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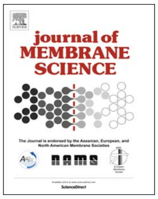

Modeling of cross flow hollow fiber ultrafiltration for treatment of effluent from Railway Workshop

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ABSTRACT

Industrial oily water containing oil, grease and dust has been treated using stage-wise filtration, first by sand bed followed by cross-flow ultrafiltration hollow fiber membrane. The sand bed removes majority of suspended particles and reduces the turbidity from 13.6 NTU to 2.6 NTU. Effects of transmembrane pressure drop and cross flow rate on ultrafiltration performance were investigated. A transport phenomena based model under the framework of boundary layer theory was developed to quantify the flux decline and oil transport through the membrane during cross flow filtration in hollow fiber. The model results matched remarkably well with the experimental data. The mechanism of filtration was analyzed and found to be governed by cake formation. Formation of cake-layer was supported by scanning electron micrography of fresh and fouled membranes and Fourier Transform Infrared spectroscopy. The modeling of separation mechanism and estimates system parameters will aid in scaling up of the filtration set-up to industrial scale for treatment of industrial effluent containing oil.

1. Introduction

Oil and grease are integrated components of many industrial effluent streams. Nature of the oily contaminant varies widely from vegetable oils to hydrocarbons and mineral oils depending on the source. Typical concentration of oil in effluent from petroleum industry varies between 10 and 3200 mg/l, whereas, the same in case of steel and aluminum industries range between 5000 and 50000 mg/l [1,2]. Car production effluent contains even higher oil and grease in the range 200 g/l [3]. Oil in such effluent includes hydrocarbons which, even in trace quantities, may harm the marine life. Oil-in-water emulsions in industrial effluent are generated from equipment wash water, rinsing baths, compressor condensates, etc., and considerable amount of such oily effluent cannot be treated using biochemical degradation [4]. The maximum permissible limit of oil in discharge stream is categorized based on the source and nature of contaminant. To cite a few, according to the US regulations, the limit of oil in effluent stream from petroleum refinery is limited to 5 mg/l [5], whereas, the same for hardware industries is 35 mg/l for one day and cannot exceed 17 mg/l over a period of month [1]. Existing Indian standard for discharge of oily water to surface is 10 mg/l oil concentration and is proposed to be reduced further to 5 mg/l [6]. This makes the removal of oil more crucial even in traces.

Treatment of oil from waste water can be divided broadly into two categories, namely, primary treatment and secondary treatment [2]. Primary treatment aims at removing floating oil and to some extent emulsified oil, whereas, secondary treatment is used to remove oil present in low concentration. Several conventional techniques are employed for removal of oil and grease from waste water streams including gravity settling, API separator, centrifugal settling, de-emulsification using chemical agents, electrostatic coalescence, skimming, air floatation, flocculation etc. [1,7–9]. Each of these conventional techniques possesses advantages and disadvantages of its own. Gravity settling, API separator, skimming, etc., are effective in removing larger droplets and emulsions but result very low efficiency for smaller droplets. Flotation and coagulation (both chemical and electrostatic) methods typically employ chemical agents generating large amount of sludge [1,10]. The major drawback of these conventional techniques is that their efficiency falls when the droplet size in emulsion is below 10 μm and concentration is less than 1% by volume [2,5].

In case, where effluent stream is a dilute solution containing micron range particles, membranes are attractive alternative. Applicability of membranes in removal of oil-water emulsions is increasing rapidly due to stable filtrate quality and small area requirement [10]. Also membrane based processes do not require external chemicals and hence, generate negligible amount of sludge. Cheryan et al., have provided significant review of various methods being followed for removal of oil from water with the help of polymeric membranes [1]. According to

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Nomenclature

a and b	Pressure dependence parameters of mass transfer coefficient, unit of b [Pa^{-1}]
B	Solute permeability through the membrane [$\mathrm{kg/(m^2\ s)}$]
c	Oil concentration [mg/l]
c_{avg}	Average solute concentration in the membrane phase [mg/l]
c_c	Oil concentration in cake layer [mg/l]
CFR	Cross flow rate [l/h]
c_p	Oil concentration in permeate [mg/l]
$c_p{}^s$	Oil concentration in permeate at steady state [mg/l]
c_0	Oil concentration in feed [mg/l]
D	Diffusivity of oil in water [$\mathrm{m^2/s}$]
d	Hollow fiber inner diameter [μm]
J	Permeate flux at any time point [$\mathrm{l/(m^2\ h)}$]
J^s	Permeate flux at steady state $\mathrm{l/(m^2\ h)}$]
$J^{s,cal}$	Steady state permeate flux: calculated values [$\mathrm{l/(m^2\ h)}$]
$J^{s,exp}$	Steady state permeate flux: experimental data points [$\mathrm{l/(m^2\ h)}$]
J_0	Initial permeate flux [$\mathrm{l/(m^2\ h)}$]
k	Mass transfer coefficient [m/s]
k_c	Filtration coefficient [Unit of k depends on value of n]
k_1	Effective mass transfer coefficient [m/s]
L	Cake thickness [μm]
l	Length of the hollow fiber cartridge [cm]
M	No. of data points at each operating condition [dimensionless]
m	Compressibility of the cake layer [dimensionless]
MWCO	Molecular weight cut-off [kDa]
N	No. of steady state data points [dimensionless]
ΔP	Trans-membrane pressure drop [Pa]
PAN	Polyacrylonitrile
q and ε_{c0}	Pressure dependence parameters of cake porosity [dimensionless]
R_c	Cake layer resistance [m^{-1}]
Re	Reynolds number [dimensionless]
R_m	Membrane Hydraulic resistance [m^{-1}]
Sc	Schmidt number [dimensionless]
Sh	Sherwood number [dimensionless]
t	Time [s]
TDS	Total dissolved solids [mg/l]
TMP	Trans-membrane pressure [Pa]
UF	Ultrafiltration
y	Distance from central line of hollow fiber [μm]

Greek letters

α	Specific cake layer resistance [m/kg]
α_0	Pressure independent parameter of specific cake layer resistance [m/kg]
δ	Mass transfer boundary layer thickness [μm]
ε_c	Cake porosity [dimensionless]
ρ_c	Cake density [$\mathrm{kg/m^3}$]
σ	Reflection coefficient [dimensionless]

them, oil present in water can be categorized into 3 groups depending on the droplet size. If the droplet size is > 150 μm, it is termed as free oil and is termed as emulsion, if droplet size is < 20 μm. Third category is dispersed oil having droplet size between 20 and 150 μm. Membrane technology is highly efficient compared to the conventional methods and its efficiency depends on the feed characteristics and membrane properties [9]. Most commonly used polymeric membranes are polysulfone, polyethersulfone, polyvinylidene fluoride, polyacrylonitrile (PAN) and cellulose acetate. Microfiltration (MF) and ultrafiltration (UF) membranes with molecular weight cut-off between 50 and 200 kDa have been employed widely for removal of oil and grease from effluent streams. Chakrabarty et al., studied filtration of synthetic oily water using different UF membranes of varying selectivity [5]. Karakulski et al., used tubular UF membrane modules of different materials for treatment of harbor and simulated emulsions and compared the efficiency of the treatment process [11]. Salahi et al., used five different types of membranes (two MF and three UF) for treatment of oily effluent from Tehran refinery and modeled the flux decline using Hermia's model and cake filtration was found to be the predominant mechanism of flux decline [8]. Daiminger et al., used membranes to separate oil from water by inducing coalescence [12]. Similar feed was treated by Rezaei et. al., using ceramic filtration modules and thus observed total organic carbon (TOC) removal efficiency of above 95% [7]. Ceramic MF membranes were also employed by Hua et al., for treatment of oily water and the effect of various parameters on separation efficiency was studied [10]. Matos et. al., carried out ultrafiltration of oily waste water and optimized the performance to find suitable parameters in total recycle mode [13]. Al-obeidani et. al., investigated effects of operating conditions on microfiltration of oily water using hollow fiber membranes [14]. However, all these works lack comprehensive modeling for prediction of profiles of permeate flux and oil concentration in permeate to quantify the system performance and subsequent scale up.

In the present work, real life effluent stream obtained from Railway Workshop, South Eastern Railway, Kharagpur, India, is treated to obtain clean water. The effluent was generated during washing of the railway coaches in their cleaning schedule. The major content of this effluent was oil, grease and dirt. Removal of contaminants was carried out in two stages. The effluent was pre-filtered through fine sand bed to remove dirt and suspended particles. The output of this stream was then treated by hollow fiber UF membrane to remove oil and grease. Effects of operating conditions on filtration performance were also investigated. The fouling mechanism of the membrane was identified. A model under the framework of cake controlling cross flow filtration was formulated to simulate the profiles of permeate flux and concentration of oil in permeate. Such work is envisaged to help in designing and up scaling hollow fiber based filtration systems for treatment of oily water from an industrial origin.

2. Theory

2.1. Identification of flux decline

Mechanism of flux decline can be identified by analyzing the time history of permeate flux in an unstirred dead end filtration process. Hermia et al. proposed an equation, given by Eq. (1), which represents the characteristic curves of a batch filtration process and is widely used by several researchers to identify the mode of flux decline [15,16].

$$\frac{d^2t}{dV^2} = k'\left(\frac{dt}{dV}\right)^n \tag{1}$$

where, V is the cumulative flux at any time point t and k' and n are system parameters. The value of n varies depending on the mode of filtration. Corresponding to the four types of flux decline mechanisms, following relations are derived from Eq. (1):

i. Complete pore blocking model ($n = 2$)

$$\ln\left(\frac{1}{J}\right) = \ln\left(\frac{1}{J_0}\right) + k_c t \tag{2a}$$