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Application of thin film cellulose composite membrane for dye wastewater reuse

Tiara Puspasari, Klaus-Viktor Peinemann*

Advanced Membranes and Porous Materials Center at King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

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ABSTRACT

The use of low cost membranes with high salt/dye selectivity and high flux is ideal for an economic and eco-friendly treatment of dye wastewater. Here, regenerated cellulose membranes prepared from trimethylsilyl cellulose are studied for treating artificial dye effluents. In the experiments using a feed containing Congo Red and high NaCl concentration, the membrane featured impressive dye removal with zero salt rejection combined with high flux. More interestingly, the membrane reached as much as 600 LMH flux at 80 °C and 4 bar while maintaining high dye rejection close to 98%. In prolonged experiments up to 75 h the membrane exhibited good antifouling behavior with nearly 100% flux recovery. This study may provide a promising alternative of dye effluent treatment where high amounts of monovalent salts are present.

1. Introduction

Dye wastewater is a problematic environmental issue considering its composition, condition and volume. The wastewater is visually polluted by the unfixed dyestuff and it contains large amounts of salts (primarily sodium chloride, NaCl) (40–80 g/L) [1] and high COD (from additives such as detergents, acetic acid and complexing agent), with high pH between 10 and 11 [1,2] and high temperature (above 50 °C) [1–3]. Typical effluents are also produced during salting-out process in dye synthetic industry that uses NaCl for dye precipitation [4,5]. Both discharged streams hamper the photosynthesis activity of the living ecosystem and are unsuitable for direct further use. Numerous attempts of treatment have been made, ranging from the conventional biological treatment to electrochemical approaches. However, the processes still suffer from the extensive cost per volume of the treated waste [1,6,7], while the simple biological method is ineffective as dyes are in general resistant to aerobic digestion [3,8,9]. In addition, not many could give an option for heat and brine reclamation that could provide significant savings in wastewater treatment. Dye effluents still remain a challenge.

Nanofiltration (NF) has proven capable of treating dye-containing wastewater with varying degrees of success [1,2,10–16]. A critical parameter is the selective removal of the dyestuff from the stream coupled with the opportunity to reuse the brine in economic and eco-friendly manners, not to mention its easy operation and high scalability. The optimization between membrane permeability and selectivity is the key for a successful NF separation. Numerous commercial NF membranes with excellent dye removal properties are available. The separation usually relies on size difference and charge interaction. The membranes have a molecular weight cut-off (MWCO, molecular weight of the solute that is 90% rejected by the membrane) between 200–1000 Da, well suited for separation of widely used dyes in industry with typical molecular weight between 700–1000 Da [17]. Despite the growing number of cationic membranes being currently developed [18–20], the majority of NF membranes are negatively charged [18,21–23], suggesting the benefit of electrostatic repulsion in the separation of dyes that are mostly also negatively charged. However, state-of-the-art membranes also reject monovalent salts; typical values are between 15 and 40%, which is undesirable for dye applications. Further processing is required to pursue high dye purity, and the salt-induced osmotic pressure of the feed stream has to be overcome. Another issue associated with NF processes is membrane fouling that in case of dye processes frequently occurs due dye adsorption leading to undesirable flux decline. Therefore, development of NF membranes featuring high organic rejection combined with minimum NaCl rejection and good anti-fouling behavior is of importance.

Given the potential of membrane processes to advance dye-containing wastewater treatment and taking into account the limitation of the existing membrane materials, we have developed a regenerated cellulose (RC) composite membrane in our previous

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* Corresponding author.
E-mail address: klausviktor.peinemann@kaust.edu.sa (K.-V. Peinemann).

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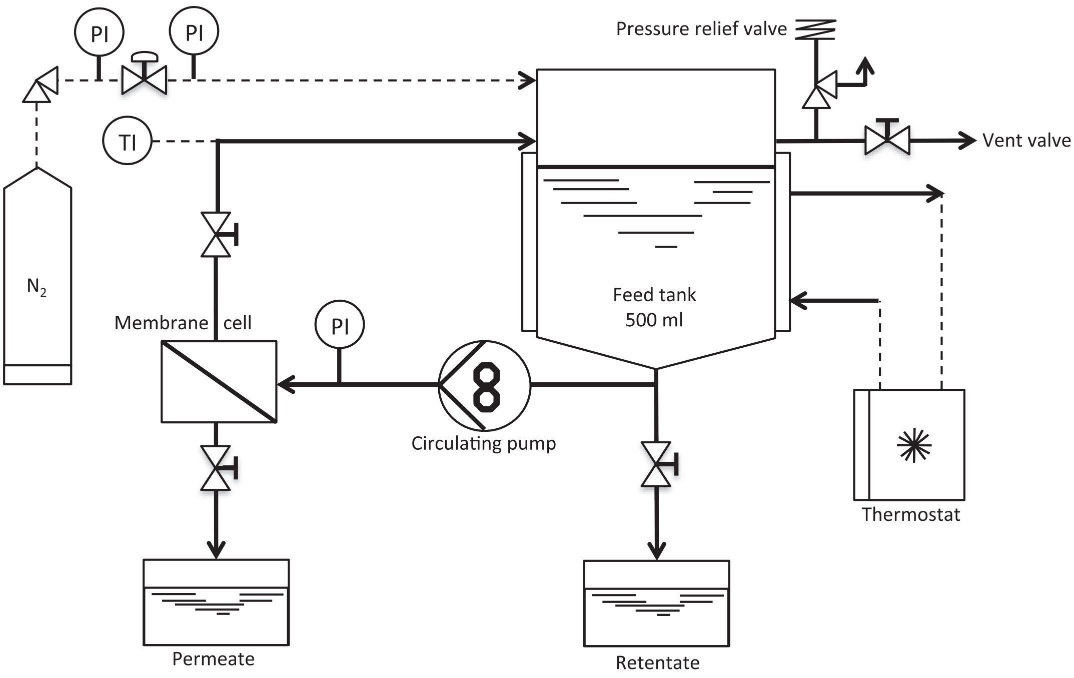

Fig. 1. Crossflow filtration setup.

work [24]. Cellulose is an important membrane material considering its abundant availability, low cost, excellent hydrophilicity and biocompatibility. We previously prepared cellulose thin film composite membranes using trimethylsilyl cellulose (TMSC) as a precursor followed by a simple cellulose regeneration method. The membranes demonstrated good isolation of sucrose from NaCl solution due to its very low NaCl rejection. In this study the membranes were evaluated to both remove the color and recover the brine of artificial dye baths containing Congo Red (CR) and high amount of NaCl. Fouling behavior was investigated in a 75-h filtration experiment.

2. Materials and method

2.1. Materials

Trimethylsilyl cellulose (TMSC) with degree of silylation of 2.2 was synthesized according to our previous work [24]. *N*-Hexane (Sigma Aldrich), hydrochloric acid (HCl, Sigma Aldrich), sodium chloride (NaCl, Sigma Aldrich), all polyethylene glycols (PEGs) and dyes (Sigma Aldrich) were used as received. Porous support material of polyacrylonitrile ultrafiltration membranes with water flux between 110 and 150 LMH/bar was received from GMT GmbH (Germany).

2.2. Membrane preparation

The following is a typical preparation procedure. About 1% TMSC was dissolved in *n*-hexane by simple stirring. Spin coating was performed on the support membranes for 1 min with a speed and an acceleration of 4500 rpm and 2500 rpm s^{-1} respectively. The as-prepared membranes were then exposed to the vapor of 10% HCl in a closed petri dish for 15 min for cellulose regeneration.

2.3. Membrane characterization

The ATR-IR spectra of membranes were collected using a Fischer Scientific Nicolet iS10 spectrometer and were recorded in the range between 650 and 4000 cm^{-1}. The top surface and cross-section morphology of the membranes were imaged by an FEI Magellan scanning electron microscope. The samples for cross section analysis were fractured in liquid nitrogen. A 3-nm iridium coating was applied to the membranes to minimize charging effects during imaging. Membrane surface zeta potential was determined using SurPASS electrokinetic analyzer (Anton Paar, Austria) with a background of 10 mM NaCl solution. The pH was adjusted using 0.1 M HCl and 0.1 M NaOH solutions.

2.4. Dye-NaCl separation

Performances of the membranes were evaluated using a commercial cross-flow filtration apparatus (P-28, Celfa Membrantechnik, Switzerland) equipped with an effective membrane area of 28 cm^2 (Fig. 1). A heating jacket surrounding the feed tank was used to control the temperature. The composition of feed in dye-NaCl experiment was 100 mg/L CR and 50 g/L NaCl unless otherwise mentioned. The water flux (J_w, LMH) was calculated using Eq. (1)

$$J_w = \frac{V}{At} \qquad (1)$$

where V is the volume of the permeate (L), A is the effective membrane area (m^2) and t is the time (h) for permeate collection. Rejection and salt/dye selectivity were calculated using Eqs. (2) and (4), where C_p and C_f are the concentration of permeate and feed solution, respectively. All experiments were performed at volume reduction (ratio between the volume of permeate withdrawn and the initial feed volume) of 20%.

$$\text{Rejection (\%)} = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \qquad (2)$$

$$\text{Selectivity (\%)} = \frac{\frac{C_{p,salt}}{C_{f,salt}}}{\frac{C_{p,dye}}{C_{f,dye}}} = \frac{100\% - R_{salt}}{100\% - R_{dye}} \qquad (3)$$

Six representative anionic dyes (listed in Table 1) were employed. Dye concentration was analyzed using a Lambda 1050 UV/vis spectrophotometer (Perkin Elmer, USA). The concentration of NaCl was analyzed using an Oakton® pH/CON 510 conductivity