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Molecularly imprinted organic solvent nanofiltration membranes – Revealing molecular recognition and solute rejection behaviour

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ABSTRACT

A new class of organic solvent nanofiltration (OSN) membranes featuring molecular recognition sites has been fabricated by a phase inversion molecular imprinting technique. Polybenzimidazole (PBI) was employed as a functional polymer for molecular imprinting for the first time. Apart from acting as a functional polymer, PBI exhibits excellent chemical and solvent stability and can be used as a nanofiltration membrane, acting both as shape-specific adsorbent and size-exclusion membrane. The molecularly imprinted organic solvent nanofiltration (MI-OSN) membranes fabricated in this study showed both nanofiltration membrane performance, and excellent molecular recognition ability. The model system comprised roxithromycin pharmaceutical, 2-aminopyrimidine building block and N,N-dimethylaminopyridine catalyst, which are retained, adsorbed and permeated through the MI-OSN membrane, respectively. The effect of both dope solution concentration and applied pressure on the molecular recognition behaviour of MI-OSN membranes has been investigated by employing Sips and Freundlich adsorption isotherms, as well as examining the physical morphology of the membranes. The rate of adsorption was investigated, revealing that the adsorption follows second-order kinetics and is not limited by diffusion. The imprinted membrane exhibited fourfold higher flux whilst maintaining the same rejection performance in comparison to the control membrane. It is shown that increasing the transmembrane pressure across the MI-OSN membrane irreversibly suppresses the molecular recognition whilst maintaining the rejection and flux performance.

1. Introduction

Organic solvent nanofiltration (OSN) is a pressure-driven separation technology capable of discriminating between molecules dissolved in organic media based on their size and shape in the range of 100–2000 g mol^{-1}. OSN membranes are usually characterized by their molecular weight cut off (MWCO), which is the molecular weight of a solute with a rejection of 90%, and it is usually estimated experimentally by interpolation of calibrated solutes from the same chemical family. OSN is capable of separating the solutes of a feed solution into two fractions, namely the permeate and the retentate. Several applications of OSN have been reported including solvent recovery, purification, chiral separations, reactive synthesis and catalyst recycle [1]. On the other hand, a molecularly imprinted membrane (MIM) is a result of the combination of molecular imprinting technology and membrane technology. The basic principle behind molecular imprinting is the incorporation of a template molecule in a polymer matrix by chemical and physicochemical interactions [2]. Having removed the template, a binding site is left behind which can selectively recognise the template molecule. Compared to conventional size-exclusion membranes where the mode of separation is the difference in solute sizes, MIMs bear an additional advantage: a specific solute can be selectively transported. Typically, molecular imprinting requires high crosslinking allowing high selectivity, recyclability and robustness. However, these materials are too rigid and brittle to fabricate large-scale membrane modules required for OSN [3].

Hence, phase inversion imprinting (Fig. 1) was followed in the present study: direct addition of template molecule to the polymeric dope solution which when cast results in simultaneous formation of binding sites and membrane morphology [4,5]. Benzimidazole is an excellent candidate for host–guest type coordination chemistry, fulfilling several important functions in biological systems, and polybenzimidazole (PBI) was recently proposed for membrane material for separations in organic solvents [6]. Hence

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Nomenclature

2AP	2-aminopyrimidine template
A_m	membrane area
API	active pharmaceutical ingredient
APTMS	3-Aminopropyl trimethoxysilane
B	bound concentration of the solute on the membrane at equilibrium
B_t	bound concentration of the solute on the membrane at time t
C_{2AP}	concentration of 2AP in the dope solution
$C_{F,x}$	concentrations of compound x in the feed
$C_{P,x}$	concentrations of compound x in the permeate
δ	thickness of the dope solution film upon casting
d_{dope}	density of the dope solution
DMAP	N,N-dimethylaminopyridine dummy-template
ϕ	theoretical number of binding sites
F	free concentration of the solute in the solution at equilibrium
IF	imprinting factor
J	solvent flux
K_i	binding capacity for either MIM or NIM
k_1	rate constant for the first-order kinetic model
k_2	rate constant for the second-order kinetic model
k_a	affinity constant
k_d	rate constant for the intraparticle diffusion kinetic model
MIM	imprinted membrane
MI-OSN	molecularly imprinted organic solvent nanofiltration membrane
MOF	metal–organic framework
MWCO	molecular weight cut off
n	heterogeneity index
NIM	non-imprinted membrane
OSN	organic solvent nanofiltration
PBI	polybenzimidazole
PF	permeability factor
q	binding site density
Roxi	roxithromycin
R_x	rejection of compound x
S_{BET}	BET specific surface area
SF	selectivity factor
$S_{Langmuir}$	Langmuir specific surface area
t	time
V_{perm}	permeate volume
V_{pore}	pore volume

PBI was chosen as the functional polymer for the present study. The main challenge in combining MIM and OSN technologies lies in the fact that two different pore populations have to be fabricated simultaneously: one for template recognition and another one for controlling the MWCO of the nanofiltration membrane. The hypothesis which is examined in this work is that phase inversion after the self-assembly of the template and the functional polymer in the dope solution will promote the formation of such a pore network. The aim of the present study is to test this hypothesis and explore the factors influencing the molecular recognition behaviour of MI-OSN membranes such as dope solution concentration and applied pressure.

Pharmaceutical regulatory authorities show increasing concerns over genotoxic impurities (GTI) in active pharmaceutical ingredients (API) due to their adverse effect on patients [7]. Pharmaceutical manufacturers have to address these concerns by detecting, controlling and eventually implementing additional purification steps to achieve ultra-low GTI levels. Both nanofiltration [8,9] and molecular imprinting [10,11] have been proposed for such purposes. Moreover, a hybrid process featuring OSN and molecularly imprinted adsorbents has been proposed for API purification [12]. Hence, 2-aminopyrimidine (2AP), 4-dimethylaminopyridine (DMAP) and roxythromycin (Roxi) were selected for the present study as a model potentially genotoxic building block, catalyst and API, respectively (Fig. 2). Roxi is a macrolide antibiotic used to treat respiratory tract, urinary and soft tissue infections. The MI-OSN hybrid strategy consists of permeating the solvent and the catalyst (DMAP) through the membrane and adsorbing the building block (2AP), whilst retaining the API by the membrane (Fig. 3). Afterwards 2AP can be eluted and the membrane regenerated. The rationale behind the selection of the model system lies in the MW differences. The MW gap between Roxi and either 2AP or

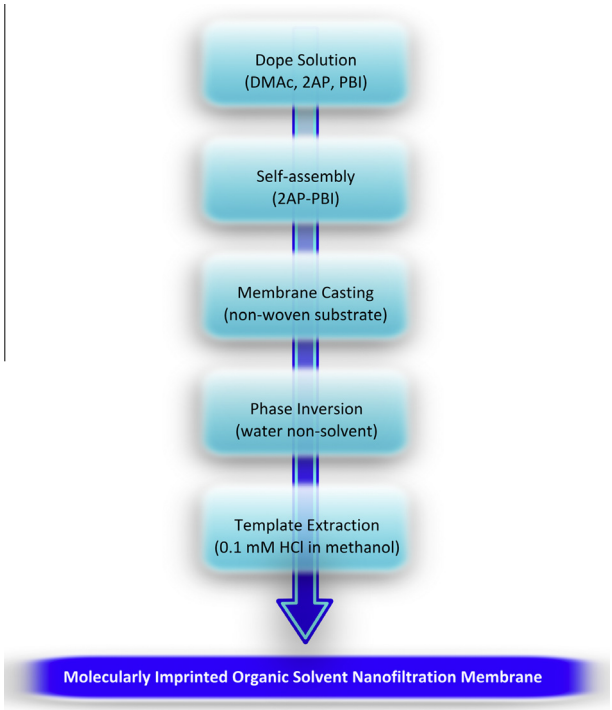

Fig. 1. Schematic representation of molecularly imprinted membrane fabrication by the phase inversion method.

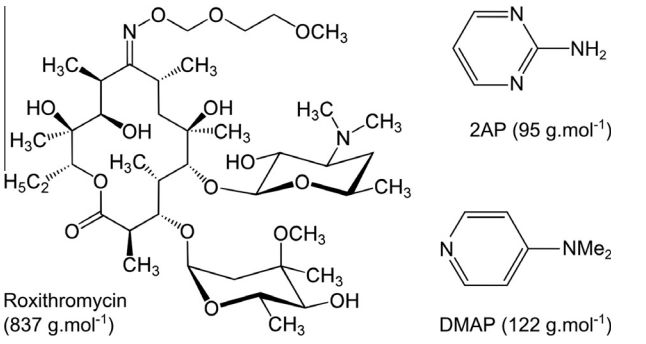

Fig. 2. Chemical structure of the model compounds: roxithromycin (API), 2-aminopyrimidine (GTI and template) and 4-dimethylaminopyridine (GTI and dummy-template).