

# Temperature, pH and concentration effects on retention and transport of organic pollutants across thin-film composite nanofiltration membranes

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Received 22 December 2006; accepted 7 January 2007

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## Abstract

The aim of this work is to study the concentration, temperature and pH dependences on retention for phenol and malonic acid single solutions and their mixtures. Crossflow filtration experiments were performed to measure transport of these organic compounds across a commercially available thin-film composite nanofiltration membrane (NF-90) in the temperature range 20–41°C. The influence of the feed solution pH on the rejection of phenol was verified as well. In addition, the contribution of the membrane-solute interactions on solute retention has been established.

*Keywords:* Nanofiltration; Organic pollutants; Retention

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## 1. Introduction

Phenolic compounds are frequently present in wastewaters deriving from many industrial processes such as food, textile, paper mills, pharmaceutical, fine chemical and petrochemical industries. Because of their toxicity and low biodegradability these aromatic hydrocarbons are of environmental concern, so many studies are devoted to achieve their ready elimination.

Among phenolic substances, phenol is usually taken as a model compound for wastewater

treatments. Catalytic and photocatalytic oxidation of phenol in aqueous solution has been extensively investigated [1–3] as both types of processes have proven to be promising methods for the elimination of this organic pollutant. In most studies, however, it is observed that the rate-limiting step to achieve the complete conversion of phenol to carbon dioxide is often the oxidation of the short chain carboxylic acids (malonic, maleic, oxalic, acetic, and so on) formed as intermediates. In this way, membrane processes can be a useful tool in order to separate compounds that are refractory to oxidation from the original phenol solution [4,5]. However, the retention selectivity for phenol

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Table 1  
Physico-chemical properties of studied compounds

Compound	Formula	MW (g/mol)	MWd (Å)	p <i>K</i> <sub>a</sub>	log <i>P</i>	Chemical structure
Phenol	C <sub>6</sub> H <sub>5</sub> OH	94.11	2.66	9.95	1.45	
Malonic acid	C <sub>3</sub> H <sub>4</sub> O <sub>4</sub>	104.03	2.01	2.83 5.69	-0.91	

and the organic acids resulting from its oxidation is usually deficient. Various studies have reported the influence of both solutes properties (size, acidity and charge) and membrane properties (charge, hydrophobicity and pore size) on the retention of organics by nanofiltration [6,7]. In addition, the influence of chemical properties of the feed solutions upon the membrane surface charge has been also examined [8–10].

On this basis, in the present work we have studied the influence of organic solute concentration, temperature and pH value of the feed solution on the performance of NF-90 polyamide membrane for retention of phenol and malonic acid.

## 2. Materials and methods

Phenol (Sigma–Aldrich, ≥99%) and malonic acid (Scharlau, synthesis grade, ≥99%) were used without further purification. Table 1 summarizes some relevant physico-chemical properties of both compounds.

NF-90, a nanofiltration membrane manufactured by FilmTec–Dow, was tested in this work. Its main physico-chemical properties are summarized in Table 2. Nanofiltration experiments were performed in an equipment at laboratory scale with a commercial crossflow filtration test cell (SEPA II, Osmonics, Minnetonka, MN). Flat sheet membranes with an effective membrane area of 0.014 m<sup>2</sup> were used and both permeate flux and selectivity retention were evaluated.

The storage tank contained 10 L organic solution prepared from Milli-Q water. Permeate and

concentrate were recycled to the tank to obtain a constant concentration of the feed solution. At the beginning of each experiment, the feed solution containing predetermined concentrations of the organic compounds was circulated through the membrane system about 40 min in order to achieve a stabilized concentrate. The permeate flux was determined by measuring the mass (well-known density) of permeate collected at given time intervals.

Pressures up to 1.66 MPa were used with an estimated feed cross flow velocity around 0.5 m/s. The temperature range of circulating feed solution was from 20 to 41°C. In each experiment, the pH was kept at a fixed value in the range 2.5–5.4 by addition of nitric acid (HNO<sub>3</sub>). The pH measurements were carried out with a Crison Multimeter MM40.

Membrane efficiency was evaluated before and after every experiment by permeate flux and retention tests with aqueous sodium chloride (2000 mg/L) at 0.48 MPa (70 psi). Sodium chloride

Table 2  
Manufacturers' characterization of NF-90 membrane

Membrane type	Polyamide NF
MWCO (Da)	200
NaCl rejection (%)	95
Test pressure (psi)	70
Pure water permeability [L/(m <sup>2</sup> day kPa) at 25°C]	2.49
Contact angle (°)	63.2
Mean roughness (nm)	63.9

concentration was measured in terms of conductivity by using the multimeter above mentioned. At the end of each experiment, the membranes were rinsed with deionised water at low pressure to recover at least 90% of the initial water permeation flux.

Retention values for each organic compound solution were determined within the initial concentration range of 100 to 500 mg/L. Phenol and malonic acid amounts in single solutions were measured with a Total Organic Carbon (TOC) analyzer (model TOC-V CSN Shimadzu). Solutions containing both organic compounds were analyzed by HPLC (Varian Polaris Prostar 320) with the UV–Visible detector set at 215 nm. The retention of the dissolved organic compound was calculated as:

$$R = \left( 1 - \frac{C_p}{C_f} \right) \%$$

where  $C_p$  and  $C_f$  are the permeate and feed concentrations (mg/L), respectively.

### 3. Results and discussion

Fig. 1 displays permeate flux data against transmembrane pressure for pure water and solutions of phenol and malonic acid (200, 300 and

400 mg/L). As expected, according to the solution-diffusion model [11], permeate flux increases as pressure raises. It can be observed that the permeate flux ( $J_v$ ) for both organic compounds is steadily reduced with solute concentration. For example, the permeate flux at 1.52 MPa decreases around 30% respect to pure water for both organic compounds solutions at the higher tested concentration. In addition, at the same operating conditions of pressure and organic concentration, the permeate flux for the malonic acid solution is slightly lower than the phenol one.

This behaviour is mainly related to the organic solute adsorption on the membrane surface. Van der Bruggen et al. [7] have shown that molecules with molecular weights around 100 g/mol exhibit a high tendency to adsorb on polyamide nanofiltration membranes. In agreement, phenol and malonic acid would be adsorbed on the NF-90 surface and the more of each component is adsorbed on the membrane, the larger the flux declines.

Because the solute concentrations are rather low the effect of osmotic pressure should be insignificant. Conversely, taking into account the acidic behaviour of the two organic solutes under study, it seems the contribution of the solution pH on the membrane response must not be negligible, as discussed below.

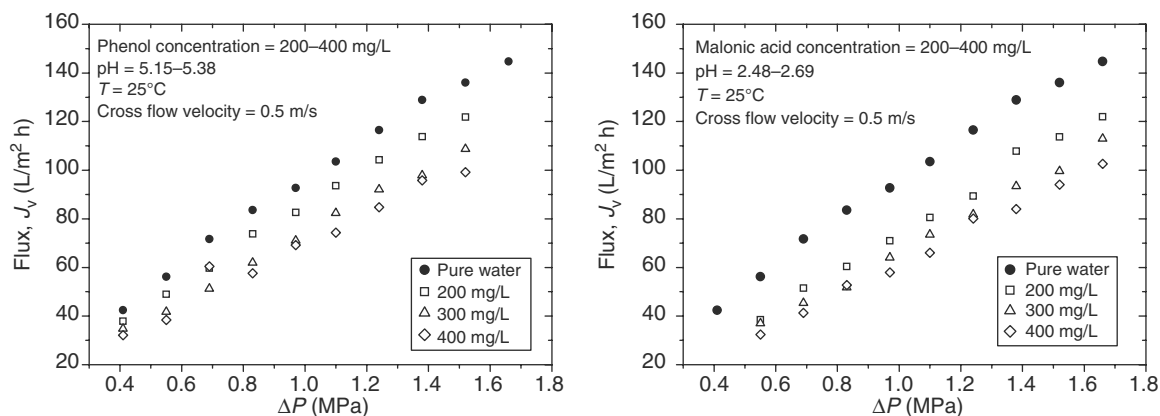


Fig. 1. Effect of transmembrane pressure on permeate flux of pure water and aqueous solutions of phenol and malonic acid.

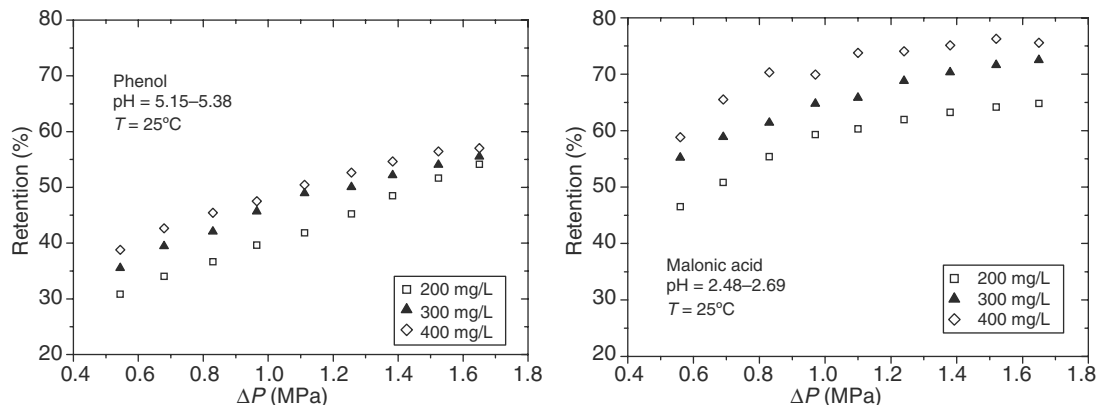


Fig. 2. Effect of transmembrane pressure on retention of phenol and malonic acid.

The retention of organic compounds against the operation pressure has been plotted in Fig. 2. Retention steadily increases with applied pressure for both compounds, as expected from the diffusion-solution model. In addition, retention percentage also enlarges with solute concentration.

As seen in Fig. 2, the retention of phenol is lower than the corresponding to malonic acid. Fig. 2 also shows that the membrane retention capability for malonic acid raises up to an apparent limiting value. The distinctive behaviour of phenol and malonic acid becomes apparent in Fig. 3

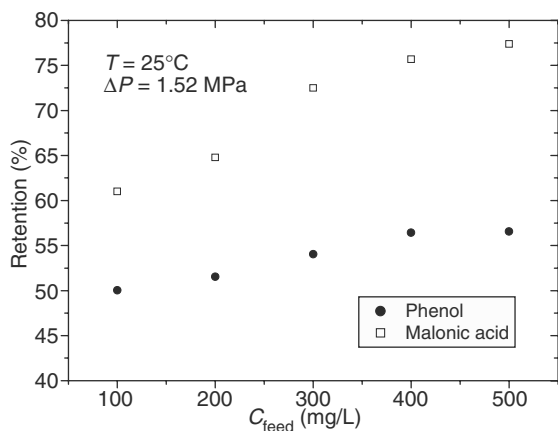


Fig. 3. Effect of organic concentration on retention at constant pressure.

where solute retention is displayed against organic concentration in the range 100–500 mg/L.

In a previous report we have analyzed the differential retention for these organic compounds [4]. We concluded that the distinction cannot be only explained by a single descriptor, such as steric hindrance exclusion (MW, MWd), solute dissociation constant ( $pK_a$ ) or hydrophobicity ( $\log P$ ). In any case, Fig. 3 illustrates that the overall interaction membrane–malonic acid is largely depending on solute concentration, a trend not found for phenol.

Temperature is a relevant factor that influences the membrane performance during filtration [12]. To study the effect of temperature on retention of phenol and malonic acid, we measured the retention at 1.52 MPa for three concentrations in the temperature range 20–41°C. The results, displayed in Fig. 4, show that phenol retention is largely reduced with temperature increase. Conversely, malonic acid retention, which is widely dependent on solute concentration, exhibits a rather steady behaviour against temperature.

If we look at the physico-chemical properties of phenol and malonic acid, a significant distinction between them is just the value of their dissociation constants ( $pK_a$ ). Thus, pH of feed solutions with similar initial concentration should be quite different for these two compounds. It is

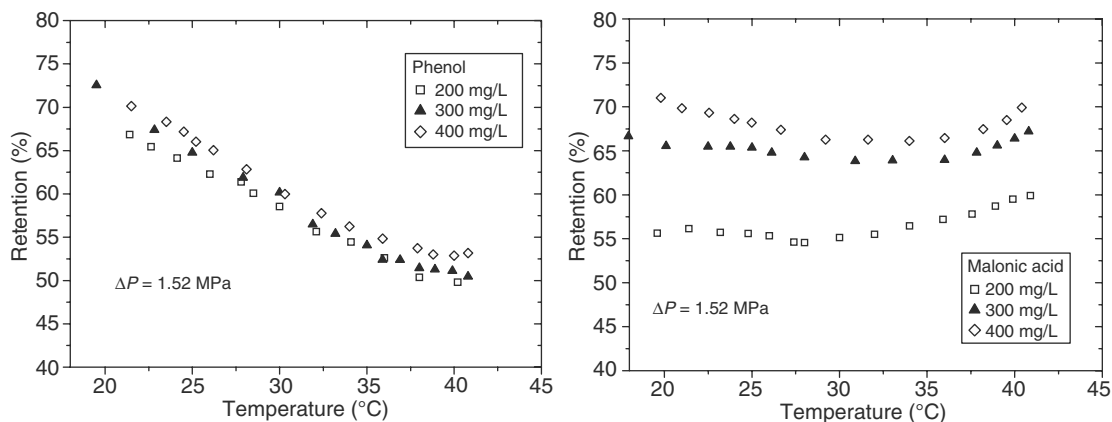


Fig. 4. Effect of solution temperature on retention of phenol and malonic acid at constant pressure.

well-known [8–10] the importance of the solution pH on the performance of the membrane retention, especially related to possible changes on the surface charge of membrane. Ku et al. [10] found that the charge of the membrane surface was shifted from negative to positive for acidic solutions with pH less than 5.0. Akbari et al. [9] observed that differences in electrical charge between the membrane and solute caused concentration polarization phenomenon, blocking the diffusion of solute.

So, a significant part of the differences that we have found between phenol and malonic acid behaviour could be attributed to pH considerations. To check this effect we carried out experiments of phenol retention at constant pressure for different pH and temperature conditions. In order to evaluate the influence of solution pH and proton source, we used mixtures of phenol with both malonic and nitric acids. In Fig. 5 we have plotted our experimental data. It is apparent that phenol retention is quite dependent on solution pH and this behaviour is maintained in the whole temperature range of this investigation.

However, the acidic source seems of minor importance on phenol retention since experimental data are quite similar for malonic acid and nitric acid. In a future work we intend to explore both

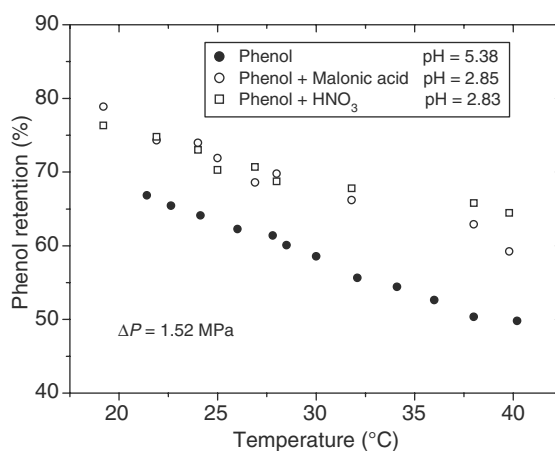


Fig. 5. Effect of solution pH on phenol retention from aqueous solution (200 mg/L).

the effect of pH on malonic acid retention and the phenol and malonic acid competition for adsorption and permeation on nanofiltration membranes.

#### 4. Conclusions

Nanofiltration experiments have been performed with aqueous solutions of phenol and malonic acid. The operational variables were: organic concentration (100–500 mg/L), transmembrane

pressure (up to 1.66 MPa), temperature (21–40°C) and pH (2.8–5.3). In all cases permeate flux was increased by raising the operating pressure and decreased by increasing the organic concentration. The retentions of both organic compounds were enhanced as the pressure was raised. Under similar operating conditions, malonic acid had higher retentions compared to phenol. Temperature and pH showed a different influence on the retention behaviour of the tested molecules. Whereas the increase of temperature had a negative effect on the retention of phenol at 1.52 MPa, no significant influence was obtained for malonic acid. A decrease of the pH of the solution significantly increased the retention of phenol, independently of the protons source used.

### Acknowledgements

This work was supported by Ministry of Education and Science of Spain under the CICYT/PPQ2003/039884 research project and Comunidad de Madrid under the P-AMB-000395-0505 (REMTAVARES) research project. The authors also wish to thank Genesys Membrane Product, S.L. for its valuable contribution to this work.

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