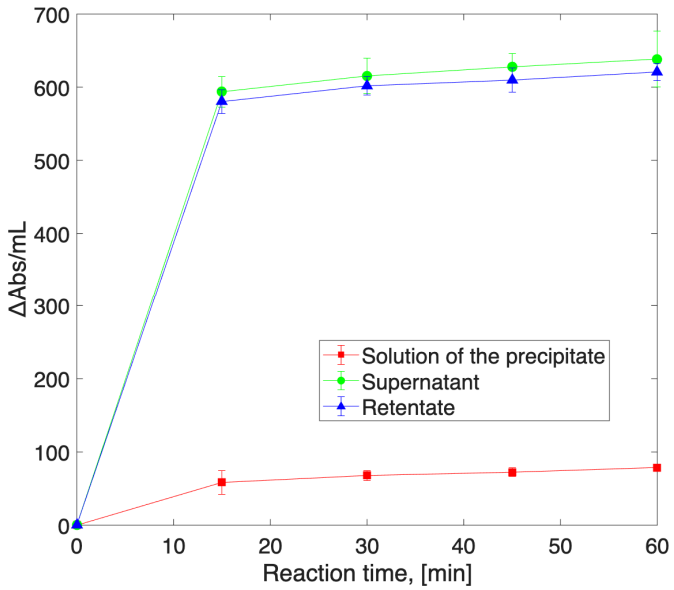

Figure 7. Kinetics of the radical scavenging reaction between DPPH• and the samples obtained from the precipitation process: retentate, supernatant, and solution of the precipitate (solid content 24.0 g/L).

During the initial stage of the reaction, all fractions exhibited a rapid increase in $\Delta Abs/mL$ values, reflecting an intensive radical scavenging phase within the first 30 min. Subsequently, the curves reached a plateau, suggesting depletion of the reactive compounds or attainment of equilibrium.

The solution of the precipitate exhibited the lowest antioxidant activity ($\Delta Abs/mL$ = 78.80), indicating a relatively low content of soluble active compounds and, consequently, a low antioxidant potential. Therefore, the precipitate can be regarded as a residual by-product. In contrast, the supernatant displayed the highest $\Delta Abs/mL$ value (638.5), surpassing that of the retentate (620.6), exhibiting an approximately 3% higher antioxidant activity, most likely due to its higher content of phenolic compounds. Since these compounds are well soluble in the 40% ethanol solvent, they remain predominantly in the supernatant. The obtained results confirm the efficiency of the precipitation process in refining the membrane-concentrated polyphenolic fraction.

3.6. DS Determination

Table 2 presents the DS results for the extract from spent lavender biomass, in the membrane concentration fractions (retentate and permeate), as well as in the samples derived from the lavender retentate precipitation.

Table 2. Results of DS determination and compositional analysis.

Fraction	DS, [g/L]	Concentration of Component in Sample, [g/L]		Component Content in Sample, [%]		Relative Content of Identified Components (%)
		Rosmarinic Acid	Luteolin	Rosmarinic Acid	Luteolin	
Feed	16.6 ± 0.500	0.071	0.097	0.428	0.584	1.01
Permeate	0.732 ± 0.012	0.021	0.057	2.87	7.83	10.7
Retentate	132 ± 0.540	0.437	0.386	0.331	0.292	0.623
Supernatant	115 ± 2.70	0.526	0.404	0.457	0.351	0.809
Solution of precipitate	24.0 ± 0.001	0.11	0	0.458	0	0.458

The results show that the DS content in the retentate (132 ± 0.540 g/L) is approximately eight times higher than that in the feed (16.6 ± 0.500 g/L), clearly confirming the successful eight-fold membrane concentration. The results of the antioxidant activity analysis of the membrane-concentrated fractions of the spent lavender extract ($\Delta Abs/mL$ values for: feed—78.05; permeate—1.01; and retentate—620.55) are consistent with the permeate's low DS content (0.732 ± 0.012 g/L).

The membrane rejection coefficients calculated based on DS content further support the efficiency of the concentration process, yielding $R_{4,DS}$ = 95.6%, $R_{5,DS}$ = 99.4%, and $R_{6,DS}$ = 98.5%. The close correspondence between the DS-based ($R_{4,DS}$, $R_{5,DS}$, and $R_{6,DS}$) and antioxidant activity-based rejection coefficients (R_1, R_2, and R_3) indicates a strong correlation between dry solids content and the concentration of antioxidant constituents in the fractions. Overall, these findings confirm that both $\Delta Abs/mL$ and DS serve as reliable and mutually consistent indicators of membrane rejection and concentration performance.

The component analysis of the DS illustrates that the antioxidant compounds (rosmarinic acid and luteolin) represent a higher percent of the composition of the dissolved matter in permeate compared to the one in feed and retentate. This allies with the experimentally determined lower rejection coefficients for the KBAC compared to those for DS and total antioxidant activity.

The DS concentration in the C_{SN} supernatant, obtained after precipitation of the concentrate, was found to be 115 g/L. The dry mass of the precipitate m_{RPR} in a 20 mL sample was 0.480 g, indicating a substantial accumulation of insoluble components. For the determination of key biologically active components, the precipitate was re-dissolved in 40% v/v ethanol in a volume equivalent to that of the retentate from which it was obtained. The DS content in the resulting solution was calculated as 24.0 g/L. According to the HPLC results, the majority of luteolin and rosmarinic acid was detected in the liquid phase, or supernatant, whereas only a small amount of rosmarinic acid was present in the precipitate after precipitation. This demonstrates that the precipitation of lavender retentate allows for further concentration of antioxidant constituents in the liquid fraction. These findings align with the antioxidant activity measurements of the precipitation samples, as the supernatant displayed roughly 3% higher antioxidant capacity. The loss of small amounts of rosmarinic acid in the precipitate can be explained by the removal of high-molecular-weight compounds, which tend to form a semi-solid precipitate that entraps soluble substances. This behavior is consistent with the well-documented "dewaxing"

phenomenon, in which insoluble or partially soluble macromolecules separate from the ethanolic extract. Examples of such macromolecules include waxes, pectins, and other polysaccharides. As a result of the dewaxing process, a refined polyphenolic fraction enriched in low-molecular-weight bioactive compounds is obtained [35,36], potentially enhancing the stability, solubility, and bioavailability of the extract.

The deviation in the material balance for DS during the precipitation process was determined using Equation (16):

$$Err = \frac{C_R V_R - (m_{RPR} + C_{SN} V_{SN})}{C_R V_R} 100, [\%] \quad (16)$$

where C_R is the DS concentration in the retentate (132 g/L), V_R is the volume of the retentate (0.020 L), C_{SN} is the DS concentration in the supernatant (115 g/L), and V_{SN} is assumed to be equal to V_R, since the amount of precipitate is negligible and does not significantly affect the total liquid volume.

The material balance deviation obtained after the precipitation process was 11.9%. The relatively high deviation can be attributed to the partial loss of material due to the volatilization of minor components during drying of the precipitate and the assumption for equality between the volumes of the supernatant and the retentate subjected to precipitation.

4. Conclusions

The present study demonstrates the feasibility of applying membrane filtration as an effective method for concentration of the hydroalcoholic liquid extracts from spent lavender plant biomass. The benefits from its accomplishment with other gentle downstream processes such as spray drying and low-temperature precipitation were experimentally demonstrated.

Building upon previous work, the membrane concentration step was performed at an increased degree of feed volume reduction (DFVR from 2 to 8) in dead-end batch membrane filtration mode. The extract was successfully concentrated without the formation of a solid phase at 20 °C and 20-bar operating pressure. The results confirm that the X201 membrane operates reliably under such conditions and maintains stable performance. This outcome is particularly important for potential industrial implementation, where the use of spiral-wound membrane modules requires stable operation without membrane fouling or membrane element blockage due to spontaneous solids precipitation. The practically achieved eight-fold concentration of the fresh extracts with respect to both total antioxidant activity and dry solids content correlates with the experimentally determined membrane rejection coefficients of 100% and 98.5% for antioxidant activity and dry solids content, respectively. Despite the nearly four-fold decrease in the permeate flux immediately after contact of the membrane with the extract, caused by increased intrinsic membrane process resistance, during the batch concentration, the permeate flux remained in the range from 2.25 to 0.201 L m^{-2} h^{-1}, which is sufficient for practical applications. The flux decline versus retentate concentration was successfully modeled by a resistance-in-series model.

Suitable operating conditions for the spray drying process were identified, resulting in minimal loss of antioxidant activity. A crucial step was decreasing the drying temperature from 120 °C down to 85 °C, which warranted less than 6% loss of antioxidant activity. Furthermore, the precipitation step selectively removed non-active, high-molecular-weight constituents, yielding a refined polyphenolic concentrate enriched in low-molecular-weight bioactive compounds.

Overall, the combined approach—membrane filtration, precipitation, and spray drying—offers a robust and scalable strategy for the valorization of spent plant biomass while preserving the biological activity of the recovered antioxidant constituents. The

experimental evidence in the present work opens perspectives for the scale-up of a process for valorization of waste lavender plant material based on the membrane concentration of the solvent extracts.

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