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Fractionation of direct dyes and salts in aqueous solution using loose nanofiltration membranes

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ABSTRACT

In the textile industry, high salinity waste streams are a challenge urging for the recovery and purification of dyes and salts (e.g., NaCl), requiring a treatment going beyond the classical filtration by e.g., reverse osmosis to produce pure water. In this work, two commercial loose nanofiltration (NF) membranes (Sepro NF 6 and NF 2A, Ultura) are proposed to fractionate dye/salt aqueous mixtures. It was observed that both NF membranes have a salt rejection $<33.3\%$ in solutions with 0.1–40.0 g L^{-1} of NaCl at 6 bar. Furthermore, both membranes have $>99.6\%$ retention of direct dyes (direct red 80, direct red 23, and congo red), even though 40.0 g L^{-1} NaCl is present, indicating salt addition has no obvious impact on the dye retention. The combination of a low salt rejection and a high dye rejection indicates the feasibility for the reuse of salt from fractionation in forward osmosis and bipolar membrane electrodialysis. Application of diafiltration for an aqueous mixture containing direct red 80 (1000 ppm) and NaCl ($\sim$20 g L^{-1}) by both membranes demonstrates that above 95% of NaCl is removed from aqueous mixture, and <0.9 g L^{-1} NaCl remains after the addition of pure water with a volume factor of 4.0 in the feed solution. At the premise of excellent diafiltration performance, concentration as the post-treatment for dye recovery expectedly indicates direct red 80 is concentrated by a factor of 4.0 for both membranes while keeping the salt concentration with a very slight increase. Over 99.9% dye retention in both diafiltration and concentration procedures yields a very high recovery since $<0.045\%$ of dye is permeated. These results indicate that loose nanofiltration membranes have potential for dye/salt fractionation.

1. Introduction

In the chemical industry, waste streams with high salinity are often generated during the synthesis and application of target organic materials [1,2]. The presence of salt is due to salt-generation reactions, solution neutralization by acid/base or salt addition for promoting a chemical reaction [1,3]. On one hand, the direct disposal of these organic solute/salt mixture fluids containing a large quantity of organic solutes without an appropriate treatment leads to water pollution. The lack of recovery of the large amount of organic materials that is present in those steams contributes to the loss of valuable organic products. On the other hand, the mass of salts in these streams leads to many challenging problems. For instance, the high content in salts limits the proliferation of microorganisms that are of interest for the biodegradation of organic solutes, and also increases human health risks by excessive unintended intake of salts [4]. With the emergence of new technologies, such as forward osmosis (FO), pressure retarded osmosis (PRO), reverse electrodialysis (RED) and bipolar membrane electrodialysis (BMED), the concentrated saline liquor can be regarded as a renewable resource [5–8]. From the point of view of recycling of resources, the massive quantity of salt would allow the use of those streams as the draw solution for FO and PRO processes or salt resource for the concentrate for RED and base/acid production by BMED technology [8–11]. Thus, fractionation of

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salts from organic solute/salt aqueous system closes the water cycle and valuable material can be reused through process integration.

Nanofiltration (NF) technology can be an alternative to achieve this objective instead of the conventional processes, such as adsorption, biological treatment, and chemical degradation [12,13]. NF membranes are semipermeable with a pore size from ~0.5 to 2.0 nm in diameter, which lies between the typical values found in ultrafiltration and conventional reverse osmosis membranes [14,15]. This provides an excellent opportunity for fractionation of different solutes, allowing salts to partially pass through the membrane and retaining molecules with larger size, based on the mechanisms of a sieving effect as well as Donnan (electrostatics) repulsion for ion fractionation [16]. At present, NF technology is applied to separate small organic solute from salt solutions, such as the removal of micropollutants (e.g., pharmaceutical compounds, pesticides, and hormones) from surface water for drinking water production [17–21], the desalination of glyphosate neutralization liquor [22], saccharide solution [23], heterocyclic drug derivative aqueous system [24], as well as other organic acid production [25].

In the majority of the organic solute/salt mixture systems found in the chemical industry, dye/salt mixtures are one of the most common liquid streams [26,27]. It is estimated that over 10,000 types of commercial dyes with annual productivity of 7×10^5 t have been applied in the industry, including textile, rubber, paper, plastic, and leather tanning [12,28–30]. In the dye synthesis process, a large amount of salt, mainly NaCl, is generated, deminishing the purity of dye products [31]. In addition, inorganic salts, such as NaCl (~6.0 wt%) or Na_2SO_4 (~5.6 wt%), are added to enhance the dye uptake by the fabric when the dyeing procedure takes place [32–34]. However, the presence of salts with high concentrations compromises dye recovery and purification.

Several commercial NF membranes have been utilized to perform the desalination of a dye solution. Asymmetric cellulose acetate NF membranes achieved >99.0% rejection for five reactive dyes (i.e., reactive orange 12, reactive red 24, reactive black 5, reactive blue 74, and reactive blue 13) and moderate salt retention (~10% for 30 g L^{-1} NaCl solution; ~40% for 10 g L^{-1} Na_2SO_4 solution) [3]. Similarly, the commercial DK (Osmonics) NF membrane was investigated for reactive dye desalination and purification, in view of water recycling. Above 96.0% rejection for reactive black 5 and 21.1% retention for the salt were observed [35]. Furthermore, the application of the commercial DK 2540F NF membrane with MWCO of ~300 Da in the treatment of real dye bath streams (direct dyes and reactive dyes contained) illustrated that NF membrane can completely remove the dyes with 47–52% rejection of salts [36]. The unsatisfying fractionation of dye/salt mixtures for these commercial dense NF membranes is due to the high salt content that remains in the feed. Simultaneously, these NF membranes also suffer a high risk of flux decline due to the complexity of the mixture. Van der Bruggen et al. [34] demonstrated that a high salt content in the feed solution results in a dramatical decrease of the membrane flux due to a higher osmotic pressure, which may strongly limit the applicability of NF technology for direct treatment of dye baths. In order to overcome the drawbacks of commercial dense NF membranes, different novel membranes have been developed. Tubular ceramic-based multilayer NF membranes synthesized by layer-by-layer assembly were observed to allow for salt fractionation from a dye/salt mixture liquor [31]: over 96.0% rejection for congo red (1000 ppm) and ca. 3.0% retention for NaCl (5.0 g L^{-1}) were obtained. Two nanofiltration hollow fiber membranes with 4500 and 2000 Da molecular weight cut-off (MWCO), synthesized by photografting of vinyl monomer sodium p-styrene sulfonate, were found to have potential for fractionation of different dyes/salt solutions (e.g. acid orange 10 and direct red 80) [37]. The NF membrane with 4500 Da MWCO had >97.0% rejection for direct red 80, with <30.0% rejection for acid orange 10. The NF membrane with 2000 Da MWCO showed above 81.7% rejection for acid orange 10. These two membranes had a salt rejection below 7.0% (10.0 g L^{-1} NaCl) [37]. The newly developed thin-film composite hollow fiber NF membrane by Yu et al. [12] through the coating of carboxymethyl cellulose outperformed the previously synthesized membranes mentioned above for filtration of anionic dye solutions. Due to the low MWCO of 700 Da, it allowed 99.9% congo red and 99.7% methylene blue rejection combined with a low rejection, ca. 2.0%, for NaCl. However, this lab-made membrane suffered from a relatively low membrane permeability of 7.0 L h^{-1} m^{-2} bar^{-1}. Significantly, the ultrathin (22–53 nm thick) graphene NF membrane fabricated by Han et al. [38] via simple filtration-assisted assembly enhanced the solution flux. This special NF membrane exhibited the merits of high permeability (19.5 L h^{-1} m^{-2} bar^{-1}) and rejection (above 99.2%) for methylene blue and direct red 81. However, the moderate retention of 20–60% for salts still poses a challenge for dye desalination [38]. Simultaneously, newly developed positively charged NF membranes made by self-assembly of polyetherimide/sulfonated polyether ether ketone blend membrane have potential for the removal of cationic dyes (methylene blue) [39]. However, it suffers from a high rejection for salts such as $MgCl_2$ and NaCl [13]. Sulfonated polyphenylenesulfone NF membranes with positive charges obtain over 99.6% rejection for the dye of safranin O with >92% rejection for $MgCl_2$ and >55% rejection for NaCl [40]. The novel hollow fiber nanofiltration membranes fabricated by Sun et al. through interfacial polymerization of hyperbranched polyethyleneimine and isophthaloyl chloride have a double repulsion effect, retaining over 98.7% of both positively (safranin O) and negatively charged (Orange II sodium) dyes [41]. Similarly, the high salt rejection (~85% for NaCl and ~95% for $MgCl_2$) also poses a challenge for the fractionation of dye and salt mixtures. The cross-linked polyamide-imide hollow fiber NF membrane developed by Ong et al. obtained a >98% rejection for reactive dye (e.g. reactive blue 19, reactive black 5, and reactive yellow 81), showing the potential high salt permeation (<20% salt rejection) [42]. In general, a long stage is inevitably required to circumvent the tradeoff between permeability and selectivity for lab-synthesized membranes, in the perspective of industrial application.

In industry, diafiltration by NF is a vital approach for removing permeable impurities (salts, solvents, tiny molecule, etc.) from a mixture to maximize the purity of desired substances such as iminodiacetic acid, soy sauce, acid whey, saccharides, glyphosate, dye, etc. [2,43–46]. However, the high salt rejection of typical commercial NF membranes compromises the tremendous water and energy consumption to reduce the content of impurities, solely resulting in a partial desalination of the mixture streams. Wang et al. stated that only high salt permeation through the NF membranes can facilitate the desalination of high salinity fluids, as well as diminish the water consumption. This corresponds to the desalination procedure of iminodiacetic acid/salt streams using diafiltration [45,46]. Otherwise, it is very difficult to effectively fractionate the salt from the organic solutes, indicating that there is no possibility for the recycling of salt in the permeate. Therefore, nanofiltration of waste streams with high salinity, such as dye wastewater, should concentrate on facilitating the free passage of salt, in view of improving the dye purity and salt recycling.

This study aims at evaluating the fractionation of salt and dye retention from a dye/salt mixture liquor by applying two loose commercial NF membranes (Sepro NF 2A and 6 membrane from Ultura, USA) in view of promoting dye recovery with high purity. The rejection of those NF membranes for single components (NaCl or dyes) in solution was further examined at different operating conditions to assess the feasibility for salt leakage and dye