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# New possibilities for the valorisation of waste aqueous fractions from the essential oil industry using nanofiltration

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## Theoretical prediction

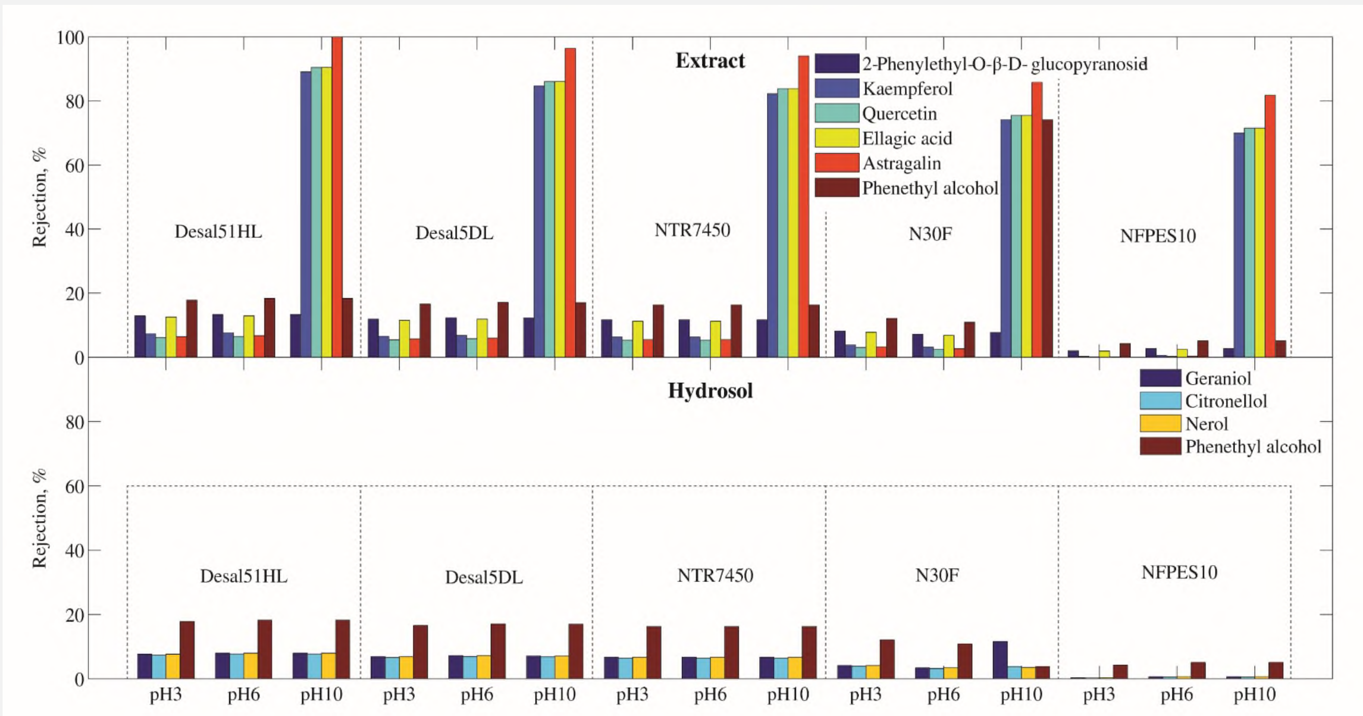


**Fig. 1.** Nanomembrane selectivity against key components of extracts and hydrosols from hydrodistillation of *Rosa × damascene* petals

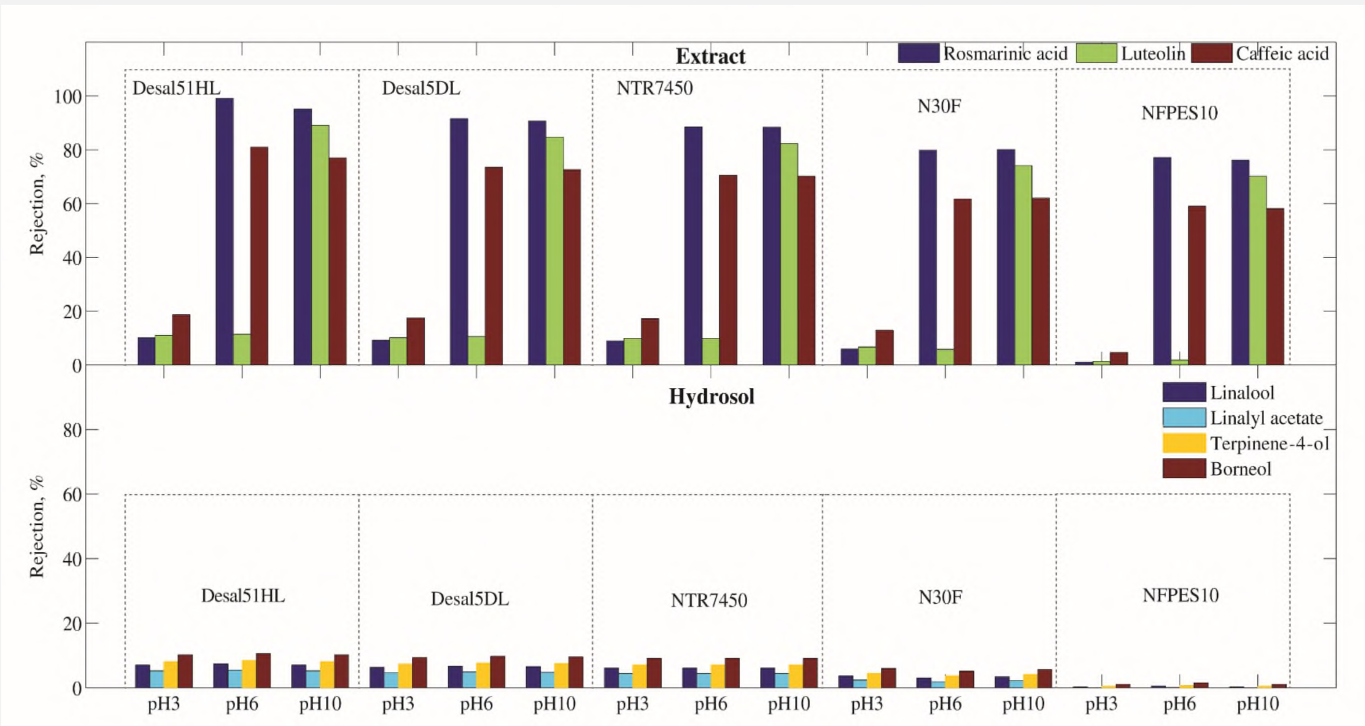


**Fig. 2.** Nanomembrane selectivity against key components of extracts and hydrosols from steam distillation of *Lavandula angustifolia*

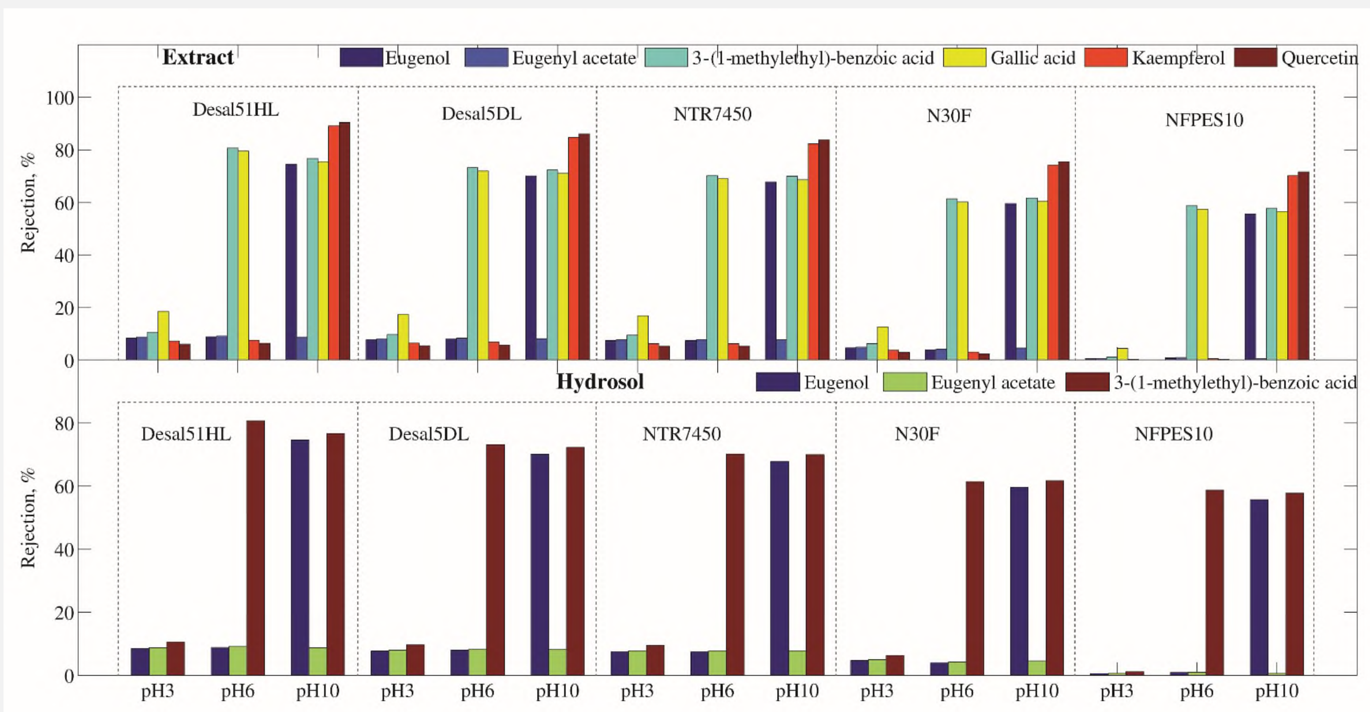


**Fig. 3.** Nanomembrane selectivity against key components of extracts and hydrosols from steam distillation of *Clove*

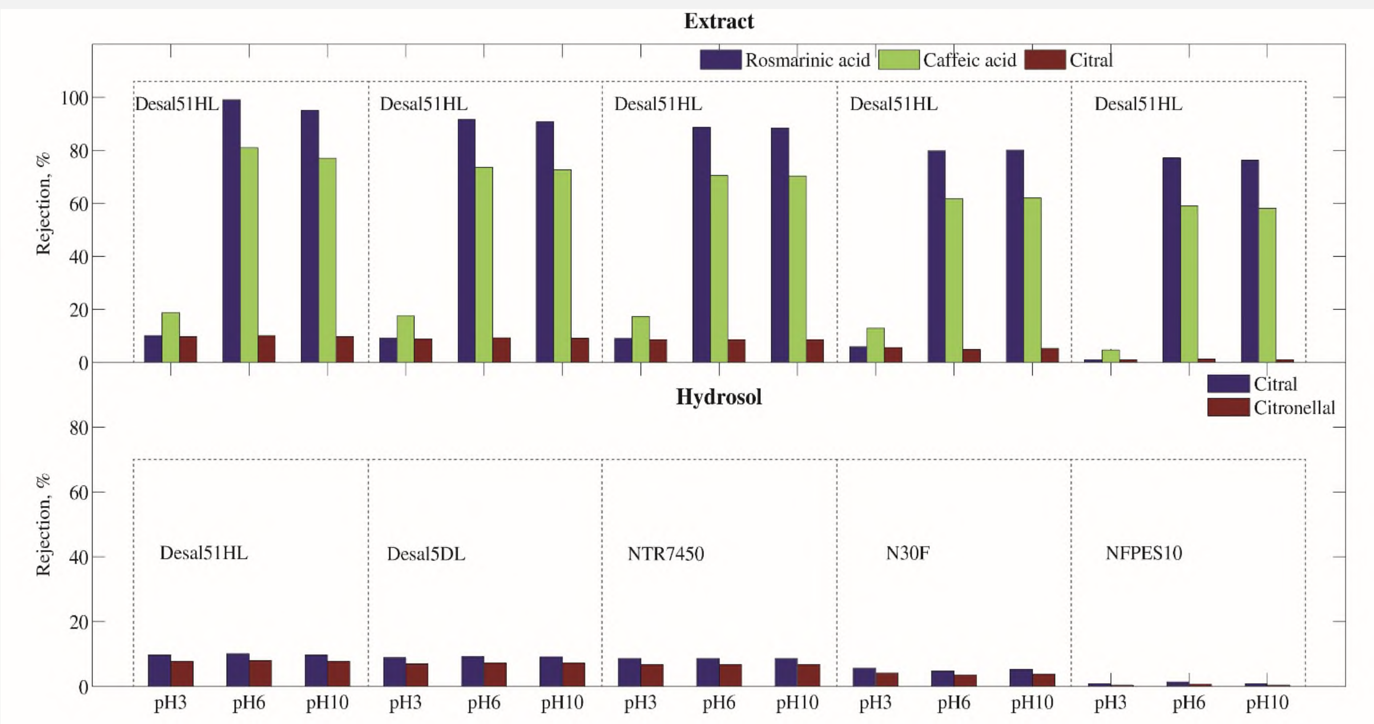


**Fig. 4.** Nanomembrane selectivity against key components of extracts and hydrosols from steam distillation of *Lemon balm*

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. 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 ºC and Kaw values permitting theoretical concentration in the extracts higher than 100 ppm. Only compounds with solubility at 30 ºC higher than 40 ppm were considered in the model mixtures representing the hydrosols.

**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 |
| Desal 51HL | 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 |

**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 | | |
|---|---|---|---|---|---|---|---|
| | | | | | pH 3 | pH 6 | pH 10 |
| Rosa x Damascena | Extract | 2-Phenylethyl-O-β-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 augostifolia | 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 | N/A | 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) | N/A | 3.06 | 0 | 0 | 0 |
| | Hydrosol | Citral (Neral and Geranial) | N/A | 3.06 | 0 | 0 | -1 |
| | | Citronellal | N/A | 3.54 | 0 | 0 | 0 |
| Syzygium aromaticum (Cloves) | Extract | Eugenol | 7.4 | 3.34 | 0 | 0 | -1 |
| | | Eugenyl acetate | N/A | 3.27 | 0 | 0 | -1 |
| | | 3-(1-methylethyl)-benzoic acid | 4.27 | 2.86 | 0 | -1 | -1 |
| | | Gallic acid | 4.21 | 1.4 | 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 | N/A | 3.27 | 0 | 0 | 0 |
| | | 3-(1-methylethyl)-benzoic acid | 4.27 | 2.86 | 0 | -1 | -1 |

For more infotmation visit: http://www.nanoessential.eu/

## Experimental evidence

**Batch nanofiltration**
$V_F$ - 100 ml; $V_R$ - 50 ml; $V_P$ - 50 ml
Degree of feed volume reduction (DEVR) = 2

**Table 3** Experimental data

| Membrane Name | $Ec_{50}F$, ml (feed solution)/ml (sample) | $Ec_{50}P$, ml (permeat solution)/ml (sample) | $Ec_{50}R$, ml (retentat solution)/ml (sample) | Deviation from material balance | $R_1$ | $R_2$ |
|---|---|---|---|---|---|---|
| NP030 Mycrodin-Nadir | 0.00349 | 0.0142 | 0.00172 | 13.74 | 0.765 | 0.864 |
| DESAL 5DL | 0.00282 | 0.0122 | 0.00166 | 1.79 | 0.754 | 0.879 |

The membrane rejection (R) of *Rosa x Damascena* extract was calculated in two different ways:

$$R_1 = 1 - \frac{Ec_{50}F}{Ec_{50}P} \quad \text{(a)}$$

$$R_2 = 1 - \frac{Ec_{50}R}{Ec_{50}P} \quad \text{(b)} \qquad (1)$$

The deviation from the material balance ($Err$) was also calculated:

$$Err = \frac{V_F\left(\frac{1}{Ec_{50}F}\right) - \left[\left(V_P\left(\frac{1}{Ec_{50}P}\right) + V_R\left(\frac{1}{Ec_{50}R}\right)\right]}{V_F\left(\frac{1}{Ec_{50}F}\right)} . 100 \qquad (2)$$

## Conclusions

- The theoretical 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 x damascena* and *Cloves*.
- The experimental data for the antioxidant power was expressed as $Ec_{50}$ value of feed, permeat and retentat solution.
- The experimental results of the separation performance of the two membranes are in agreement with the theoretical prediction at pH 10.
- Part of the *Rosa x damascene* extract constituents were adsorbed within the NP030 Mycrodin-Nadir membrane matrix.

## Acknowledgements

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