

Theoretical assessment of the use of nanofiltration for fractionation of waste aqueous fractions from the essential oil industry

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The possibility to fractionate hydrosols and extracts (residual waters) from the distillation of representative essential oil plants using nanofiltration was investigated. The rejections of five commercial nanofiltration membranes with respect to key bioactive components were predicted based on regression models. Membranes of different Molecular Weight Cut-Off (MWCO), structure and composition were analyzed. Descriptors in the models were the membrane MWCO and zeta potential, as well as the molecular weight (Mw), octanol-water partition coefficient (log P) and acidity constant (pKa) of the solutes. For consistency, log P and pKa of all studied components were calculated according to the COSMO-RS method, which has the quantum-chemical basis of the Conductor-like Screening Model (COSMO). The distribution of the key components in the two types of effluents under the process conditions was also predicted using COSMO-RS for modelling of the solid-liquid, liquid-liquid and vapor-liquid equilibrium. The calculations were performed using the BIOVIA COSMOsuite software package. The results showed that independently of the membrane material, the polymeric membranes exhibit high retention capability against charged solutes such as the phenolic acids contained in the residual waters. Since the pKa of the phenolic compounds, representatives of the flavonoid family, is within the range of pH of the aqueous extracts, their retention or permeation could be controlled by slight variations of the pH. The essential oil components dissolved in the aqueous fractions are easily permeating through the membranes.

Keywords: nanofiltration, membrane, fractionation, hydrosol, residual water, COSMO-RS

INTRODUCTION

The intensively changing lifestyle and technological developments in recent decades have led to the significant presence of synthetic and semi-synthetic functional ingredients in food and cosmetics, leading to adverse effects on human health and quality of life. As a result, the demand for organic foods and beverages, as well as cosmetics and pharmaceuticals with a high content of natural ingredients, has been significantly increased in recent years as an alternative to synthetic ones. Crude and refined plant extracts rich in phenolic compounds are increasingly applied as natural colorants, antioxidants, preservatives and nutritional supplements. At the same time, plants rich in valuable essential oils are also the main sources of natural antioxidants, but according to market forecasts, annual consumption of essential oils on the world market is growing steadily, reaching 403 thousand tons in 2025 [1]. Since essential oils make up a very small fraction of the mass of the respective plants, from a few percent for typical representatives of the *Lamiaceae* family [2,3] to as little as 0.03% for *Rosa × damascena* [4], this means that tens of millions of tons of waste fractions are generated each year, that is becoming an environmental problem in areas with traditions

in the production of essential oils. At the same time, valuable substances with biological activity are being lost.

The steam distillation remains a major technology, ensuring a high and sustainable quality of the extracted oils [5]. Depending on the mode of contact between the plant material and the steam and/or water three types of process are distinguished - dry steam distillation, direct steam distillation and hydrodistillation [5]. In all the three cases, besides the waste vegetable mass and the essential oil, there are two more liquid fractions - aqueous condensate (hydrolat, hydrosol) and extract (residual water). The hydrosol is obtained by the separation of the distillate into an oil fraction and an aqueous fraction. It contains small amounts of volatile aromatic substances, which in the case of some plant species makes it an end product for aromatherapy, ingredient into cosmetic compositions or raw material for further distillation in order to increase the yield of essential oils. In many cases, however, it is discarded into the environment without further processing. The residual water is generally considered waste and disposed of in the environment. The amount varies depending on the steam distillation mode and the operating parameters. Typical values per kilogram

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of essential oil produced can be stated as 100 kg in dry steam distillation [6] and 12000 kg in the hydrodistillation of *Rosa × damascena* petals [7]. These waste fractions have traditionally been underestimated as a source of high value-added substances due to their low concentration and the susceptibility of the contained biologically active substances to oxidation and degradation at high temperature. Hence, traditional thermal separation methods, such as distillation and evaporation, are considered economically unprofitable and often lead to reduced product quality. Therefore, alternative separation methods are required to allow for softer conditions during concentration or fractionation, so as to increase the quality of the products obtained and at the same time reduce the cost of their recovery.

Separation processes at the molecular level, and in particular nanofiltration have in recent years been the subject of intense research regarding their application for the utilization of by-products of the food- and agro-industries [8, 9]. Up-to-date report on the trends in nanofiltration and nanofiltration membrane research in the last decade highlights their application to wastewater treatment and clean water production as main topics [10]. The factors determining the selectivity and permeate flux of nano- and ultra-filtration membranes for isolation, fractionation and concentration of phenolic compounds with biological activity, extracted from products of the agricultural and food industry have been studied [9]. Significant discrepancies between the retention capacity of commercial membranes and their nominal MWCO were established during separation of aqueous solutions of polyphenolic compounds [9], which is explained by specific interactions between the membrane and the components of the separated mixtures. These interactions consist of components adsorption on the membrane surface, hydrophobic or electrostatic interactions with the membrane, which cannot be influenced by the process parameters. Some physicochemical and structural characteristics of water-soluble organic substances and membranes have been used as descriptors in empirical quantitative models to predict membrane rejection and permeate flux during nanofiltration, taking into account the effects of membrane fouling [11, 12]. Nevertheless, studies on the capability of typical commercial nanofiltration membranes for fractionation or concentration of hydrosols and aqueous extracts from the steam distillation of essential oils, with regard to their specific composition, have not been carried out.

The aim of the present study was to assess the separation performance of typical commercial nanofiltration membranes aiming at their application for fractionation or concentration of effluents from the essential oil industry using available models for the membrane rejection. To achieve this aim, subject of theoretical analysis was a set of plant materials, which are emblematic and of economic interest for Bulgaria, as well as representative for a wide range of aromatic plants in terms of their phytochemical composition and technological parameters of the steam distillation of their essential oils. The distribution of key components in the waste fractions under the process conditions was predicted using universal models of statistical thermodynamics (Conductor-like Screening Model Real Solvents, COSMO RS) [13-15] for modelling of the solid-liquid, liquid-liquid and vapor-liquid equilibrium.

METHODS

Prediction of physico-chemical properties using COSMO-RS

Analysis of the distribution of the most significant valuable substances and essential oil components in the waste aqueous streams was carried out using quantum chemistry and statistical thermodynamics methods to optimize the molecular structures of interest and predict the required physicochemical properties of the multicomponent mixtures, as well as to describe the phase equilibrium. The components solubility, Vapour-Liquid Equilibrium (VLE) diagrams, pKa and logP were predicted using the COSMO-RS method, which is available in many commercial molecular simulation software packages. Some of them (e.g. Turbomole, Gaussian, DMOL3, GAMESS-US, PQS, Molpro, Columbus, ORCA, Q-Chem) can be used to calculate a discrete surface around a pre-optimized at the required level molecular structure surrounded by an imaginary conducting medium with an infinite dielectric constant. Each element of this surface is characterized by the size of its surface and the so-called Screening Charge Density (SCD). The liquid is regarded as a set of closely situated ("packed") molecules, whereby macroscopic thermodynamic and physical properties are predicted based on the statistical averaging of possible electrostatic interactions between segments with different SCD [13-15]. To implement the last step, specialized software, COSMOtherm [14], is available, which uses the SCD distribution data for the studied structure and its total energy obtained as a result of quantum-chemical simulations. In this work, the BP-TZVP-

parameterized BIOVIA COSMObase 2020 Golden database supplied with the BIOVIA COSMOtherm 2020 Golden software (Dassault Systèmes SE, France) was used for all databank components. So as to parameterize all non-databank compounds at the same computational level, a simulation sequence was developed using the Turbomole Version 7.4 software (Dassault Systèmes SE, France). The initial structure was generated from the compounds SMILES *via* the software graphical user interface TmoleX 4.3. The initial structure was pre-optimized at a semi-empirical AM1 (MOPAC 7) level with the SVP basis set in vacuum. The resulting structure was further optimized at DFT level using the BP86 density functional and TZVP basis set and subjected to COSMO calculation in order to obtain the charge screening on the molecular surface and the respective .cosmo file, considering solvent effects through the conductor-like polarizable continuum model. In this way the compound structure was parameterized at a computational level compatible with the BP-TZVP-parameterized COSMObase 2020 database. The new component was added to the COSMObase 2020 by importing from the obtained .cosmo file. Component solubilities and VLE were analyzed by means of the COSMOtherm application. LogP partition coefficients and pKa for all components were predicted using the COSMO-RS theory *via* the COSMOquick (Dassault Systèmes SE, France) program and COSMOfrag approach [16]. The COSMO-RS theory allowed for prediction of logP at user-defined temperature as opposed to commonly used QSAR (quantitative structure activity relationship) methods.

Regression models for membrane rejection

A limited number of studies reported QSAR models for prediction of the rejection and permeate flux of commercial nanofiltration membranes during filtration of aqueous solutions of organic solutes that account for the solute-solvent-membrane molecular interactions [11, 12]. In a study covering a range of organic solutes and variety of nanofiltration membranes empirical models for prediction of the amount of solute adsorbed by the membranes, the permeate flux and the solute rejection are derived [12]. In this study five commercial nanofiltration membranes with different MWCO, structure and composition were

used: Desal51HL and Desal5DL (GE Osmonics, USA), N30F and NFPES10 (MICRODYN-NADIR, Germany), NTR7450 (Nitto-Denko, Japan). Desal51HL and Desal5DL have a polyamide top layer while in N30F, NFPES10 and NTR7450 the selective layer is made of (in the case of NTR7450, sulfonated) polyethersulfone (PES). MWCO, porosity of the surface layer (represented as the volume fraction of the pores with small and large size), roughness of the active surface, water contact angle, water permeability and membrane charge (expressed as zeta potential of the membrane at three pH values) were used as membrane descriptors. Independent models were obtained for the cases of nanofiltration of uncharged and charged organic solutes dissolved in water. In this work the membrane rejection coefficients for the key components of the extracts and hydrosols were predicted using the regressions reported in [12] for uncharged, Eq. (1), and charged, Eq. (2), solutes:

$$Rejection = (5.73 - 0.71\text{Log}P - 0.002\text{MWCO})^2 \quad (1)$$

$$Rejection = -82.75 + 26.13 \ln(Mw) + 5052.63/\text{MWCO} - 18.54/\text{Membrane charge} \quad (2)$$

The membrane rejection coefficient is defined based on the ratio of the concentration in the permeate, C_P , and retentate, C_R , streams as follows [13]:

$$Rejection = 1 - C_P/C_R \quad (3)$$

Membrane-related model parameters in Eqs. (1) and (2) are the MWCO and *Membrane charge* expressed as zeta potential at a specific pH. Their values for the studied membranes are summarized in Table 1. Solute-related descriptors are the M_w in the case of charged and LogP in the case of uncharged organic compounds. The charge of the solutes in the present work was estimated at the respective pH based on their pKa value. The compounds containing either carboxyl (-COOH) or hydroxyl (-OH) functional groups at pH higher than their pKa are preferably deprotonated and thus negatively charged. At pH lower than pKa these compounds are assumed to be neutral as none of them contains basic groups as also confirmed by our simulations. Some of the components contain neither acidic nor basic groups and are considered as neutral independently of the pH.

Table 1. Summary of the membrane-related parameters in the models for membrane rejection at different pH values [12].

Membrane	pH 3		pH 6		pH 10	
	MWCO, Da	Membrane charge (Zeta potential), mV	MWCO, Da	Membrane charge (Zeta potential), mV	MWCO, Da	Membrane charge (Zeta potential), mV
Deasal51HL	220	4	190	-13	220	-17
Desal 5DL	290	7	260	-17	270	-21
NTR 7450	310	1	310	-15	310	-19
N30F	590	1	680	-14	630	-18
NFPES10	1300	1	1200	-10	1300	-15

RESULTS AND DISCUSSION

Biologically active constituents of the essential oil cultures and their distribution amongst the aqueous extracts and hydrosols

This study focusses on the water-soluble biologically active components of the essential oil cultures, as well as on the major constituents of their essential oils. Due to their relatively high solubility in warm water, phenolic compounds in plants are also the major bioactive components in aqueous decoctions or infusions from medicinal plants. Often the total phenolic fraction from the plant (anti-inflammatory agents [4, 7, 17]), purified and standardized polyphenolic fractions (venoactive drugs [18], phytoestrogens [19], hepatoprotective drugs [20]) or individual phenolic compounds (medications for acute and chronic liver diseases, cancer and haematological diseases [21], drugs and materials for dental medicine [22]), are the active component of medicines and medical materials. In Table 2 are summarized the key polyphenolic and essential oil components of crops that are highly popular, cultured and processed in high volumes due to their formidable benefits to human health - *Rosa × damascena*, aromatic plants of the *Lamiaceae* family (lavender, lemon balm) and cloves. Bulgaria is a leading country in the world for lavender cultivation and processing and in 2017 accounts for 52% of world essential oil production. *Rosa Damascena*'s cultivation and processing is an emblematic sector for Bulgaria.

Studies on the phytochemical profile of the aqueous extract from hydrodistillation of *Rosa × damascena* petals showed that it contains phenolic compounds, representatives of different subclasses of the flavonoid family (flavan-3-ols, flavanones, flavonols and flavones) [7]. The quantitative analysis proved that predominant phenolic compounds in both the waste water and the residual biomass [4] are flavonol glycosides containing campherol and quercetin in their structure, as well as flavonol, ellagic acid, flavone, quercetin and kaempferol. The molecular weights of the phenolic

components in the water extract range from about 280 g/mol for kaempferol to about 637 g/mol for multiflorin A [7], thus covering a significant part of the selectivity spectrum of nanofiltration membranes (200-1000 g/mol). Under conditions of boiling in water, a high content of high molecular weight pectic polysaccharides can be expected in the water extract [23]. Depending on the source and method of extraction, the molecular weight of recovered pectic polysaccharides varies in a wide range from about 30,000 to about 250,000 g/mol, fall outside of the nanofiltration membranes range of selectivity and were not considered in the present work. Major constituents of the essential oil from *Rosa × damascena* are monoterpenes (geraniol, citronellol, nerol), phenethyl alcohol and hydrocarbons (nonadecane) with molecular weights mostly below the nanofiltration range [24-26].

Lavender and lemon balm are aromatic herbs belonging to the *Lamiaceae* family, which are characterized by a high content of polyphenolic compounds. In extracts with polar organic solvent from plant waste remaining after steam distillation of lavender [3, 27, 28] and in aqueous extracts from lemon balm [29, 30] flavonoid glycosides, similar to those in the *Rosa × damascena* hydrodistillation waste streams, have been identified. Their structures contain luteolin and apigenin in the case of lavender or myricetin and quercetin in the case of lemon balm. In addition to the content of flavonoids, these fractions are rich in polyphenolic acids, such as caffeic, gallic, chlorogenic and rosmarinic acids. Dominant with respect to all phenolic constituents in both herbs is the rosmarinic acid, which is also a major contributor to the antioxidant capacity of the aqueous extracts. Despite the variations in the composition of the essential oils, primary components are linalool and citral in the case of lavender and lemon balm, respectively. Other common constituents of lavender essential oil are linalyl acetate, trans- β -ocimene, terpinen-4-ol and borneol [24, 31, 32]. In

Table 2. Key polyphenolic (PF) and essential oil (EO) components, their thermodynamic properties and distribution amongst aqueous extracts and hydrosols.

Plant	Fraction	Key component	COSMO parametrization	Mw, Da	$m_{100} \times 10^6$	$m_{30} \times 10^6$	y^* at 100 °C $\times 10^6$	K_{AW} at 100 °C
<i>Rosa × damascena</i>	PF	2-Phenylethyl-O-β-D-glucopyranoside	User	284.3	3588.0	361.3	0	0
		Kaempferol	User	286.2	1300.7	178.2	0	0
		Quercetin	User	302.2	1522.0	305.0	0	0
		Ellagic acid	User	302.2	6720.1	1546.1	0	0
		Kaempferol-3-O-glucoside (Astragalol)	User	448.4	163.1	4.871	0	0
		Kaempferol-3-O-glucosylrhamnoside (Multiflorin B)	User	594.5	8.4	0.1	0	0
		Quercetin-3-O-rhamnosylglucoside (Rutin)	User	610.5	3.4	0	0	0
	Kaempferol-3-O-acetylglucosylrhamnoside (Multiflorin A)	User	636.6	3.3	0.1	0	0	
	EO	Geraniol	BIOVIA	154.3	974.4	592.8	8381.1	73.77
		Citronellol	BIOVIA	156.3	578.1	310.2	8405.1	126.4
Nerol		BIOVIA	154.3	1188.0	709.0	15032.2	108.5	
Phenethyl alcohol		BIOVIA	122.2	37570.0	24261.7	15930.7	2.79	
Nonadecane		BIOVIA	268.5	0	0	NA	NA	
<i>Lavandula angustifolia</i>	PF	Rosmarinic acid	User	360.3	12900.1	1806.2	0	0
		Luteolin	User	286.2	740.5	25.3	0	0
		Caffeic acid	User	180.2	135479.9	23161.1	0	0
	EO	Linalool	BIOVIA	154.3	607.8	322.6	22449.1	316.1
		Linalyl acetate	BIOVIA	196.3	93.5	43.0	4741.0	553.3
		Trans-β-ocimene	User	136.2	65.8	15.9	164681.6	19240
		Terpinen-4-ol	BIOVIA	154.3	529.3	61.5	7347.9	119.2
Borneol	BIOVIA	154.3	759.3	67.7	4888.5	55.27		
<i>Melissa officinalis</i>	PF	Rosmarinic acid	User	360.3	12900.1	1806.2	0	0
		Caffeic acid	User	180.2	135479.9	23161.1	0	0
		Rutin	User	610.5	3.4	0	0	0
	EO	Citral (Neral and Geranial)	BIOVIA	152.2	2261.1	3082.2	12588.7	47.49
		Germacrene D	BIOVIA	204.4	4.8	0.1	1420.9	3379
		β-Caryophyllene	BIOVIA	204.4	13.6	2.5	2878.3	2400
		Citronellal	BIOVIA	154.3	417.6	246.0	33679.5	695.7
D-Limonene	BIOVIA	136.2	93.4	23.7	86305.1	7051		
<i>Syzygium aromaticum</i> (Cloves)	PF	Eugenol	BIOVIA	164.2	1479.9	677.3	4569.4	28.33
		Gallic acid	BIOVIA	170.1	278190.0	89312.9	0	0
		Kaempferol	User	286.2	1300.7	178.2	0	0
		Quercetin	User	302.2	1522.0	305.0	0	0
		Tamarixetin 3-O-β-D-glucopyranoside	User	478.4	81.5	2.0	0	0
	EO	Eugenol	BIOVIA	164.2	1479.9	677.3	4569.4	28.33
		Eugenyl acetate	BIOVIA	206.2	533.5	179.1	152.441	3.275
		β-Caryophyllene	BIOVIA	204.4	13.6	2.5	2878.3	2400
		3-(1-Methylethyl)-benzoic acid	BIOVIA	164.2	3017.5	344.8	657.0	2.002
α-Humulene	BIOVIA	204.4	6.0	0.2	851.1	1604		

m_{100} - solubility in water at 100 °C (maximum concentration in aqueous extracts), mass fraction; m_{30} - solubility in water at 30°C (concentration in hydrosols), mass fraction; K_{AW} - air–water partitioning coefficient (y^*/x_{sat}); x_{sat} – mole fraction of component in saturated solution; y^* - concentration of vapor phase at equilibrium with saturated solution in mole fraction.

addition to citral, the oil from lemon balm contains germacrene D, β -caryophyllene, citronellal and D-limonene [24, 33-35].

The aromatic flower buds of the tree *Syzygium aromaticum* (cloves), in addition to being widely used as a spice, food preservative and in medicine, are also one of the popular raw materials for the preparation of essential oil by steam distillation [36-38]. This is due to their high content of biologically active polyphenolic and aromatic substances. Eugenol is the main constituent of the essential oil [36-38] and also the biologically active component with the highest content per unit mass of plant material - up to approximately 10 wt. % [37]. In a systematic study on methanolic extracts of 26 aromatic plants belonging to 12 botanical families with pronounced antioxidant activity, the flower buds of *Syzygium aromaticum* were found to have the highest total phenolic content [37]. A key representative of the polyphenolic compounds is gallic acid (783.5 mg/100 g dry plant mass) and its derivatives (2375.8 mg/100 g dry plant mass), flavonoids (caempferol, 23.8 mg/100 g and quercetin, 28.4 mg/100 g dry plant mass) [37] and their glycosides (tamarixetin 3-O- β -D-glucopyranoside [38]). Apart from eugenol, the essential oil contains also significant amounts of eugenyl acetate, β -caryophyllene, 3-(1-methylethyl)-benzoic acid and α -humulene [36, 39, 40].

To be able to discuss the effects from nanofiltration of the extracts and hydrosols from the distillation, a preliminary appraisal of their composition is required. As an estimate for the magnitude of a component concentration in the extracts is assumed its predicted solubility in water at 100 °C shown in Table 2. This approximation is justified since the operating pressure is usually close to atmospheric one while the plant material is in contact with boiling water during hydrodistillation or eventually in contact with aqueous condensate leading to the formation of extract during steam distillation. The plant materials have to contain required amount from the respective component to achieve the equilibrium concentration in water at the said temperature as an additional prerequisite. However, the solubility at 100 °C is not a sufficient criterion for presence of the respective compound in the extract. In the course of a typical process for the studied essential oil plants (duration is in the range from 40 min to 4 hours [68]), highly volatile compounds would be stripped from the extract and quantitatively transferred in the distillate. For this reason, the isobaric VLE was also simulated and the results are

illustrated in Table 2. The VLE diagram $y=f(x)$ was a linear relationship (coefficient of linear correlation more than 0.9996 in all cases) for all studied volatile components within the ranges for x with a slope equal to y^*/x_{sat} (Table 2). The latter represents the air-water partitioning coefficient, K_{AW} , and indicates that Henry's law for dilute systems holds in the range of essential oils components solubility at 100 °C and 1013.25 mBar. A smaller value of K_{AW} implies high reflux ratio and multiple stages, thus inefficient separation of the essential oil components *via* distillation. In the case of simple distillation, which depicts the process of hydrodistillation of essential oil cultures and can be used as an approximation for the case where steam distillation of the biomass is accompanied by formation of aqueous condensate (extract), small K_{AW} would require distillation of large fractions of the feed solution in order to achieve sufficient yield of the essential oil components in the distillate. As a result, components with the highest partitioning coefficients are expected to be quantitatively transferred in the distillate and consequently distributed between the hydrosols and essential oil fraction, while these with extremely low partition coefficient may also be present in the aqueous extracts. Hence, in Table 3 as constituents of the extracts are listed only components that have solubility at 100 °C and K_{AW} values permitting theoretical concentration in the extracts higher than 100 ppm.

The hydrosols will contain dissolved components of the respective essential oils in concentrations corresponding to their solubility at the emulsion decantation temperature (28-35 °C) [16, 41]. The solubility of essential oil components in this work was predicted at a reference temperature of 30 °C (Table 2) and only compounds with solubility higher than 40 ppm were considered in the model mixtures representing the hydrosols from the distillation of the essential oil cultures (Table 3).

Parameters of the membrane rejection models

The values for the membrane MWCO and zeta potential at different pH were taken from the literature and listed in Table 1. The only solute specific model parameter is LogP. For each of the suggested key components of the extracts and hydrosols, the COSMO-RS predicted value is included in Table 3. In contrary with the generally accepted simplified approach of the so-called "sieve" mechanism of membrane separation, in which the ability of the membrane to separate

certain substances is determined by its MWCO, Eq. (1) reveals that for the range of LogP values in this work, the hydrophobicity of the organic solutes expressed as LogP has an impact on the membrane rejection in an order of magnitude equal to that of the MWCO.

Even though not explicitly present in the model equations, pKa is another physicochemical property of the organic solutes predetermining their membrane rejection. A quick observation of the theoretical predictions demonstrated that only polyphenolic acids are negatively charged at neutral pH. In a moderately basic environment of pH 10, all polyphenolic constituents except phenylethyl-glucopyranoside will exist in a deprotonated form and behave as negatively charged solutes permeating the membranes. The components of the hydrosols are either aprotic or have a pKa higher than 14 (except phenethyl alcohol and 3-(1-

methylethyl)-benzoic acid) that make them practically uncharged within a feasible range of pH.

Membrane fractionation of the waste aqueous fractions from the steam distillation

The predicted membrane rejection coefficients against all individual components of the aqueous fractions are plotted in Figs. 1 - 4. An overview of the results reveals that none of the nanofiltration membranes is capable to retain the uncharged organic compounds to a level permitting their practical implementation for component concentration. An exception is phenethyl alcohol in *Rosa × damascena* hydrosols where a suitable process configuration may render nanomembrane concentration feasible. In contrast, the negatively charged components at certain pH were as a rule highly rejected by all studied commercial membranes independently of their MWCO, morphology or composition of the selective layer.

Table 3. Suggested composition of extracts and hydrosols from the investigated cultures and summary of the solute-related parameters in the models for membrane rejection at different pH values.

Plant	Fraction	Component	pKa	LogP	Component charge		
					pH3	pH6	pH10
<i>Rosa × damascena</i>	Extract	2-Phenylethyl-O-β-D-glucopyranoside	11.8	2.39	0	0	0
		Kaempferol	6.74	3.66	0	0	-1
		Quercetin	6.27	3.96	0	0	-1
		Ellagic acid	7.65	2.48	0	0	-1
		Kaempferol-3-O-glucoside (Astragalín)	6.74	3.89	0	0	-1
		Phenethyl alcohol	13.9	1.51	0	0	0
	Hydrosol	Geraniol	15.5	3.55	0	0	0
		Citronellol	15.7	3.63	0	0	0
		Nerol	15.5	3.55	0	0	0
Phenethyl alcohol		13.9	1.51	0	0	0	
<i>Lavandula angustifolia</i>	Extract	Rosmarinic acid	3.22	2.98	0	-1	-1
		Luteolin	6.27	2.76	0	0	-1
		Caffeic acid	4.4	1.36	0	-1	-1
	Hydrosol	Linalool	19.2	3.71	0	0	0
		Linalyl acetate	NA	4.23	0	0	0
		Terpinene-4-ol	19.2	3.44	0	0	0
		Borneol	17.7	2.95	0	0	0
<i>Melissa officinalis</i>	Extract	Rosmarinic acid	3.22	2.98	0	-1	-1
		Caffeic acid	4.4	1.36	0	-1	-1
		Citral (Neral and Geraniol)	NA	3.06	0	0	0
	Hydrosol	Citral (Neral and Geraniol)	NA	3.06	0	0	0
		Citronellal	NA	3.54	0	0	0
<i>Syzygium aromaticum</i> (Cloves)	Extract	Eugenol	7.4	3.34	0	0	-1
		Eugenyl acetate	NA	3.27	0	0	0
		3-(1-Methylethyl)-benzoic acid	4.27	2.86	0	-1	-1
		Gallic acid	4.21	1.40	0	-1	-1
		Kaempferol	6.74	3.66	0	0	-1
		Quercetin	6.27	3.96	0	0	-1
	Hydrosol	Eugenol	7.4	3.34	0	0	0
		Eugenyl acetate	NA	3.27	0	0	0
		3-(1-Methylethyl)-benzoic acid	4.27	2.86	0	-1	-1

This phenomenon can be explained only if a mechanism of membrane retention controlled by intermolecular solute-membrane, solute-solvent and solvent-membrane interactions rather than sieving is assumed. As expected, the rejection for uncharged solutes in both extracts and hydrosols is consistently decreasing with increasing the membrane MWCO. Due to their relatively low hydrophobicity (based on their low LogP values), phenethyl alcohol, caffeic acid and gallic acid are the most highly rejected uncharged components with predicted rejection coefficients of up to about 20% for polyamide composite membranes.

The results on extracts from *Rosa × damascena* (Fig. 1) illustrate the potential of nanofiltration for both isolation and concentration of the contained flavonoid polyphenols and ellagic acid from their mixture with other phenolic compounds and phenethyl alcohol when the process is held at elevated pH of 10. The pH susceptibility of the nanomembranes performance may be further exploited to claim that a single set-up and membrane can be used for purification of the phenolic fraction *via* removal of high molecular weight compounds such as pectin at neutral pH, followed by further fractionation of the phenolic fraction at basic pH. Despite the relatively low rejection for phenethyl alcohol, its concentration in hydrosols can be practically achieved *via* design of multistage nanofiltration operation [42] with membranes such as Desal51HL or Desal5DL. In

lavender extracts, the negligible rejection at normal pH and high rejection at pH 10 for luteolin along with the high rejection for the two phenolic acids in both cases reveals the opportunity to separate the phenolic acids from the flavonoid components and concentrate them (Fig. 2). Rosmarinic and caffeic acids are also key components of the extracts from lemon balm and the data in Fig. 3 demonstrate the possibility for their direct purification and concentration at normal pH of the environment using preferably Desal membranes. Due to the negligible rejection for essential oil components in the hydrosols from both lavender and lemon balm (Figs. 2, 3), the nanofiltration of their hydrosols would not bring any benefits. Predicted performances of the nanofiltration membranes are favorable for efficient fractionation of the biologically active constituents of both clove extracts and hydrosols (Fig. 4). At pH 6 nanofiltration can selectively remove organic acids from the extracts. If the permeates are subjected to nanofiltration with the same membranes at pH 10, this would allow for isolation of the flavonoids fraction together with eugenol in the retentates. Since eugenol is the target bioactive component of cloves and at the same time due to its high water solubility is contained in high concentrations in the hydrosols, nanofiltration appears as a feasible technology to recycling eugenol from this waste stream from the steam distillation of cloves. As is

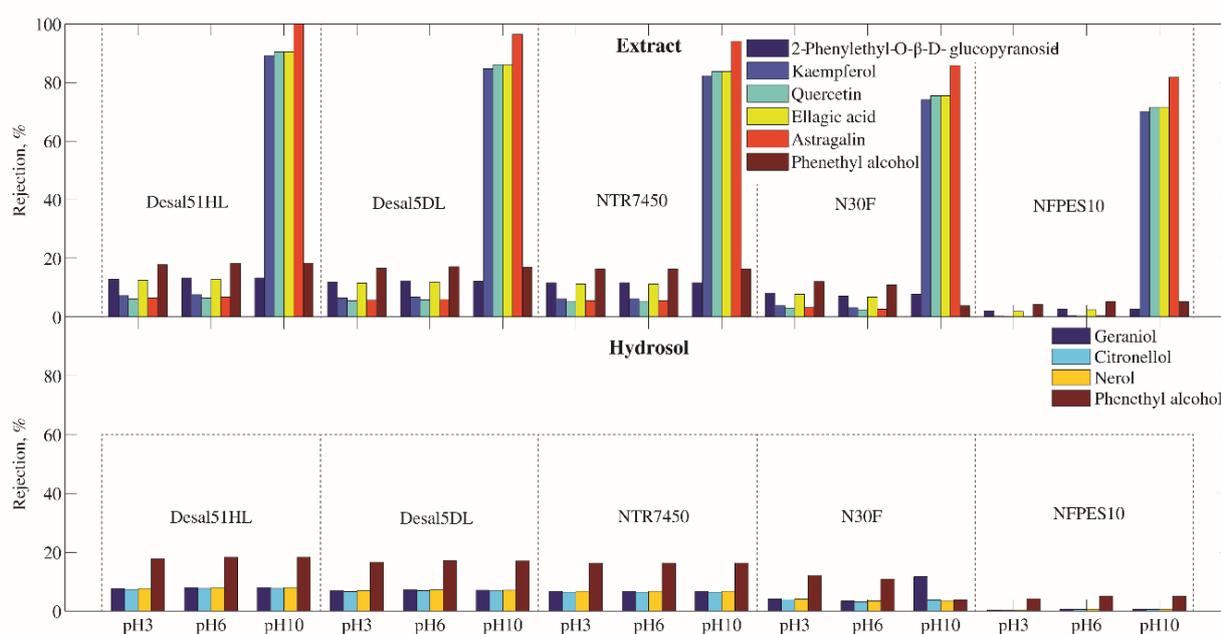


Fig. 1. Nanomembrane selectivity against key components of extracts and hydrosols from hydrodistillation of *Rosa × damascena* petals

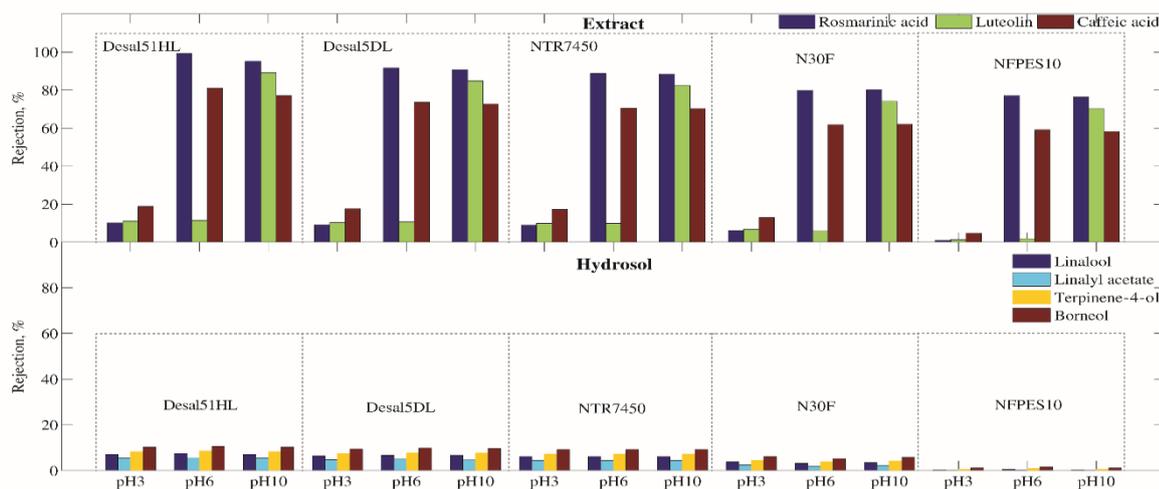


Fig. 2. Nanomembrane selectivity against key components of extracts and hydrosols from steam distillation of *Lavandula angustifolia*

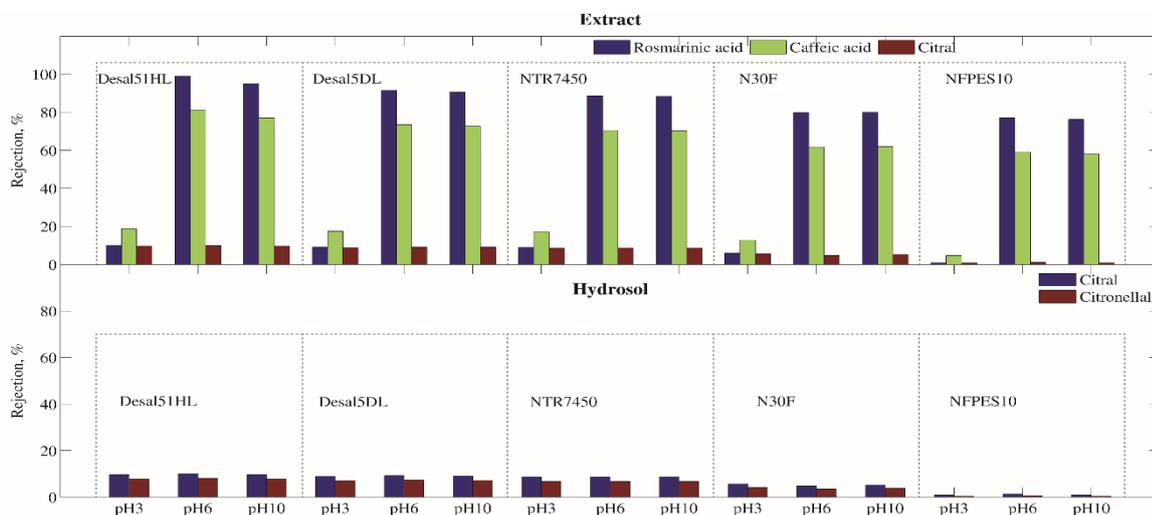


Fig. 3. Nanomembrane selectivity against key components of extracts and hydrosols from steam distillation of *Melissa officinalis*

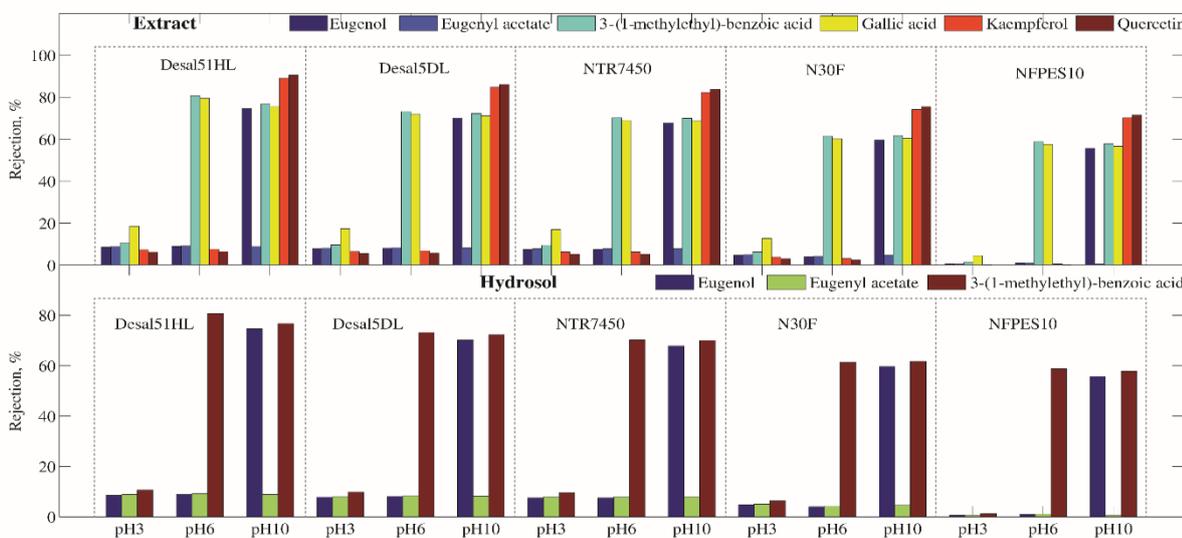


Fig. 4. Nanomembrane selectivity against key components of extracts and hydrosols from steam or hydrodistillation of *Syzygium aromaticum* (Cloves)

obvious from Figure 4, eugenol in hydrosols can be isolated by their nanofiltration at neutral pH aiming to purify it in the permeates. The obtained permeates can be concentrated by nanofiltration at pH 10 using the same membranes.

CONCLUSIONS

The selectivity with respect to key biologically active constituents of effluents from the essential oil industry of five representative commercial nanofiltration membranes with different MWCO, structure and composition was predicted based on empirical models. The theoretical analysis was performed on a set of emblematic and of economic interest for Bulgaria essential oil cultures such as *Rosa × damascena*, *Lavandula angustifolia* and *Melissa officinalis*. Flower buds from *Syzygium aromaticum* (Cloves) has also been selected due to encouraging in the scope of the present research specifics in its phytochemical composition and technological parameters of the steam distillation of its essential oil. The key biologically active constituents of the selected plants were summarized based on literature review. Their presence in the waste aqueous fractions from the steam distillation was assessed *via* prediction of the components solubility, VLE diagrams, pKa and LogP using the COSMO-RS universal models of statistical thermodynamics. The membrane selectivity was expressed in terms of membrane rejection coefficient. The most significant parameters affecting the membrane rejection were the hydrophobicity of the solutes and pH of the nanofiltered aqueous mixtures. The results clearly demonstrated the viability of nanofiltration for isolation of refined polyphenolic fractions from the extracts effluents and for recovery of phenethyl alcohol and eugenol from hydrosols of *Rosa × damascena* and cloves, respectively.

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