

# Abstract

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Several conventional treatment methods have been used to treat the wastewater from different paper mills. Previous studies and applications have shown that conventional methods are not capable to comply with the most stringent environmental regulations on effluent quality and/or for the process water to be reused in papermaking (Shankar et al., 2014).

Faced with the necessity for process optimization membrane separation technology has attracted more and more attention as an alternative way to treat paper mill wastewater. Some nanofiltration (NF), ultrafiltration (UF) and reverse osmosis (RO) plants have been installed in pulp and paper mills to purify secondary and tertiary effluents using external biological treatment. The major advantage of the membrane separation technology is that it can save energy, reduce the carbon footprint and simplify operation. Many reports have demonstrated the applicability of membrane technology to pulp and paper mill wastewater (Pokhrel and Viraraghavan, 2004a). Additionally, UF can be used as an advanced tertiary treatment to remove suspended solids and dissolved and colloidal substances (DCS) during the treatment of paper industry effluent.

However, membrane fouling is a major drawback that limits widespread and full-scale applications of UF and, currently, this treatment technology can only be used to filter paper mill effluent that has been pre-treated and meets discharge standards (Puro et al., 2011a). To help minimize membrane fouling, it is important to understand the effect of operating conditions on process and investigation the chemical composition and possible origins of membrane foulants.

The overall goal of this research has been divided into three main parts: i) describes how to find optimal operating conditions of four controlling parameters, such as transmembrane pressure (TMP), cross-flow velocity (CFV), temperature and molecular weight cut-off (MWCO) for maximizing the average permeate flux ( $\bar{J}_p$ ) and chemical oxygen demand (COD) rejection, and minimizing the cumulative flux decline (SFD) using Taguchi method and utility concept for a cross-flow UF in pilot scale, used to remove DCS from a paper mill treated effluent (PMTE), ii) flux decline and fouling mechanisms of UF membranes fouled with PMTE were examined by theoretical

modelling. The results from UF tests were expressed in terms of permeate flux ( $J_p$ ) as a function of time to check modified Hermia's models adapted to crossflow filtration and cake formation in constant-pressure filtration, and iii) describes the Identification, characterization and possible origins of UF membrane foulants. Techniques such as chemical analysis, FESEM, SEM-EDS, ATR-FTIR and 3DEEM analysis were applied to understand which fraction of the foulants caused the fouling.

This research found that the TMP and MWCO have the greatest contribution to the average permeate flux and SFD. In the case of the COD rejection rate, the results showed that MWCO has the highest contribution followed by CFV. The optimum conditions were found to be the second level of TMP (2.0 bar), the third level of the CFV (1.041 m/s), the second level of the temperature (15 °C), and the third level of MWCO (100 kDa). Under these optimum conditions  $\bar{J}_p$ , COD rejection and SFD resistance of 81.15 L/m<sup>2</sup>/h, 43.90% and 6.01 (around 28.96 % of  $\overline{FD}$ ), respectively, were obtained and they were within of the predicted range at the 95% confidence interval.

Furthermore, the results showed that the predictions of the modified Hermia's models adapted to cross-flow UF had good agreements with experimental data, under different conditions tested for PMTE. Therefore, it can be concluded that for all cases the best fit (higher accuracy) to the experimental data corresponds to the complete (coefficient of determination  $R^2 > 0.97$ ) and intermediate ( $R^2 > 0.96$ ) blocking, followed by the cake layer formation ( $R^2 > 0.94$ ). Moreover, measurements of particle size distribution and zeta potential near the isoelectric point, showed a substantial reduction in colloidal compounds.

The 3DEEM analysis revealed that the majority of the organic foulants with fluorescence characteristics on the fouled membranes were colloidal proteins (protein-like substances I+II) and macromolecular proteins (SMP-like substances). Further, polysaccharide (cellulosic specie), fatty and resin acid substances were identified on the fouled membrane by the ATR-FTIR analysis and they play an important role in membrane fouling. In addition, the membrane SEM-EDS analysis showed accumulate and adsorbed onto the membrane surfaces of inorganic foulants, such as multivalent metal ions and especially Ca<sup>2+</sup> (acts as a binding agent) that could accelerate cake layer formation on the membrane.