Theoretical assessment of the possibility for fractionation of waste aqueous fractions from the essential oil industry using nanofiltration.

Dimitar Peshev[1], Nevena Lazarova-Zdravkova[2], Chavdar Chilev[1]

[1] Department of Chemical Engineering, Faculty of Chemical and System Engineering, UCTM, Sofia, Bulgaria

[2] Department of Biotechnology, Faculty of Chemical and System Engineering, UCTM, Sofia, Bulgaria

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) for modelling of the solid-liquid, liquid-liquid and vapour-liquid equilibrium.

The rejections of five commercial nanofiltration membranes with respect to key bioactive components were predicted based on regression models. Membranes of different MWCO, structure and composition were analysed. Descriptors in the models were the membrane MWCO and zeta potential. Their values for the studied membranes are summarized in Table 1.

Solutes related descriptors are the molecular weight (Mw) in the case of charged and the octanol-water partition coefficient (LogP) in the case of uncharged organic compounds.

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

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

The predicted membrane rejection coefficients against all individual components of the aqueous fractions are plotted in Figs. 1 - 4. The results showed that independently on the membrane material, the polymeric membranes exhibit high retention capability against charged solutes such as the contained in the residual waters phenolic acids. 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 dissolved in the aqueous fractions essential oil components would be easily permeating through the membranes.

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

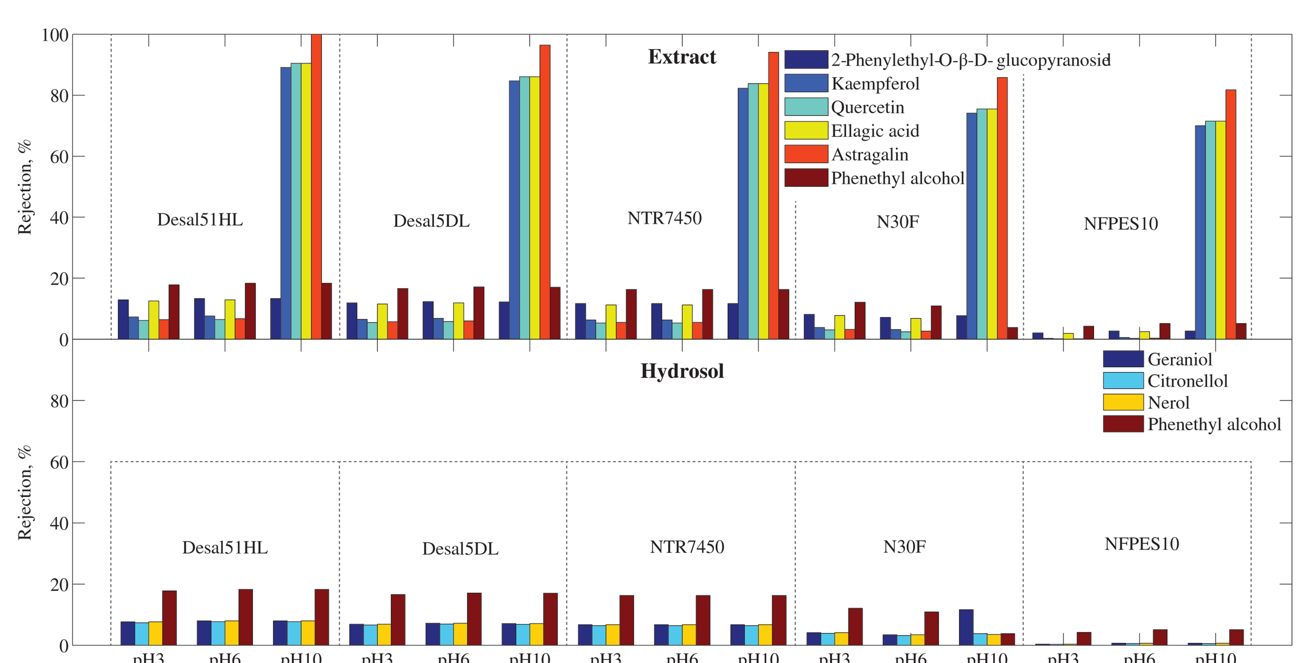


Fig. 2 Nanomembrane selectivity against key components of extracts and hydrosols from steam distillation of *Lavandula angustifolia*

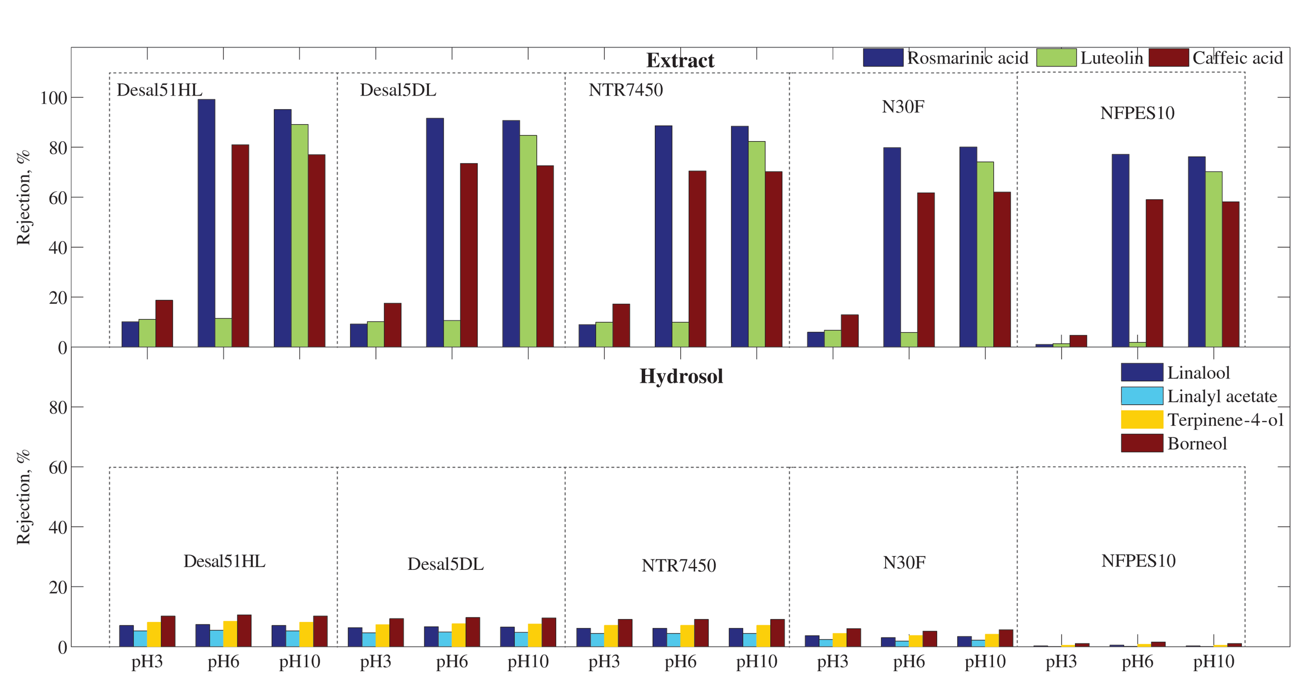
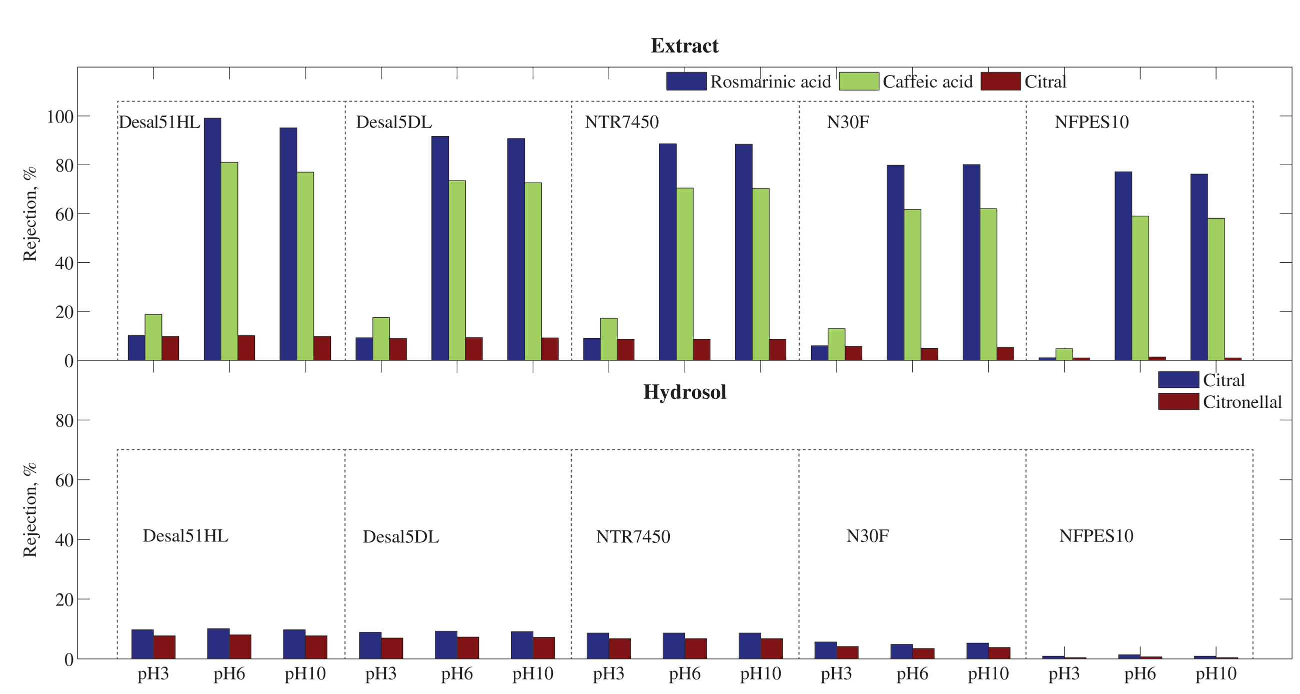


Fig. 3 Nanomembrane selectivity against key components of extracts and hydrosols from steam distillation of *Melissa officinalis*



The charge of the solutes in the present work was estimated at the respective pH based on their pKa value.

Key polyphenolic and essential oil components of highly popular, cultured and processed in high-volumes crops due to their formidable benefits to human health - Rosa × damascena, aromatic plants of the Lamiaceae family (lavender, lemon balm) and cloves were observed. 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.

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 calculations were performed using the BIOVIA COSMOsuite software package.

In Table 2 as constituents of the extracts are listed only components that have solubility at 100 ⁰C and Kaw values permitting theoretical concentration in the extracts higher than 100 ppm. Only compounds with solubility at 30 ⁰C higher than 40 ppm were considered in the model mixtures representing the hydrosols.

Table 2 Suggested composition of extracts (E) and hydrosols (H) from the investigated cultures and summary of the solutes related parameters in the models for membrane rejection at different pH values.

Plant	Fraction	Component	pKa	LogP	Component charge		
					pH3	pH6	pH10
Rosa × damascena	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 (Astragalin)	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
Lavandula angustifolia	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
Melissa officinalis	Extract	Rosmarinic acid	3.22	2.98	0	-1	-1
		Caffeic acid	4.4	1.36	0	-1	-1
		Citral (Neral and Geranial)	NA	3.06	0	0	0
	Hydrosol	Citral (Neral and Geranial)	NA	3.06	0	0	0
		Citronellal	NA	3.54	0	0	0
Syzygium aromaticum (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

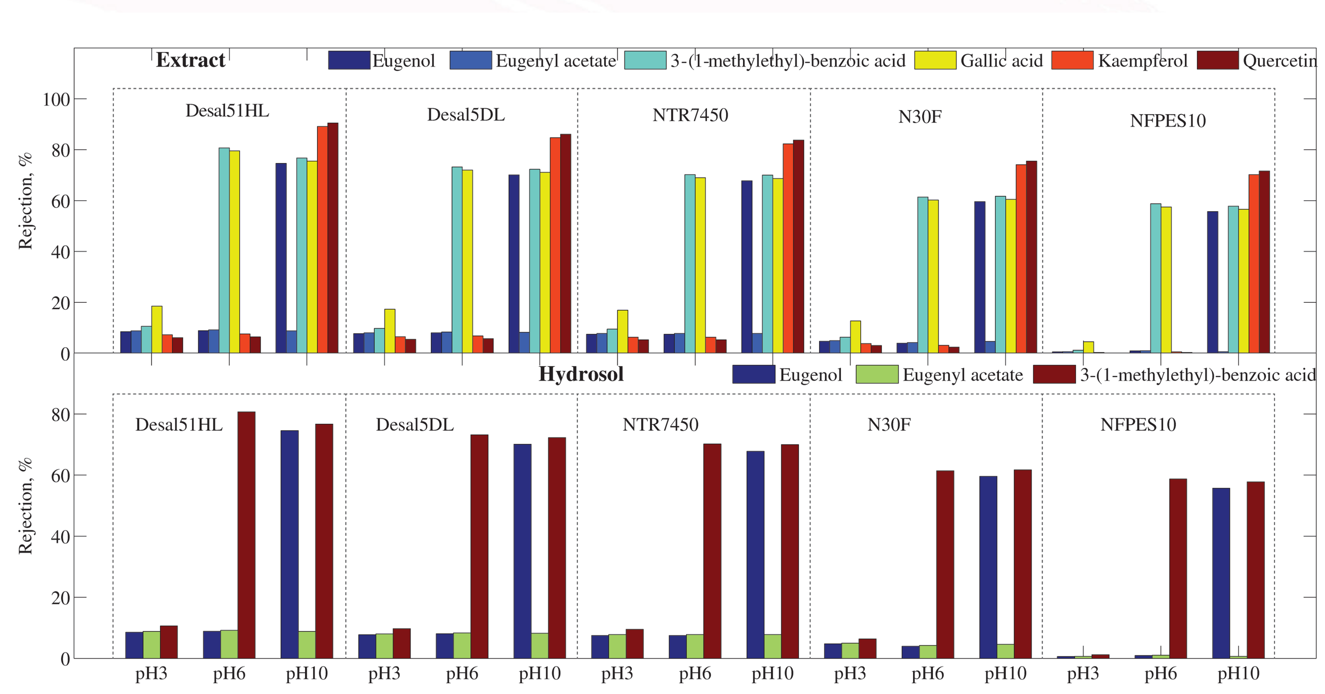


Fig. 4 Nanomembrane selectivity against key components of extracts and hydrosols from steam or hydrodistillation of *Syzygium aromaticum* (Cloves)

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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