Supporting information

Nanofiltration membrane for bio-separation: process-oriented materials innovation

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Membrane type	Permeance	Separation performance	Application	Refs
	$(Lm^{-2}h^{-1}bar^{-1})$			
NTR7450	5.3	Molasses decolorization	Bio-product decolorization	[1]
		rate: >90%		
HNTs-SO ₃ H/PES	18.7	Reactive black rejection: > 90%;	Bio-product	[2]
		Na ₂ SO ₄ rejection: <10%	decolorization	
TiO ₂ -HDMI	15.3	Congo red rejection: 97.4%;	Bio-product	[3]
modified PES		Methyl blue rejection: 99.1%;	decolorization	
membrane		Na ₂ SO ₄ rejection: 6%		
PEI-PI	37.4	Jansu green B rejection: 98.7%;	Bio-product	[4]
			decolorization	
ZTFCMs	8.4	Erythromycin rejection: 96.5%;	Biomolecules	[5]
	12.2	NaCl rejection: 14.4%	separation	5.63
PEI-g-SBMA/TMC	13.2	Orange GII rejection:90.6%;	Bio-product	[6]
		Na ₂ SO ₄ rejection: 50.4% ;	decolorization	
DA DSEn	14.8	Nacl rejection: 7.1%	Diamalagulas	[7]
rA-r Shii	14.0	Normoxacin rejection: ~90%,	separation	[/]
N-hexane post-	16.7	Clindamycin rejection: 95%	Bio-product	[8]
treated PA	10.7	NaCl rejection: 19%	desalination	[0]
membrane			acsumation	
Ethanol	19.3	Clindamycin rejection: 92%;	Bio-product	[8]
post-treated PA		NaCl rejection: 12%	desalination	
membrane		·		
HGMX	89.6	Rhodamine B rejection: >97%;,	Bio-product	[9]
		Methyl blue rejection: >97%	decolorization	

Table S1 Bio-separation performances of various NF membranes prepared with innovate membrane materials

Abbreviations: Halloysite nanotubes (HNTs); 1, 6-hexamethylene diisocyanate (HDMI); polyimide-Extem (PI); zwitterionic polyamide thin film composite nanofiltration membranes (ZTFCMs); Sulfobetaine methacrylate (SBMA); Polysulfone (PSF); GO-based NF membrane intercalated with TiO₂ nanoparticles (HGMX).

Membrane type	Anti-fouling performance	Regulation mechanisms	Refs
PEG-4arm-NH ₂ /TM C	• Flux recovery ratio >90% after fouling with BSA	• PEG enhances the surface hydrophilicity	[10]
PEI-g-SBMA/TMC	• Number of <i>Escherichia coli</i> adhered on to surface is significantly lower than the control membrane	• Zwitterionic monomer provides a hydrophilic and electroneutral membrane surface	[6]
ZA-modified PA membrane	• Flux recovery ratio >99% after fouling with BSA	 Groups of ZA improve the hydrophilicity of membrane The self-restrictive diffusion effect of PIP/ZA obtained from the reaction of PIP and ZA result in smooth membrane surface 	[11]
P(AA-co-Ada)/PAH	• <i>Escherichia coli</i> and <i>Staphylococcus aureus</i> killing ratio >95%	• Quaternary ammonium salt groups on the surface inhibit the growth of bacteria	[12]
FPA/PES	• Total flux decline ratio is 9.9% and 4.9% after fouling with BSA and HA, respectively	• The covalently bonded perfluoro groups effectively lower the surface free energy of the membrane	[13]
PDADMAC-PSS	• The flux almost keeps constant after fouling with BSA for 24 h	• Biocatalytic activity removes adsorbed proteins from modified membrane surface.	[14]

Table S2 Fouling bahavior of various membranes and the corresponding anti-fouling mechanisms

Abbreviations: Polyethylene glycol (PEG); bovine serum albumin (BSA); zoledronic acid (ZA); piperazine (PIP); Poly(acrylic acid-co-1-adamantan-1-ylmethyl acrylate)/Poly(allylamine hydrochloride) (P(AA-co-Ada)/PAH); fluorinated polyamide (FPA); poly(diallyl dimethyl ammonium chloride) (PDADMAC); poly(acrylic acid) (PAA).

References

[1] Luo, J., Guo, S., Qiang, X., Hang, X., et al., Sustainable utilization of cane molasses by an integrated separation process: Interplay between adsorption and nanofiltration. *Sep. Purif. Technol.* 2019, *219*, 16-24.

[2] Wang, Y., Zhu, J., Dong, G., Zhang, Y., et al., Sulfonated halloysite nanotubes/polyethersulfone nanocomposite membrane for efficient dye purification. *Sep. Purif. Technol.* 2015, *150*, 243-251.

[3] Zhang, L., Guan, H., Zhang, N., Jiang, B., et al., A loose NF membrane by grafting TiO2-HMDI nanoparticles on PES/ β -CD substrate for dye/salt separation. *Sep. Purif. Technol.* 2019, *218*, 8-19.

[4] Xia, Q.-C., Yang, W.-J., Fan, F., Ji, M., et al., Encapsulated Polyethyleneimine Enables Synchronous Nanostructure Construction and In Situ Functionalization of Nanofiltration Membranes. *Nano Lett.* 2020, *20*, 8185-8192.

[5] Weng, X.-D., Ji, Y.-L., Ma, R., Zhao, F.-Y., et al., Superhydrophilic and antibacterial zwitterionic polyamide nanofiltration membranes for antibiotics separation. *J. Membr. Sci.* 2016, *510*, 122-130.

[6] Ma, T., Su, Y., Li, Y., Zhang, R., et al., Fabrication of electro-neutral nanofiltration membranes at neutral pH with antifouling surface via interfacial polymerization from a novel zwitterionic amine monomer. *J. Membr. Sci.* 2016, *503*, 101-109.

[7] Yang, Z., Wang, F., Guo, H., Peng, L.E., et al., Mechanistic Insights into the Role of Polydopamine Interlayer toward Improved Separation Performance of Polyamide Nanofiltration Membranes. *Environ. Sci. Technol.* 2020, *54*, 11611-11621.

[8] Guo, S., Chen, X., Wan, Y., Feng, S., et al., Custom-Tailoring Loose Nanofiltration Membrane for Precise Biomolecule Fractionation: New Insight into Post-Treatment Mechanisms. *ACS Appl. Mater. Interfaces*. 2020, *12*, 13327-13337.

[9] Han, R. and Wu, P., High-performance graphene oxide nanofiltration membrane with continuous nanochannels prepared by the in situ oxidation of MXene. *J. Mater. Chem. A.* 2019, *7*, 6475-6481.

[10] Cheng, X.Q., Liu, Y., Guo, Z. and Shao, L., Nanofiltration membrane achieving dual resistance to fouling and chlorine for "green" separation of antibiotics. *J. Membr. Sci.* 2015, *493*, 156-166.

[11] Cao, X.-L., Zhou, F.-Y., Cai, J., Zhao, Y., et al., High-permeability and anti-fouling nanofiltration membranes decorated by asymmetric organic phosphate. *J. Membr. Sci.* 2021, *617*, 118667.

[12] Wei, T., Zhan, W., Cao, L., Hu, C., et al., Multifunctional and Regenerable Antibacterial Surfaces Fabricated by a Universal Strategy. *ACS Appl. Mater. Interfaces*. 2016, *8*, 30048-30057.

[13] Qian, Y., Wu, H., Sun, S.-P. and Xing, W., Perfluoro-functionalized polyethyleneimine that enhances antifouling property of nanofiltration membranes. *J. Membr. Sci.* 2020, *611*, 118286.

[14] Dizge, N., Epsztein, R., Cheng, W., Porter, C.J., et al., Biocatalytic and salt selective multilayer polyelectrolyte nanofiltration membrane. *J. Membr. Sci.* 2018, *549*, 357-365.