Supporting Information

Transport of *N*-nitrosamines through Reverse Osmosis Membrane: Role of the Molecular Size and Nitrogen Atoms

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Table S1 – Properties of the selected chemicals.

Group	Number of Nitrogen atom	2	1	0
A	Name	NDMA	DMF	IBAL
	Molecular formula	$C_2H_6N_2O$	$C_3H_7N_1O$	C_4H_8O
	Log *D* at pH7[a] [-]	0.04	-0.6	0.9
	Strongest basic pKa[a] [-]	3.5	-1.3	Unionizable
	Hydrogen bond acceptor count[a] [-]	2	1	1
	Dipole moment[a] [Debye]	6.3	4.8	3.0
	Van der Waals volume[a] [Å^3]	72.6	76.8	81.5
	Molecular length[a,b] [Å]	6.5	6.2	7.0
B	Name	NMEA	NEMF	2MBTL
	Molecular formula	$C_3H_8N_2O$	C_4H_9NO	$C_5H_{10}O$
	Log *D* at pH7[a] [-]	0.4	-0.3	1.3
	Strongest basic pKa[a] [-]	3.4	-1.2	Unionizable
	Hydrogen bond acceptor count[a] [-]	2	1	1
	Dipole moment[a] [Debye]	6.4	4.8	3.0
	Van der Waals volume[a] [Å^3]	89.6	93.8	98.5
	Molecular length[a,b] [Å]	7.9	6.7	8.0
C	Name	NPYR	N.A.	N.A.
	Molecular formula	$C_4H_8N_2O$		
	Log *D* at pH7[a] [-]	0.4		
	Strongest basic pKa[a] [-]	3.3		
	Hydrogen bond acceptor count[a] [-]	2		
	Dipole moment[a] [Debye]	6.6		
	Van der Waals volume[a] [Å^3]	94.9		
	Molecular length[a,b] [Å]	7.7		
D	Name	NMOR	N.A.	N.A.
	Molecular formula	$C_3H_8N_2O$		
	Log *D* at pH7[a] [-]	-0.2		
	Strongest basic pKa[a] [-]	3.1		
	Hydrogen bond acceptor count[a] [-]	3		
	Dipole moment[a] [Debye]	6.5		
	Van der Waals volume[a] [Å^3]	104.5		
	Molecular length[a,b] [Å]	8.8		

[a] Marvin software (ChemAxon, Budapest, Hungary).

[b] Maximum length perpendicular to the minimum projection area.

N.A.: Not available (not used).

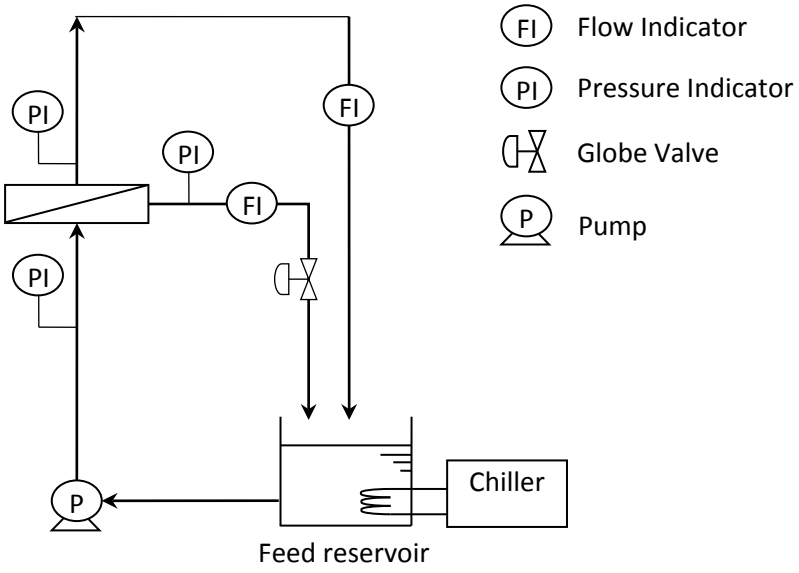

Fig. S1 – Schematic diagram of the RO treatment system.

Text S1 – RO treatment system and experimental protocol.

(a) Filtration set-up

The system comprised of a 4-in. glass-fiber pressure vessel (ROPV, Nangang, China), 65-L stainless steel reservoir, a high-pressure pump (25NED15Z, Nikuni Co., Ltd., Kawasaki, Japan), digital flow meters (FDM, Keyence Co., Osaka, Japan), digital pressure indicators (GPM, Keyence Co., Osaka, Japan), a pressure gauge, stainless steel pipes in the feed stream and PVC pipes and PTFE tubing in the permeate stream, and a titanium heat exchanging pipe connected to a chiller unit (CA-1116A, Tokyo Rikakikai Co. Ltd., Tokyo, Japan).

(b) Experimental procedure

Deionised water (resistivity = >10MΩcm) as RO feed was prepared by filtering tap water with a pure water system (Mega Unity, Organo Co., Tokyo, Japan), which comprised a pre-filter, reverse osmosis membrane, and ion exchange resin. Solution pH win RO feed was adjusted at 6–7 by adding a 1N NaOH solution. Prior to tests, stock solution of each chemical was added to obtain 700 ng/L of each *N*-nitrosamine or 14–20 mg/L for the other chemicals in the feed solution. Their concentrations were determined to enable to detect them in RO permeate at concentrations sufficiently higher than their detection limits. It is noted that concentration polarisation is not affected by solute concentration. Concentration polarisation can be affected by the hydrodynamic condition within the membrane module, however, all hydrodynamic parameters (i.e., permeate flux and cross-flow velocity) were kept constant in this study. The same RO element was used for solutes in this study to avoid any possible variation from the membrane manufacturing process. After each experiment, the RO membrane element was thoroughly cleaned with deionised water. Permeate and feed samples were collected after one hour filtration.

(c) Analysis

Concentrations of DMF and NEMF were determined using an Agilent GC-MS (GC = 6890N and MS = 5973) (Agilent Technologies, Palo Alto, CA, USA) with an InertCap Pure-WAX column (GL Sciences Inc., Tokyo, Japan). Concentrations of IBAL and MBTL were determined using GC-MS (Agilent GC-MS, GC = 6890N and MS = 5973) with an InertCap 5MS/Sil column (GL Sciences Inc., Tokyo, Japan). The method detection limits (MDLs) of NDMA, NMEA, NPYR and NMOR for a 200 µL injection volume were 0.3, 0.7, 1.4 and 0.8 ng/L, respectively. The MDLs of the other chemicals (DMF, NEMF, IBAL, and MBTL) were 0.1 mg/L.

(d) Membrane preparation for analysis

The membrane skin layer was separated from the polysulfone supporting layer soaking the membrane sample in reagent grade *N*,*N*-dimethylformamide (Tokyo Chemical Industry, Tokyo, Japan) at room temperature for one minute. After dissolving the polysulfone supporting layer, the active skin layer was rinsed with pure water to remove any residual chemicals.

Table S2: Properties and separation performance of the membranes.

Membrane	Membrane surface area [m^2]	Permeate flow[a] [m^3/day]	NaCl rejection[a] [%]	Conductivity rejection[b] [%]
ESPA2-LD-4040	7.43	9.75	99.6	98.5
LFC3-LD-4040	7.43	7.57	99.7	98.9

[a] Filtration conditions: 1,500 ppm (NaCl concentration), 1.03 MPa for ESPA2 and 1.55 MPa for LFC3 (applied pressure), 25 °C (operating temperature), 15% (permeate recovery), and pH 6.5 - 7.0 (solution pH).

[b] Conductivity rejection was obtained using tap water at a permeate flux of 20 L/m^2h, recovery of 20%, and feed temperature of 25 °C.

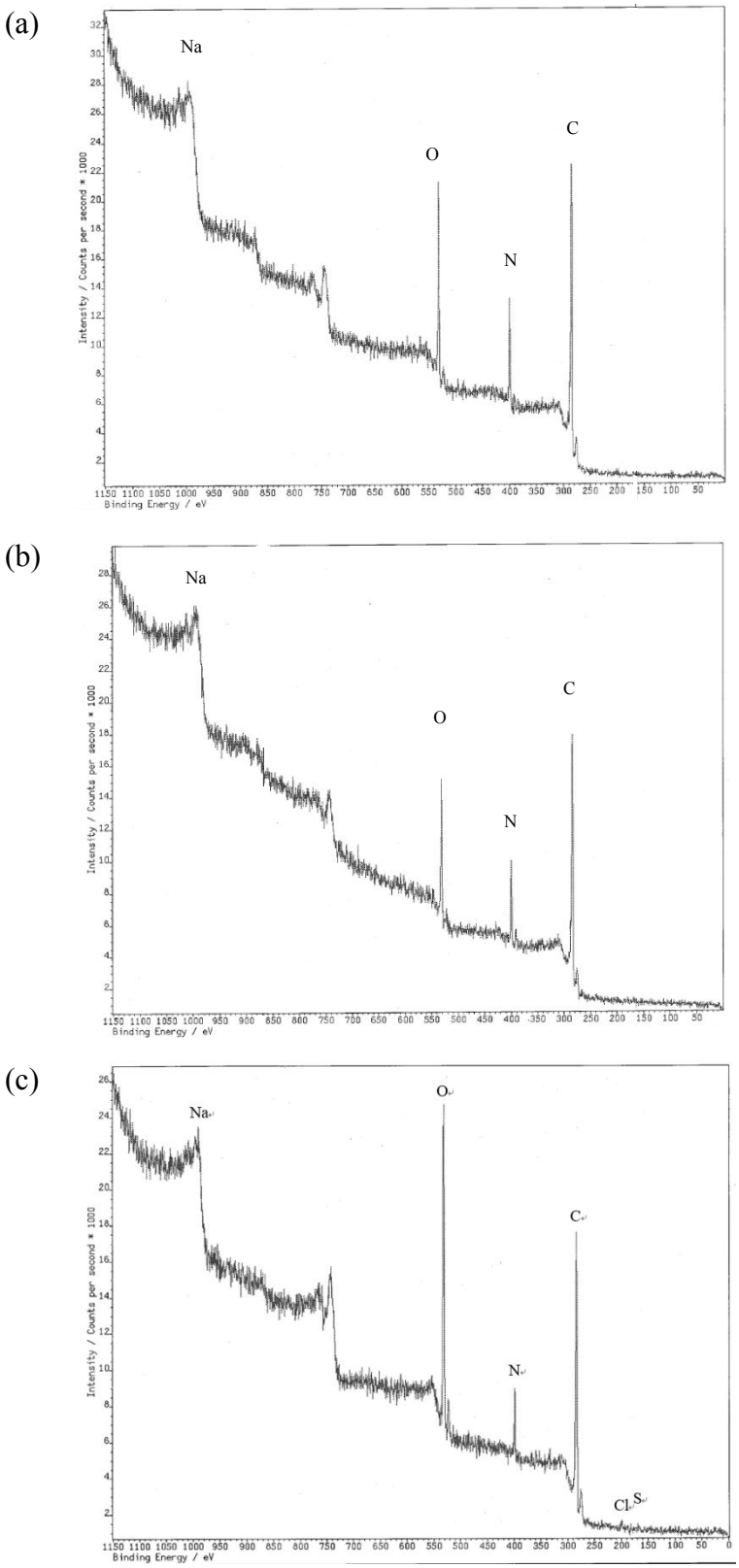

Fig. S2 – XPS data: (a) face and (b) reverse side of ESPA2 and (c) face side of LFC3 membranes.

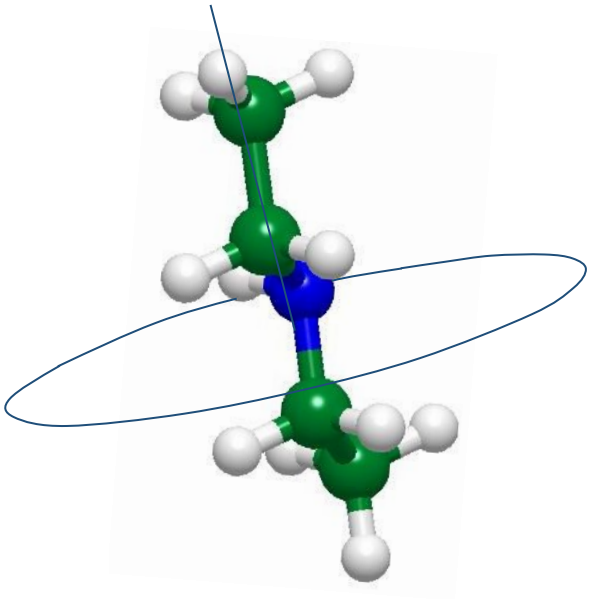

Fig. S3 – Schematic figure of minimum projection area. The line perpendicular to the circular disk represents the centre axis of the minimum projection area.

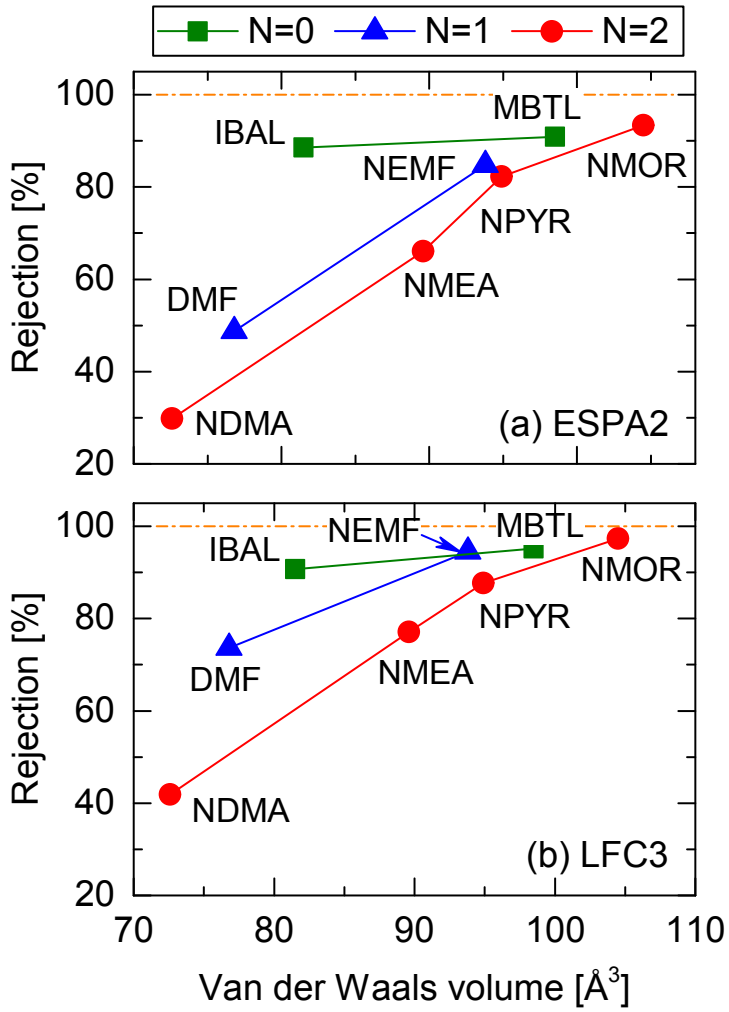

Fig. S4 – Rejection of the selected chemicals in pure water by (a) ESPA2 and (b) LFC3 RO membranes as a function of Van der Waals volume.

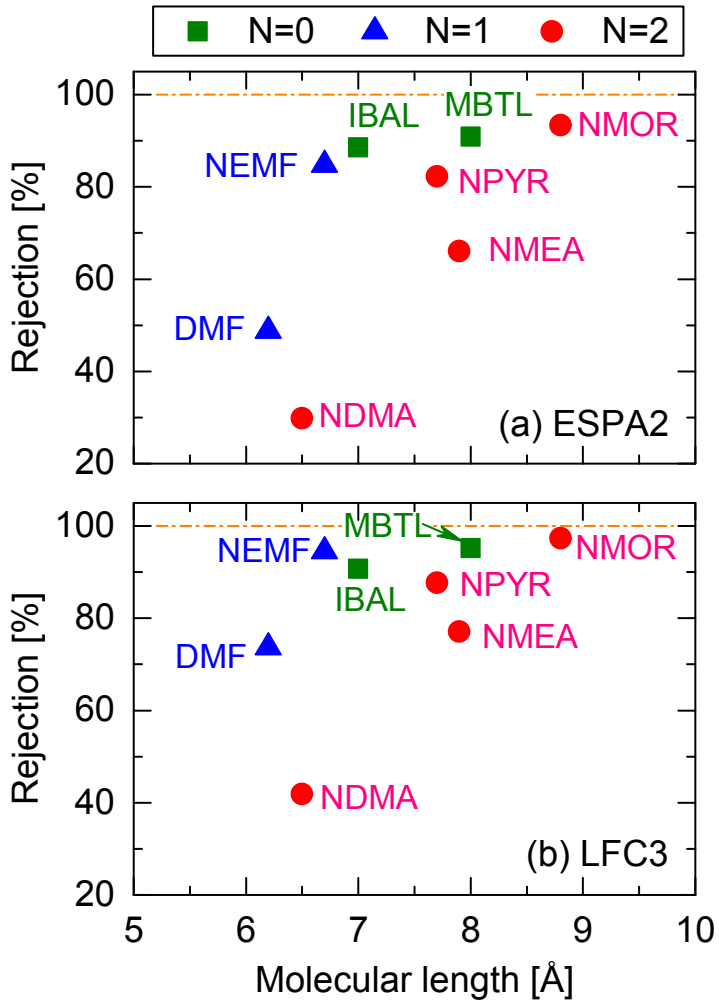

Fig. S5 – Rejection of the selected chemicals in pure water by (a) ESPA2 and (b) LFC3 RO membranes as a function of molecular length.

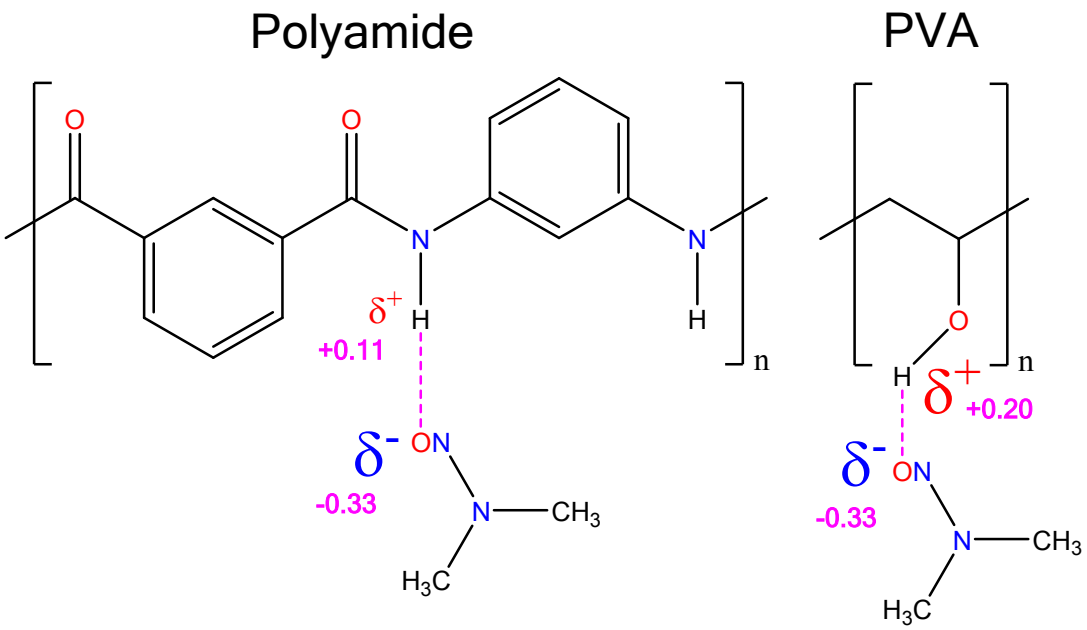

Fig. S6 – Elements of a hydrogen bonding between hydrogen bond acceptor on NDMA and hydrogen bond donor on a polyamide and PVA chains. Partial charge [e^-] was calculated based on Hückel method of ChemDraw software (PerkinElmer, Waltham, MA, USA).