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Modelling approach to an ultrafiltration process for the removal of dissolved and colloidal substances from treated wastewater for reuse in recycled paper manufacturing

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A B S T R A C T

In this work, ultrafiltration (UF) is used to remove dissolved and colloidal substances (DCS) from a secondary clarifier effluent from a wastewater treatment plant (WWTP) in a papermaking factory. The approach has been to examine and model the decline in permeate flux resulting from membrane fouling. Effluent from a WWTP at a papermaking factory, previously filtered, was used as feed. UF experiments were carried out in a laboratory-scale plant using a 10 kDa polyethersulfone (PES) UF membrane in a flat sheet module with an active area of 154.8 cm^2. The transmembrane pressure (TMP) (1–3 bar) and crossflow rate (1.5–4.5 L/min) were varied during the experiments, at constant temperature (22 ± 0.5 °C). Experimental results from UF tests were expressed in terms of permeate flux (Jp) as a function of time to check modified Hermia's models adapted to crossflow filtration. The parameters of these models were theoretically estimated. The predicted results were compared with experimental data with a high goodness of fit. The results showed that the phenomenon controlling fouling, under most of the conditions tested, was intermediate blocking ($R^2 > 0.96$). Measurements of particle size distribution and zeta potential near the isoelectric point, showed a substantial reduction in colloidal compounds. Additionally, given that COD was removed down to 110 mg/L, it could be said that UF is suitable for producing water that can be reused in different papermaking processes.

1. Introduction

The pulp and paper (P&P) industry represents one of the most important industries of the European economic sector. According to data from 2010 the sector had a total turnover of 76.4 billion euros, employing about 225,000 people directly [1]. According to Key Statistics 2014-CEPI, Europe is the second largest producer of paper and paperboard with 22.7% (91.39 million tons) of world production (Asia 45.3% and North America 21.1%), and the third largest consumer with 18.9% (76.28 million tons), behind Asia the leader with 46.6%, and North America with 19.2%. These industries commonly produce considerable amounts of wastewater and face challenges to comply with stringent environmental regulations. In this regard, the European Commission has described the best available techniques (BAT) to be adopted by P&P mills [2].

Wastewater from the paper industry contains a high biodegradable organic matter loading and its volume is high in relation to production. Paper mill wastewater carries significant quantities of fibre (losses with effluent 0.5–5% of total fibre amount), filler, fines and other wet-end additives that contribute to total suspended solids (TSS), chemical oxygen demand (COD) and biological oxygen demand (BOD). TSS varies significantly from mill to mill, based on the type of internal clarification equipment used, equipment arrangement and design philosophy. COD depends on the amount of suspended solids such as fibre, fines, and other chemically oxidisable wet-end additives such as starch. BOD is high due to the presence of large amounts of oxidisable materials, such as fibre, fines, starch, wet and dry strength resins, drainage aids, dyes, sizing materials and other dissolved organics [3]. Furthermore, the volume, properties and characteristics of P&P generated wastewater depend on several factors such as the type of paper production (packaging paper, corrugated cardboard, light-weight coated paper, printing and writing paper), the raw materials used in the manufacturing process, which can be from virgin fibre or recovered fibres (RCFs), the production process employed, applied technologies, additive chemicals and the amount of water consumed. It is important to mention that the wastewater generated in a RCF mill is quite small compared to that from a virgin P&P production process [4,5].

In fact, P&P industry recovery of waste papers such as mixed office waste, old cardboard, old newsprint and old corrugated containers has increased over recent decades, due of a number of favourable factors

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Nomenclature

A	Membrane surface (m^2)
C_O	Feed concentration of particles ($kg.m^{-3}$)
C_g	Gel concentration (volume fraction) (%)
J_p	Permeate flux (m/s)
J_{SS}	Steady-state permeate flux (m/s)
J_O	Initial permeate flux (m/s)
k	Constant of hermia's model [units depend on the parameter n in Eq. (2)]
K_C	Constant of complete pore blocking (m^{-1})
K_i	Constant of intermediate pore blocking (m^{-1})
K_s	Constant that corresponds to the standard blocking model ($m^{-1/2}.s^{-1/2}$)
K_{gl}	Constant of cake filtration model ($s.m^{-2}$)
K	Carmen–Kozeny constant
k_m	Mass transfer coefficient ($m^2 m^{-1}.s^{-1}$)
n	Constant of hermia's modelin Eq. (2) (dimensionless)
N_{Fc}	Critical filtration number
ΔP	Hydraulic pressure differential (Pa)
ΔP_c	Pressure drop across the concentration polarisation layer (Pa)
R_m	Membrane resistance (m^{-1})
R_{bm}	Resistance of the blocked membrane (m^{-1})
R_c	Cake resistance (m^{-1})
R_t	Total resistance (m^{-1})
R_{res}	Resistance reversible fouling (m^{-1})
r_c	Specific resistance of the cake layer (m^{-2})
T	Temperature (K)
TMP	Transmembrane pressure
t	Time (s)
PES	Polyethersulfone
μ	Permeate viscosity (Pa.s)
δ	Cake thickness (m)
ε	Porosity of membrane
a_p	Particle diameter (m)
τ	Tortuosity of membrane
ε	Porosity of membrane

such as raw material economy, natural resources saving, reductions in solid waste and effluent [6]. However, when recycled paper is used (RCF mills) the effluent is characterised by a variable loading of fibres, pulping additive chemicals and other impurities such as short fines and fillers, which are generally not very soluble. In addition, the concentration of dissolved organic pollutants is particularly high and directly related to the origin of the waste papers [7,8]. Zwain et al. [9] studied some physical-chemical characteristics of recycled paper wastewater as presented in Table 1.

Paper mills have their own wastewater treatment plants, but this treatment does not achieve the pollutant loadings permissible under current regulations. As a result, the wastewater must be sent to municipal WWTPs, causing problems in designed operational conditions. Most pulp and paper mills treat their effluent by using an activated sludge process. However, this biologically treated effluent still contains significant amounts of colour compounds, microorganisms, recalcitrant organics and a minor amount of biodegradable organics as well as suspended solids. Therefore, the biological treatment does not significantly reduce the inorganic content of the effluent. As a result, the water is still not sufficiently clean after this process for reuse in the production of most paper. Pulp and paper mill effluents can be reused for the production of different types of paper and cardboard [10], but process water cannot be recycled easily because dissolved and colloidal substances (DCS) and electrolytes become enriched with water recycling. This has the effect of adversely affecting paper machine operability and paper quality. In general, the DCS in process water comes from fibre extractives and the chemical additives consumed during manufacturing and they can also react with electrolytes Ca^{2+} and Mg^{2+} [11–14].

The degree to which these impurities need to be removed before reuse of the water is not well known. However, the higher the quality of the paper produced, the cleaner the water used in manufacturing should be [15,16]. Recently, 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) membrane filtration 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 [17]. Ultrafiltration can be used as an advanced tertiary treatment to remove suspended solids and DCS during the treatment of paper industry effluent. This allows the re-utilisation of process water and reduces fresh water consumption. However, membrane fouling limits the application and use 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 [18].

DCS might play a number of different roles in membrane fouling. Colloidal substances larger than the pores cannot pass through the membrane and they will be deposited on the membrane surface blocking the pores. Dissolved substances that are smaller than the membrane pore-size are adsorbed within the pores and/or deposited within the membrane, shrinking the pore diameter and increasing membrane resistance. In addition, once pores are blocked, other DCS can form a cake on top of the membrane, adding additional resistance via another porous layer covering the membrane [19,20].

According to research performed by Chen et al. [21], reversible membrane fouling during ultrafiltration accounted for 85.52% of total fouling. It primarily originated from retention aids, drainage aids, polyacrylamide and wet strength resins. While irreversible adsorptive fouling accounted for 14.48% and mostly came from sizing agents, coating chemicals (oxidants for polyester or resin and polyester or resin surface sizing agents) and other sources. Moreover, the presence of dissolved multivalent metal ions, especially Ca^{2+}, accelerated membrane fouling [22]. Some research aimed at reducing biofilm formation has demonstrated that bacterial cells (Pseudomonas fluorescens) on cellulose fibres can affect retention [23]. Pratima Bajpai [24] studied the types of microorganisms encountered in the papermaking process

Table 1
Physical-chemical characterization of recycled paper wastewater (from Zwain et al.).

Parameter	Range[a]
pH	6.2–7.8a
Floc size	08–300
Temperature	35–45
Chemical oxygen demand (COD)	3380–4930
Biochemical oxygen demand (BOD)	1650–2565
BOD_5/COD	0.488–0.52
Alkalinity	300–385
Ca	375–420
Mg	10–15
Total solids (TS)	3530–6163
Total dissolved solids (TDS)	1630–3025
Total suspended solids (TSS)	1900–3138
Total volatile solid (VSS)	840–2920

[a] Parameters are in mg/L except pH, BOD5/COD, temperature in °C and floc size in µm.