

# Nanofiltration for the Treatment of Bleaching Effluents from the Pulp and Paper Industry: A Case Study

Ronca A.\*, Galinha C.F., Crespo J.G.

LAQV-REQUIMTE, DQ, NOVA School of Science and Technology, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal

\*Corresponding author: [a.ronca@fct.unl.pt](mailto:a.ronca@fct.unl.pt)

**Abstract.** The present study explores the application of commercial nanofiltration (NF) membranes for the treatment of bleaching effluent from the pulp and paper (P&P) industry, within the framework of the RESURGENCE project, funded by the European Union's Horizon Research and Innovation Programme (Grant Agreement No. 101138097). The P&P industry is a major user of water, generating effluents characterised by high organic load, elevated temperature, intense colour, and the presence of priority pollutants, all of which pose significant environmental risks. The NF process was evaluated using a lab-scale plate-and-frame membrane unit operated in full recirculation mode. Three different commercial membranes were tested under identical conditions ( $P = 10$  bar, fixed temperature, 4-hour filtration time). The results demonstrate stable permeate flux and promising separation performance, with colour removal exceeding 99%, COD reduction above 85%, and retention (or partial retention) of key pollutants such as  $\text{Cl}^-$  and  $\text{Ca}^{2+}$ . This is particularly relevant in the context of water reuse within the industrial process. These findings confirm the potential of NF membranes for advanced industrial wastewater treatment, enabling both improved effluent quality and the potential for water reuse, thereby reducing the environmental impact and freshwater demand in the P&P sector.

**Keywords:** P&P industry, nanofiltration membrane, industrial wastewater treatment, water reuse.

## 1. Introduction

The pulp and paper (P&P) industry is characterized by substantial water usage, generating a diverse range of wastewater streams throughout the production cycle, including raw material and chemicals preparation, cooking, bleaching, washing, and stock preparation (Lacorte, 2003; Toczyłowska Mamińska, 2017). Each process produces a distinct type of wastewater, typically exhibiting high concentrations of COD, total suspended solids (TSS), and colour, while parameters such as pH and specific chemical compositions vary significantly. In particular, the wastewater generated from the bleaching process is characterized by extreme pH values and elevated concentration of compounds containing

chlorine, some of which are toxic to humans and the aquatic environment, including chlorophenols, adsorbed organic halogen (AOX), polychlorinated biphenyls and polychlorinated dibenzodioxins, chlorinated resin acid and chlorinated lignosulfonic acids (Esmaceli et al., 2023). The NF process has been investigated for the treatment of different wastewater streams from the P&P industry, showing interesting results in terms of water recovery for its recirculation back into the production processes and in terms of water purification. Typical performance includes a 70–90% reduction in COD and 90–97% reduction in AOX levels, along with high removal efficiencies for monosaccharides, organic acids, and colour (Mänttari et al., 2021). As in other membrane processes, effective fouling control and mitigation are essential for the development of a functioning process. This is due to the fact that the streams of the P&P industry are characterised by a high degree of heterogeneity in terms of their organic and inorganic compounds, which can act as foulants (Bokhary et al., 2018).

## 2. Nanofiltration assays

The assessment of membrane properties was carried out through different tests. The hydraulic test using distilled water is used to determinate the membrane permeability ( $L_{pw}$ ). The bleaching effluent, supplied by a Portuguese P&P company, was used for the real wastewater test. Nanofiltration assays were conducted in full recirculation mode to simulate a continuous operation, over a 4-hour operational period under a constant pressure of 10 bar. Each membrane was tested twice, once at ambient temperature and once at 45°C, to assess the effect of temperature on performance. The chemical cleaning was performed to evaluate fouling removal efficiency and the restoration of membrane permeability. The cleaning protocol included two sequential steps: an alkaline cleaning (sodium hydroxide) and an acidic cleaning (Ultrasil®) for 30 minutes each. The water quality assessment was performed using NANOCOLOR® pre-packaged test kits for COD, chloride ( $\text{Cl}^-$ ), calcium ( $\text{Ca}^{2+}$ ), magnesium ( $\text{Mg}^{2+}$ ), and total hardness. In this preliminary phase, UV-Vis spectrophotometry and fluorescence spectroscopy were

employed to analyse the optical properties of both raw and treated wastewater samples.

### 3. Results, discussion and outlooks

The three commercial membranes exhibited similar behaviour at both temperatures, with permeability increasing at higher temperatures, suggesting 45°C as the optimal operating point. This choice balances performance and energy consumption, as the wastewater stream is initially at 70–80°C. Among the membranes, NF-270 showed the best hydraulic performance but experienced a significant permeability loss after operation and chemical cleaning, similarly to NF-90. NF-DK, although initially having the lowest water permeability, maintained higher fluxes than NF-90 during real wastewater tests and showed better permeability recovery after cleaning. This suggests that NF-DK's material composition may enhance fouling resistance, requiring further investigation. Flux decline was observed for all membranes during wastewater operation. At ambient temperature, NF-DK, NF-90, and NF-270 declined moderately (from 50 to 45 LMH, 34 to 28 LMH, and 92 to 88 LMH, respectively). At 45°C, NF-90 and NF-270 showed a sharper decline, while NF-DK maintained a relatively stable flux (~65 LMH), suggesting improved operational stability and reduced cleaning needs.

Observed rejection values indicate that  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and hardness were fully rejected by all membranes. COD removal was consistent across membranes, with rejections above 0.85. As shown in [Table 1](#), conductivity and  $\text{Cl}^-$  rejection highlighted differences: NF-90 maintained high rejection, meeting purification targets, while NF-DK and NF-270 only partially rejected these ions, probably due to membrane properties like MWCO and surface charge accumulation during operation. Overall, NF-90 demonstrated the highest ion rejection but the lowest flux, while NF-270 achieved high flux without fully meeting purification standards. NF-DK offered excellent fouling resistance but insufficient  $\text{Cl}^-$  removal.

**Table 1.** Rejection to the principal solutes of the three membranes under different conditions

Membrane	Temp. condition	Rejection		
		Conductivity	COD	$\text{Cl}^-$
NF-DK	Ambient	0.68 ± 0.03	0.89	0.56 ± 0.04
	45°C	0.66 ± 0.01	0.88	0.56 ± 0.04
NF-90	Ambient	0.98	0.90	0.97
	45°C	0.98	0.89	0.97
NF-270	Ambient	0.63 ± 0.04	0.88	0.50 ± 0.05
	45°C	0.56 ± 0.01	0.86	0.47 ± 0.01

Since this NF process is expected to be scaled up to both pilot and industrial levels, an optimization of key operational parameters is required. These include

hydraulic performance, process maintenance (e.g., membrane cleaning protocols), operating pressure, module configuration, and compliance with purification standards. Given that the project's objective is focused on sustainability and improving water usage efficiency in industrial processes, one of the main goals is the reintroduction of the permeate stream into the paper production cycle.

Ongoing studies aim at collecting information that will facilitate the optimization of the NF process in a sustainable way. Additionally, a more profound examination of the fouling mitigation strategies is being conducted to facilitate the cleaning of the membrane and its recovery, thereby extending the lifespan of the membrane. This will be coupled with membrane autopsy for the identification of the compounds that act as foulants in this complex wastewater stream. Finally, and equally importantly, there is a necessity to develop techniques that can be utilized to identify the presence of micropollutants (MPs) in both the feed and the permeate. This will enable the evaluation of the potential for MPs removal through the NF process.

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