Chemical Engineering Journal 285 (2016) 304–318

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Treatment of textile plant effluent by hollow fiber nanofiltration membrane and multi-component steady state modeling

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HIGHLIGHTS

- Hollow fiber nanofiltration membranes were prepared upto cut off 360 Da.
- At pH 10, zeta potential of optimum membrane was −10 mV.
- 4 reactive dyes were removed more than 98% from a textile plant effluent.
- 42% salt recovery was attained.
- A predictive multi-component steady state model was developed.

ARTICLE INFO

Article history:
Received 5 August 2015
Received in revised form 29 September 2015
Accepted 2 October 2015
Available online 8 October 2015

Keywords:
Hollow fibers
Nanofiltration
Surface modification
Textile effluent

ABSTRACT

Polysulfone based nanofiltration (NF) hollow fibers upto 360 Da cut off were prepared by interfacial polymerization of meta-phenylenediamine and trimesoyl chloride. Hollow fibers were characterized in terms of scanning electron and atomic force microscopy, permeability, molecular weight cut off (MWCO), pore size distribution and surface zeta potential. Increase in TMC concentration reduced the MWCO and average pore size of the membrane. MWCO was decreased from 780 to 360 Da and average pore radius was reduced from 7.3 to 5 Å as TMC concentration increased from 0.1 to 1 wt%. A textile effluent containing four reactive dyes and salt was successfully treated by this hollow fiber. A completely predictive steady state multicomponent model was developed to quantify the system performance.

1. Introduction

Textile industries generate huge quantity of wastewater from dyeing and finishing processes containing 50–200 mg/L unfixed dyes [1,2]. Certain classes of dyes like reactive dyes are generally found at relatively high concentration due to their lower ability of fixation to fibers like cotton and viscose. These wastewater streams are often found to be biorecalcitrant due to presence of various additional chemicals like fixation, bleaching agents and surfactants. Large amount of salts are added to the dye baths for enhancing dye fixation [3]. In addition to salts, caustic solution of about 23% NaOH is also added to improve properties like fiber strength, shrinkage resistance, luster, and dye affinity. Therefore, dye house effluent has high chemical oxygen demand (COD) and it is a major contributor to pollution in aquatic environment, leading to stricter environmental regulations [4]. Due to high cost of treatment, small scale industries discharge the effluent directly to the surface water.

Hyper-saline effluents are often found to be resistant to biological treatment. Biological treatment systems sometimes become poisoned due to the chemicals present in these effluents. Thus, they are not efficient for dye removal [5]. Solar evaporation is one of the low-cost techniques that reduces the volume of the effluent and concentrates the salts and organic content of saline effluent [6]. Coagulation–flocculation is also used as a pretreatment of hyper saline effluent to remove COD [6,7]. However, coagu lation–flocculation is not efficient for salt removal. The conventional processes used to remove dyes from wastewater include

Abbreviations: AFM, atomic force microscopy; COD, chemical oxygen demand; CFR, cross flow rate; DMF, dimethylformamide; FRR, flux recovery ratio; FDR, flux decline ratio; MPD, m-phenylenediammine; MWCO, molecular weight cut-off; NaCl, sodium chloride; PEG, polyethylene glycol; PSF, polysulfone; SEM, scanning electron microscope; TDS, total dissolved solid; TMC, trimesoylchloride; TMP, transmembrane pressure drop; TS, total solid.

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http://dx.doi.org/10.1016/j.cej.2015.10.005
1385-8947/

Nomenclature

a_i	osmotic coefficient of ith component, Pa m^3/kg
A_0	membrane surface area, m^2
$C_{i,m}$	concentration of ith component on membrane surface, kg/m^3
C_P	concentration of permeate, kg/m^3
C_F	concentration of feed, kg/m^3
d	diameter of the hollow fiber, m
D_i	diffusion coefficient of ith component, m^2/s
J_{ss}	steady state permeate flux, L/m^2 h
J_w	pure water flux, L/m^2 h
J_{w1}	water flux of the membrane before experiment, L/m^2 h
J_{w2}	water flux of the membrane after experiment, L/m^2 h
J_1	initial flux of the membrane with dye solution, L/m^2 h
K_i	mass transfer coefficient of ith component, m/s
k_b	Boltzmann constant, 1.3805×10^{-23} J/mol K
L	length of the hollow fiber, m
L_p	membrane permeability, m/Pa s
M_i	molecular weight of ith component, g/mol
MW	molecular weight, g/mol
Q	volumetric flow rate, m^3/s
R_g	ideal gas constant, J/mol K
R	rejection, %
$R_{i,r}$	real retention of ith component
R_i	radius of ith component, m
r_s	solute radius, m
r_p	effective pore radius of the membrane, m
Re	Reynolds number ($\rho u_0 d/\mu$)
Sc	Schmidt number ($\mu/\rho D$)
Sh	Sherwood number (Kd/D), Eq. (9)
T	temperature, K
u_0	average velocity, m/s

Greek symbols

α	$a/\Delta P$, Eq. (6)
δ	film thickness, m
ΔP	transmembrane pressure drop, Pa
Δt	sampling time, s
ε	molar extinction coefficient
η	viscosity of solution, Pa s
λ	wavelength, nm
μ_p	mean effective pore radius, m
μ_s	geometric mean radius of solute, m
π_m	osmotic pressure at the membrane surface, Pa
π_p	osmotic pressure at the permeate, Pa
σ_g	geometric standard deviation of solute radius, m
σ_p	geometric standard deviation of solute radius, m

flotation [8], sedimentation [9], physical and chemical adsorption [10], advanced oxidation processes like ozonation, photocatalytic oxidation [11,12], Fenton's process, photo-Fenton oxidation [13,14], ultraviolet irradiation and electrochemical oxidation [15,16]. The limitations associated with all these conventional processes are also significant. For example, ozonation and advanced oxidation processes are expensive [17,18]. Electro-coagulation is another recently developed method for removal of dyes [19,20]. But, this process is also expensive and time-consuming. Ozkan-Yucel and Gokcay reported anaerobic oxidation for treatment of azo dye [21]. Adsorption is one of the popular methods to treat dye containing wastewater. Activated carbon, clay minerals, zeolites, metal oxides, agricultural wastes, biomass and polymeric materials are used as adsorbents by several researchers [22–31]. Low cost adsorbents, like, raw and modified rectorite [32], perlite [33], rice husk [34], marine algae [35], etc., are also used. However, adsorption is a slow and equilibrium governed process. Moreover, the powdery form of adsorbents makes their removal difficult from filtrate [36]. High operating and disposal cost are other disadvantages.

Membrane based separation processes offer an attractive alternative in this regard due to various advantages, including (i) physical separation; (ii) no additives; (iii) low energy intensive; (iv) high scalability [37]. Nanofiltration (NF) is in between reverse osmosis and ultrafiltration and is a suitable process for textile effluent treatment [38]. The operating pressure requirement for NF membranes is much less (10–20 atm) compared to reverse osmosis. Numerous reports are available in literature on the application of NF for treatment of textile effluent [39–46]. Most of the modules are in plate and frame, spiral wound or tubular configurations. On the other hand, in hollow fiber configuration, one can pack a large number of hollow fibers in a bigger tube so that a large surface area is obtained in a smaller volume, thereby, providing a higher throughput of the process. Very few reports are available in NF grade hollow fibers [47–54]. Treatment of textile effluent using NF hollow fiber is scant in literature [55,56].

Thin film composite hollow fiber NF membrane was developed by in-situ interfacial polymerization of polysulfone based ultrafiltration grade fibers using in m-phenylenediamine (MPD) and trimesoyl chloride (TMC) [50]. In that study, concentration of MPD was in the range of 0.5–2 wt% and that of TMC was from 0.01 to 0.1 wt%. With combination of 2 wt% MPD and 0.1 wt% TMC, a membrane of molecular weight cut off (MWCO) 490 Da was obtained and synthetic dyes with molecular weight 480–990 Da were successfully removed. A typical dye-house effluent contains a mixture of dyes with lower range of molecular weight as low as 400 Da. However, Maurya et al. [50] reported extremely low flux (0.01–0.035 L/m^2 h) with synthetic dye solution. Therefore, the present work has been undertaken to attain NF grade hollow fiber with low MWCO (<400 Da) by varying concentration of TMC to higher range (0.1–1 wt%) at a fixed MPD concentration (2 wt%) for interfacial polymerization of polysulfone and to achieve higher permeate flux. The developed hollow fibers are characterized in terms of surface morphology by scanning electron microscope (SEM), permeability, MWCO, pore size distribution, atomic force microscopy (AFM) and surface zeta potential. Efficiency of membranes is evaluated by treating a real life textile effluent containing four reactive dyes. Performance of filtration is analyzed in terms of physico-chemicals parameters, like, chemical oxygen demand (COD), total dissolved solids (TDS), total solids (TS), conductivity, rejection of dye and salts. A completely predictive multi component model for steady state is formulated based on film theory and osmotic pressure model. Adequacy of the model is quantified by comparing the permeate flux, permeate concentration of salt and dye with experimental data. Such simple model can be of great help to design engineers for scaling up.

2. Theory

In case of an actual textile plant effluent, a steady state model is proposed to calculate the permeate flux and permeate concentration. The solvent flow through the porous membrane can be quantified as [57],

$$J_{ss} = L_p[\Delta P - \Delta\pi] \quad (1)$$