Polymer 103 (2016) 417–456

Contents lists available at ScienceDirect

Polymer

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

Chemistry and fabrication of polymeric nanofiltration membranes: A review

Mou Paul*, Steven D. Jons

The Dow Chemical Company, Dow Water and Process Solutions, 5400 Dewey Hill Road, Edina, MN, 55439, USA

ARTICLE INFO

Article history:
Received 20 December 2015
Received in revised form
24 June 2016
Accepted 29 July 2016
Available online 12 August 2016

Keywords:
Review
NF
Nanofiltration
RO
Reverse osmosis
Membrane
Interfacial polymerization
PIP
MPD
TMC
Amine
Acid chloride
Polymer
Water purification
Flux
Salt passage
Salt rejection
NaCl
$MgSO_4$
Coating
Fouling

ABSTRACT

The review article describes research on different methods for manufacturing polymeric NF membranes. The primary focus is on NF composite membranes formed by interfacial polymerization. Within that space, topics covered in detail include the composite structure, monomeric and polymeric reactants employed to endow specific characteristics, and additives used to influence the reaction. Other approaches covered that have been commercially important are manufacture of NF membranes by phase inversion and different post-treatments (e.g. coatings, grafting) that may be applied to a more porous support. Emerging technologies also discussed include layer-by-layer coatings, incorporation of aquaporins, and use of glassy polymers with high internal porosity. Common themes include research directed to improved performance (flux, rejection, selectivity, reduced fouling) and modifications that allow for success in more challenging feeds (pH extremes, high temperature, chlorine, solvents).

Contents

* Corresponding author.
E-mail address: MPaul@dow.com (M. Paul).

http://dx.doi.org/10.1016/j.polymer.2016.07.085

1. Introduction

Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) are all pressure-driven separation processes that fall along a continuum of performance needs. MF is used for removing suspended particles greater than about 0.1 μm. UF commonly excludes dissolved molecules greater than 5000 molecular weight. RO membranes have high rejection of almost all salts and neutral species greater than 100 Da MW. And, NF is somewhere between UF and RO.

The term nanofiltration (NF) was originally coined at Filmtec Corporation to characterize "loose RO" membranes with pores diameters greater than about 1 nm in size. A more critical definition of an NF membrane may be formulated based on a number of approximate characteristics.

- Pore diameters less than 2 nm.
- Passage of an appreciable amount of monovalent ions.
- Substantially higher rejection of divalent ions than monovalents.
- Molecular weight cutoff (MWCO) for neutral species is in the 150–2000 Da range.
- Rejection of neutrals and positive ions relates principally to their size and shape.

This description is similar to the list of NF features provided by Bjarne Nicholaisen, as reiterated in the 2005 book, *Nanofiltration: Principles and Applications* [1]. It is somewhat more inclusive, as that description specified more than 30% passage of monovalents, virtually total rejection of divalents, and a molecular weight cutoff range of 150–300 Da. The NF literature is inconsistent on these points, and acceptance of a common set of defining characteristics for nanofiltration remains elusive. In any case, it is clear that one can't define a membrane in terms of its performance without also establishing the conditions of operation. (For instance, just decreasing the pressure by a factor of two might commonly double the passage of divalent ions.) Hence, using some definitions, there is a reasonable argument that whether a membrane is NF or RO could depend on the process in which it is being used. Because it is even more difficult to determine if a membrane is NF by a description of its fabrication, the authors have been fairly inclusive in this review. Nonetheless, it important to recognize particular ways in which NF is perceived as advantaged.

As compared to RO, the success of NF often results from its selective separation of one solute over another. The Méry-sur-Oise plant has been producing drinking water from the Oise river since 1999, with objectives to remove atrazine and pass a substantial fraction of calcium and bicarbonate ions [2]. In the dairy industry, NF is used to demineralize whey products by passing undesirable monovalent salts (Na, K, Cl) and simultaneously concentrating constituents such as lactose, protein, and calcium [3]. The waste streams from textile dying can comprise both dyes and salt, both of which would be removed by RO, but NF can be used to keep the valuable salts while concentrating dyes into a more manageable volume [4]. NF is also used in separation of different neutral species, e.g. the simple monosaccharides xylose (150 MW) and glucose (180 MW) [5].

NF membranes are also frequently advantaged by their ability to avoid an osmotic pressure limitation. To produce water for downhole injection on offshore oil production platforms, NF has been used to treat seawater and prevent barium sulfate scale. High recoveries are possible at reasonable pressures because the membrane passes most of the sodium and chloride ions while retaining sulfate [6]. NF is also used to remove sulfate in the chloralkali process, where concentrations of NaCl in the feed may exceed 200 g/L and would correspond to unreasonably high osmotic pressure for RO [7]. As zero liquid discharge (ZLD) is becoming more often required, NF will play a larger role in treating already concentrated RO reject streams, reducing the volume of water needing more costly final stage operations (e.g. evaporation).