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Performance characteristics of surfactant treated commercial polyamide membrane in the nanofiltration of model solution of reactive yellow 160

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ABSTRACT

Top surface modification of commercial PA-NF 150 membrane was carried out by dip-soaking the membrane swatches with predetermined concentration of aqueous solutions of sodium dodecyl sulphonate (SDS), cetyltrimethylammonium bromide (CTAB) and Triton X-100 as anionic, cationic and non-ionic surfactants, respectively. The modified flat sheet membranes were used in the nanofiltration of the Reactive yellow 160 dye waste water in a pilot plant. AFM, FTIR-ATR, and water contact angle measurements were employed to characterize the prepared membranes. Addition of surfactants resulted in membranes with superior dye rejection in comparison to untreated membranes. The percent rejection of dye was in the vicinity of 95% for both CTAB and SDS treated membranes, however the results were different for Triton X-100. CTAB treated PA-NF membrane was observed to have marginally less extent of volumetric flux reduction with time compared to other two surfactant treated membranes. Substantial removal of color was achieved in the nanofiltration experiments with a marked reduction in COD and TDS. The process allowed the production of permeate stream with great reutilization possibilities.

1. Introduction

In the past few decades nanofiltration (NF) has evolved from a novel approach into a reliable and commercially attractive standard unit operation for reclamation of waste water. The lower operating pressures compared to reverse osmosis and unique selectivity of the membranes render NF a less energy-intensive and eco-friendly downstream operation for the treatment of effluents containing many different components such as inorganic/organic salts, amino acids and peptides, oligosaccharides, molasses, reactive dyes and so on. It can significantly reduce the levels of dissolved solids, colors, organics, hardness, turbidity, divalent and multivalent ions and facilitate the required desalting of permeate streams [1,2]. While NF has a myriad of advantages and benefits to its credit, there is a flip side as well. One of the most important drawbacks of nanofiltration is the decline in flux due to concentration polarization and membrane fouling during the operation. The accumulation of solutes at the membrane surface adversely affects the membrane performance. Several studies in recent literature report the effects of the operational parameters including ionic strength, feed concentration and feed pressure on flux decline, which typically leads to higher energy requirements and ultimately reducing the lifetime of the membrane [3,4].

However, besides the operational parameters, the membrane properties such as the molecular weight cut off (MWCO), pure water permeability, surface charge, surface roughness and membrane hydrophilicity play a paramount role in separation performance of the nanofiltration membranes. Solutes are prone to get adsorbed on to the membrane surface through hydrophobic interaction, hydrogen bonding, van der Waals attraction and electrostatic interaction. Thus, an effective method to reduce membrane fouling aims at the alleviation of these adsorptive interactions and enhancing the repulsive interaction between the foulant molecules and membrane surfaces by modulating the membrane surface properties [5,6]. Membranes with a smooth and hydrophilic surface of similar charge to the foulant seem to possess good anti-fouling property [7,8]. Modified membranes with lower contact angles and lower average surface roughness compared to unmodified ones exhibit improved fouling resistances [9]. Both the top layer chemistry and surface coating can strongly affect the properties like surface charge and roughness of a thin film composite membrane, which in turn determines the membrane's long term performance [10]. Therefore, a good understanding of the impacts of surface-treated membrane properties on the

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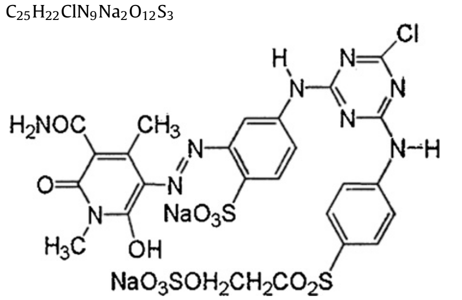
separation performance under different operational conditions is vital on the controlling of membrane fouling and successful application of NF process for dyeing wastewater treatment. The permeation and performance parameters of surface-modified membranes depend mostly on the physico-chemical characteristics of the coating material, which usually endows the modified membranes with special performance and characteristics.

A variety of surface modification strategies to mitigate membrane fouling has been reported in literature using commercial surfactants or surface active molecules. Different methods of incorporation of surfactant in to the membrane include addition from the bulk feed-solution [11], mixing with the substrate of interfacial polymerization (IP) [12,13], soaking with membrane swatch [14,15], complexation with water soluble chelating agents [16,17] and so on. These surfactants are thought to form a thin film of charged solution on the membrane surface that alters the separation either by repulsion or attraction on the surfactant film and membrane [11]. Solute separation in NF involves mainly electrostatic interaction of membrane and solutes on the membrane surface and size exclusion. Miceller enhanced separation methods have been studied for the removal of organic and inorganic pollutants. Enhanced separation by micelles is due to the adsorption of metallic ions on the polar head of the surfactants micelles surface, which normally renders surfactant concentration more than critical miceller concentration. Most of the commonly used commercial NF membranes are thin film composite (TFC) polyamide membranes with a thin film layer fabricated onto a microporous substrate via IP technique [18]. Surfactant addition is recognized as a necessary component for IP process as it facilitates the monomer in water phase moving into organic phase, thus improving polymerization efficiency as well as transport properties of formed TFC membranes [19]. Fouling behavior of membranes can be improved by increasing the hydrophilic character of the membrane surface. The idea is that before any protein or cell can adsorb to the membrane, it must first displace the water molecules that are chemically associated with the surface groups on the membrane [14]. The introduction of negative charges on the membrane surface is expected to increase the electrostatic repulsion between the membrane and the cells/proteins that are negatively charged in aqueous solution. Most studies of surfactant-modified membranes provide evidence for this general phenomenon with anionic surfactants being much more effective at reducing fouling than cationic surfactants [20]. Xiang et al. [21] investigated the role of amine salt surfactants on nanofiltration performance of TFC poly (piperazine-amide) NF membranes. Amine salt containing larger steric configuration cationic amine group resulted in better performance. Layer by layer surface modification has shown its ability to limit fouling and biofilm formation on asymmetric cellulose acetate membrane [22]. Surface treated membranes exhibit lower contact angles and lower average surface roughness than untreated membranes, suggesting these modified membranes could demonstrate improved fouling resistance [23].

Synergistic mixtures of surfactants could provide combinations of electrostatic, steric, and hydration interactions that could be optimized for the particular solutes and membranes. So, surface modification is a potential means to improve fouling resistance. While there have been quite a good number of studies on surfactant incorporation onto the membrane surface internally through IP, the effect of external surfactant coating layer on the permeation and rejection performances of commercial PA composite membranes remains to be an underexploited area of research. Keeping this is mind in the present work; membrane surface treatment was carried out by dip-soaking the membrane swatch into the aqueous solutions having predetermined concentration of cationic, anionic and non-ionic surfactants. The flux behavior as well as dye removal efficiency of surfactant-treated membranes were compared

Table 1
Characteristics of the dyes used in the study.

Characteristics	Reactive yellow 160
C.I. (color index) name	C.I. reactive yellow 160
Molecular weight	818.13 Da
Melting point	> 240 °C
Application class	Cotton
Chemical class	Azo
Absorption max (water)[a]	430 nm
Chemical formula	$C_{25}H_{22}ClN_9Na_2O_{12}S_3$
Molecular structure	
UV spectra