Textile Wastewater Treatment by Bioinspired Antimicrobial Nanofiltration Membranes

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1. Problem: Waterborne Chemical Contaminants

World water crisis:

- The United Nations has predicted that **two-thirds of the world population may face water stressed conditions** by 2025 [1].
- Waterborne chemical contaminants **deleterious to both human health and the environment** have recently emerged as serious public health concerns. Many of these molecules are too small to be removed by traditional water treatment processes.
- Textile wastewater is one type of harmful industrial wastewater.

www.biovistawaters.com/sites/default/files/textile-2.jpg www.lotusozone.com/upload/textile-waste-water-treatment-02.jpg

Textile wastewater

Sustainable approach:

- Nanofiltration membranes are increasingly used to remove waterborne chemical contaminants.
- Membrane surface functionalization with advanced nanomaterials offers tailored control and targeted design of surface properties optimal for specific separations [2, 3], such as the separation of textiles.
- Rather than removing chemicals (*e.g.*, dyes) as waste, separating chemicals from industrial wastewater (*e.g.*, textile wastewater) not only purifies industrial wastewater but also allows the reuse of chemicals.
- Textile wastewater includes salts. If dye/salt mixtures can be separated, then dyes can be removed and reused from textile wastewater while treating the water.

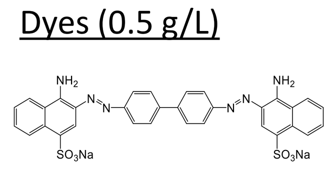
2. Methods: Membrane Preparation and Testing

Textile wastewater solutions: filtered via cross-flow filtration

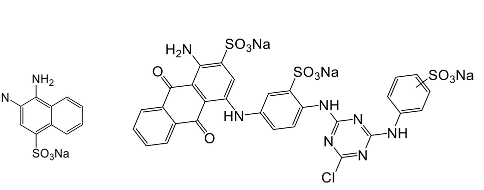
Salts (1.0 g/L)

- Na_2SO_4
- $MgCl_2$
- NaCl

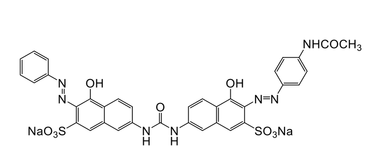
Dyes (0.5 g/L)



Congo Red (CR, MW = 696.7 Da)



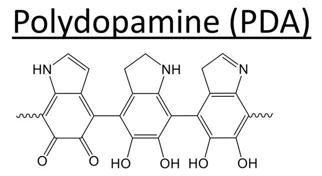
Reactive Blue 2 (RB2, MW = 774.2 Da)



Direct Red 23 (DR23, MW = 813.7 Da)

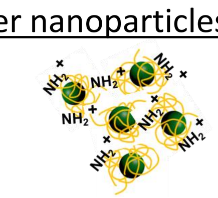
Membrane preparations

Polydopamine (PDA)



- Adhesive interfacial coating
- Mussel-inspired
- Rapid deposition (30 min)

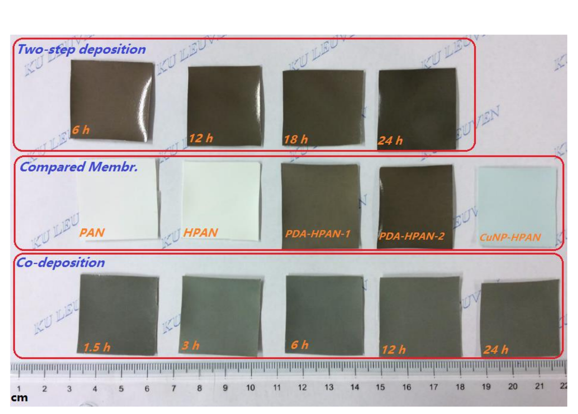
Copper nanoparticles (CuNPs)



- Inexpensive biocide
- Cationic; modified by polyethylenimine

Modifications

- Polyacrylonitrile (PAN) support
- Co-deposition or traditional two-step deposition of PDA and CuNPs for various times



Prepared membranes

Membrane	PDA deposition time (h)	CuNP deposition time (h)	Co-deposition time (h)
PDA-HPAN-1	0.5	-	-
PDA-HPAN-2	6	-	-
CuNP-HPAN	-	24	-
NF-1	0.33	24	-
NF-2	0.5	12	-
NF-3	0.5	18	-
NF-4	0.5	24	-
Co-NF-1	-	-	1.5
Co-NF-2	-	-	3
Co-NF-3	-	-	6
Co-NF-4	-	-	12
Co-NF-5	-	-	24

Assigned membrane names from various deposition times

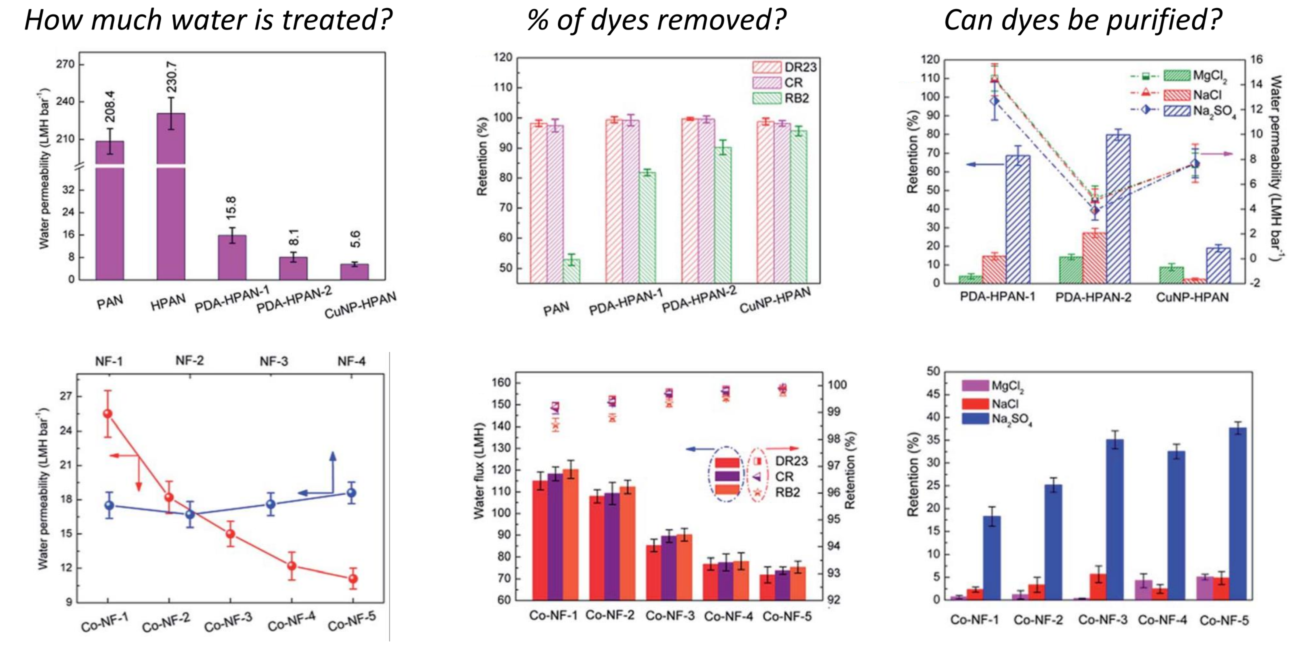
3. Results: Separation Performance

The co-deposition membranes exhibited the best separation performances.

Water permeability — *How much water is treated?*
Dye rejection — *% of dyes removed?*
Salt permeation — *Can dyes be purified?*

Pristine PAN, PDA only, and CuNP only membranes:

Co-deposition membranes:



Notable water permeability results

- Co-deposition (3 h): 18.2 L m^{-1} h^{-1} bar^{-1}
- CuNPs only (24 h): 5.6 L m^{-1} h^{-1} bar^{-1}
- PDA only (30 min): 15.8 5.6 L m^{-1} h^{-1} bar^{-1}

RB2 dye rejection

- Co-deposition (3 h): 99.0%
- Two-step deposition: 96.6%
- PDA only (30 min): 81.9%
- Pristine PAN: 52.9%

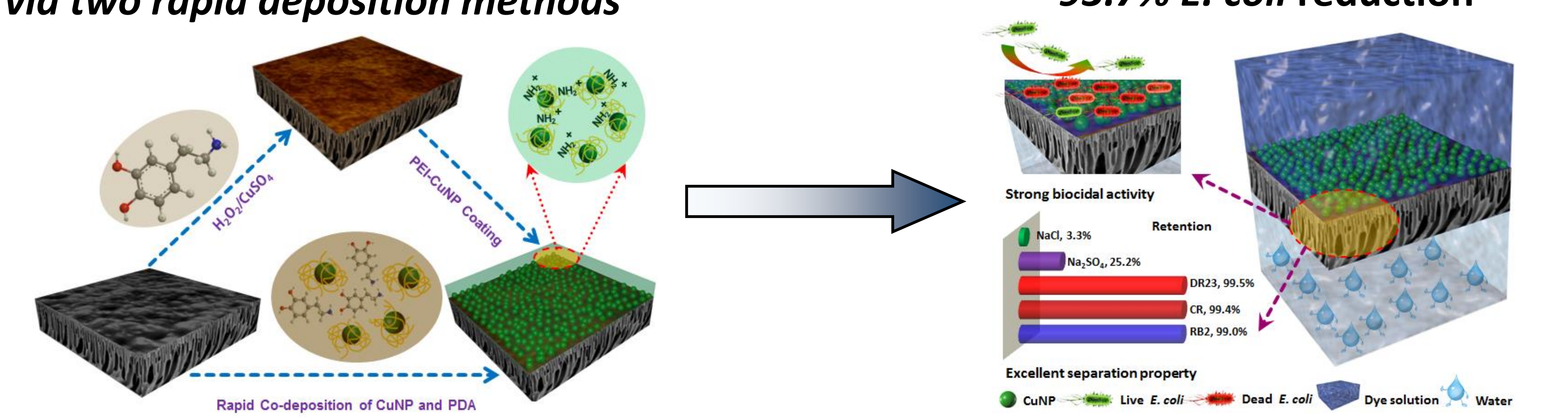
Notable salt permeation results

- Na_2SO_4: 75% for co-deposition (3 h); 30% for 30 min PDA
- NaCl: 97% for co-deposition (3 h)
- $MgCl_2$: >99% for co-deposition (3 h)

Summary

Membranes modified by PDA and CuNPs via two rapid deposition methods

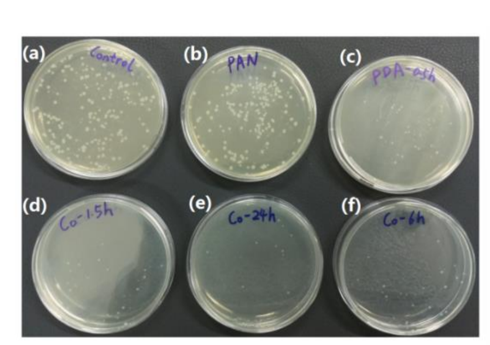
>99% dye retention, 97% NaCl permeation, 93.7% E. coli reduction

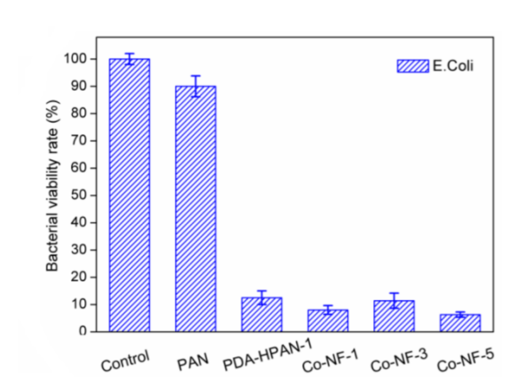


Homogeneous nanoparticle distribution, low surface roughness, high hydrophilicity, and relatively neutral surface charge provides highly efficient water purification and dye recovery in textile wastewater treatment.

4. Results: Antimicrobial Activity

Membrane biocidal activity **kills disease-inducing pathogens** that contribute to the 3.4 million water-related deaths occurring each year worldwide [4]. The inhibition of cell growth additionally **prevents membrane biofouling**, increasing long-term separation efficiency and membrane lifetimes extensively.





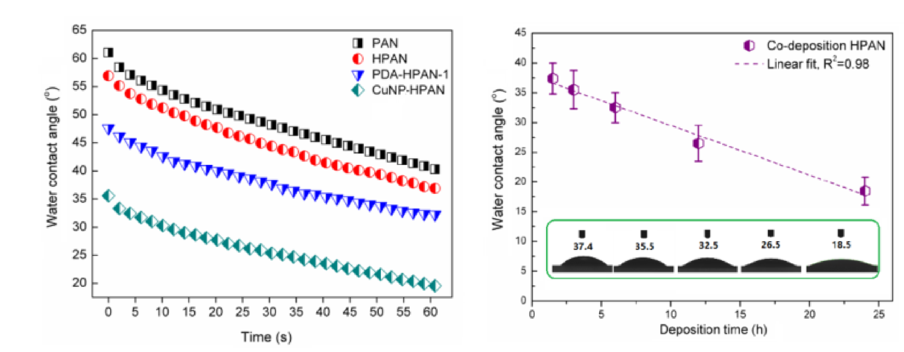
93.7% reduction in live bacteria attained by co-deposition membranes

Antimicrobial mechanism: Contact between pathogens and copper: release of cell-damaging reactive oxygen species from copper nanoparticles and ions, and intake of copper toxic to pathogens

5. Results: Materials Characterizations

Materials characterizations of the membrane surfaces corroborate the textile separation performance of the membranes with PDA-CuNP co-deposition.

Water contact angle: *High hydrophilicity, improving water permeability*



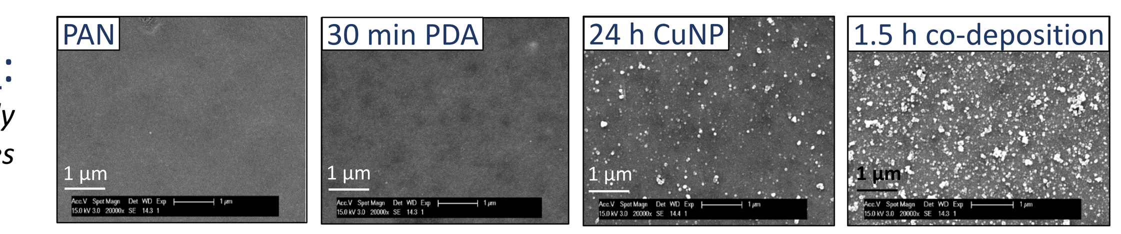
- PAN: 61°
- PDA: 48°
- CuNPs: 36°
- Co-dep: 18°

Zeta potential: *Co-deposition → more neutral charge, higher salt permeation*

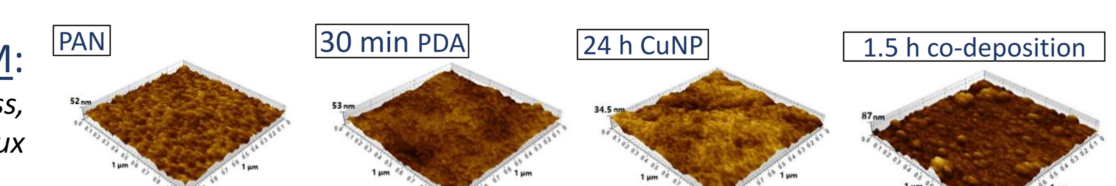
Isoelectric points:

- PAN support: 3.9
- 30 min PDA only: 3.4
- 3 h co-deposition: 4.8
- 24 h CuNP only: 5.7

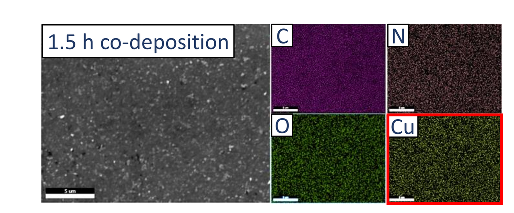
SEM: *Abundant homogeneously distributed copper nanoparticles*



AFM: *Low surface roughness, higher flux*



EDS Mapping: *Presence of copper confirmed*



Pristine PAN: 0.00% Cu
1.5 h co-deposition: 3.27% Cu

6. Conclusions, Comparisons, Future Work

Conclusions

- Of all established membranes that achieved ultra-high dye retention, **co-deposition membranes yielded highest water permeability and antimicrobial activity**
- Elevated salt transport attained makes co-deposition membranes competitive for textile wastewater separations
- Fast, facile deposition strategy faster than past PDA and CuNP depositions [10, 11] deems co-deposition method as practical

Comparison to state-of-art membranes

Membrane	Dye	Dye retention (%)	PWP[a] (LMH bar^{-1})	Salt rejection (%)	Ref.
CMCNa[b]/PP[c] NF	Methyl blue (799.8 Da) Congo red (696.7 Da)	99.6 99.8	10.8	NaCl (0.5 g L^{-1}): 28.8 Na_2SO_4 (0.5 g L^{-1}): 85.5	5
mHT[e]/PES	Reactive black 5 (991.8 Da) Reactive red 49 (576.5 Da)	95.0 90.0	6.3	NaCl (0.5 g L^{-1}): ~8.0	6
Sepro NF 6	Congo red (696.7 Da) Direct red 23 (813.72 Da)	99.93 99.8	13.7	NaCl (0.1–40.0 g L^{-1}): 2.6-17.9	7
UTC-60	Reactive blue 2 (774.2 Da)	99.9	~ 10.0	NaCl (0.6 g L^{-1}): 30.1	8
GO-PSBMA[f]/PES	Reactive black 5 (991.8 Da) Reactive red 49 (576.5 Da)	99.2 97.2	~11.98	NaCl (0.5 g L^{-1}): ~4.0 Na_2SO_4 (0.5 g L^{-1}): ~10.0	9
3 hour PDA CuNP co-deposition	**Direct red 23 (813.72 Da)** **Congo red (696.7 Da)** **Reactive blue 2 (774.2 Da)**	**99.5** **99.4** **99.0**	**~18.2**	**NaCl (0.5 g L^{-1}): 3.3** **Na_2SO_4 (0.5 g L^{-1}): 25.2**	**This work**

[a] PWP is pure water permeability; [b] CMCNa is sodium carboxymethyl cellulose; [c] PP is polypropylene; [e] mHT is modified hydrotalcite with poly(ionic liquid); [f] GO-PSBMA is graphene oxide modified with poly(sulfobetaine methacrylate)

Future Work

- Apply co-deposition membranes for separation and reuse of other emerging chemical contaminants
- Use PDA to fine-tune pore sizes and adhere antimicrobial nanomaterials
- Co-deposition for other separations, like oil-water separation or nanoscale separations

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References

[1] United Nations. (2014, November 24). *Water scarcity*. Retrieved April 1, 2016, from http://www.un.org/waterforlifedecade/scarcity.shtml. [2] J. Zhu, A. Uliana, J. Wang, S. Yuan, J. Li, M. Tian, K. Simoens, A. Volodin, J. Lin, K. Bernaerts, Y. Zhang, and B. Van der Bruggen, *J. Mater. Chem. A*, 2016, *4*(34), 13211-13222. [3] J. Wang, Y. Wang, Y. Zhang, A. Uliana, J. Zhu, J. Liu, and B. Van der Bruggen, *ACS Appl. Mater. Interfaces*, 2016, *8*(38), 25508–25519. [4] World Health Organization. (2015). *WHO World Water Day report*. Retrieved April 1, 2016, from http://www.who.int/water_sanitation_health/takingcharge.html. [5] S. Yu, Y. Zheng, Q. Zhou, S. Shuai, Z. Lü and C. Gao, *Desalination*, 2012, **298**, 49-58. [6] L. Yu, J. Deng, H. Wang, J. Liu and Y. Zhang, *ACS Sustainable Chem. Eng.*, 2016, **4**, 3292–3304. [7] J. Lin, W. Ye, H. Zeng, H. Yang, J. Shen, S. Darvishmanesh, P. Luis, A. Sotto and B. Van der Bruggen, *J. Membr. Sci.*, 2015, **477**, 183-193. [8] B. Van der Bruggen, B. Daems, D. Wilms and C. Vandecasteele, *Sep. Purif. Technol.*, 2001, **22-23**, 519-528. [9] J. Zhu, M. Tian, J. Hou, J. Wang, J. Lin, Y. Zhang, J. Liu and B. Van der Bruggen, *J. Mater. Chem. A*, 2016, **4**, 1980-1990. [10] H. Lee, S. M. Dellatore, W. M. Miller and P. B. Messersmith, *Science*, 2007, **318**, 426-430. [11] M. Ben-Sasson, K. R. Zodrow, Q. Genggeng, Y. Kang, E. P. Giannelis and M. Elimelech, *Environ. Sci. Technol.*, 2014, **48**, 384-393.