

**Selective adsorption of Malachite green (MG) and Fuchsin acid (FA)
by ZIF-67 hybridized Polyvinylidene fluoride (PVDF) membranes**

Ying Liu, Na Wang, Zhongqiao Sun, Yide Han, Junli Xu, Yan Xu, Junbiao Wu, Hao
Meng and Xia Zhang*

Department of Chemistry, College of Sciences, Northeastern University, Shenyang
110819, P. R. China.

*Corresponding author.

E-mail: xzhang@mail.neu.edu.cn.(Prof. X. Zhang)

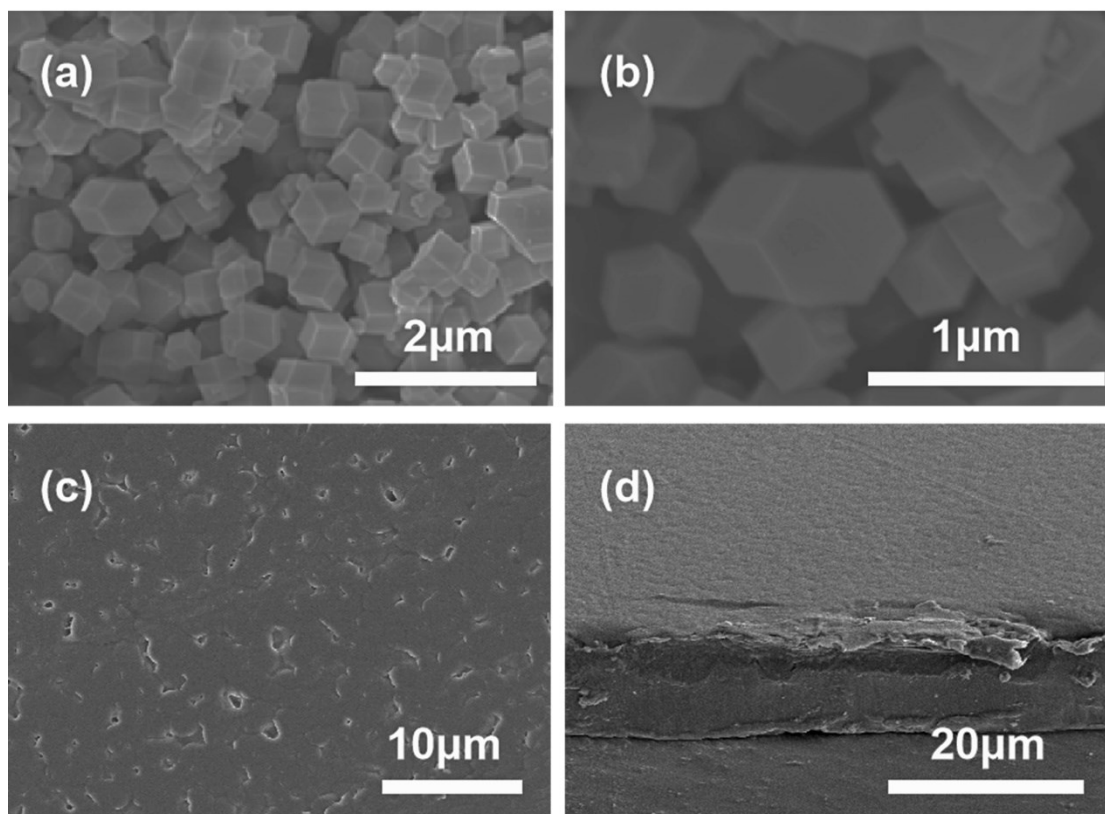


Fig.S1. SEM images of single ZIF-67 (a, b) at different magnification; SEM images of pristine PVDF (c, d): (c) front view; (d) cross section view.

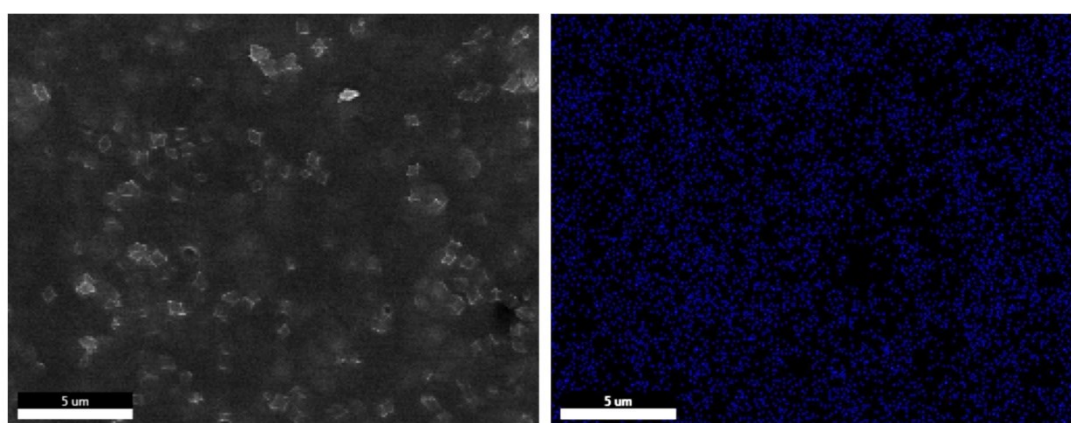


Fig.S2.SEM-EDS mapping of Co of the ZIF(4)/PVDF.

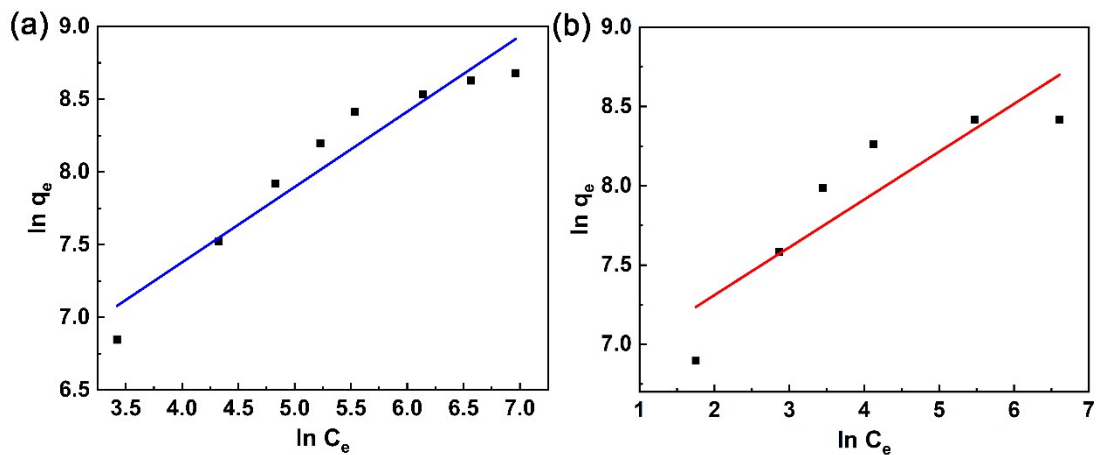


Fig.S3. Fitting curves of MG (a) and FA (b) using Freundlich model.

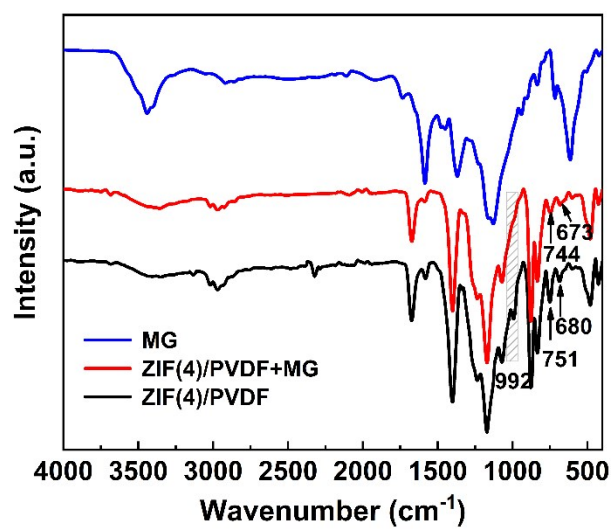


Fig.S4. FTIR spectra of MG, original ZIF(4)/PVDF and MG-adsorbed hybrid membranes.

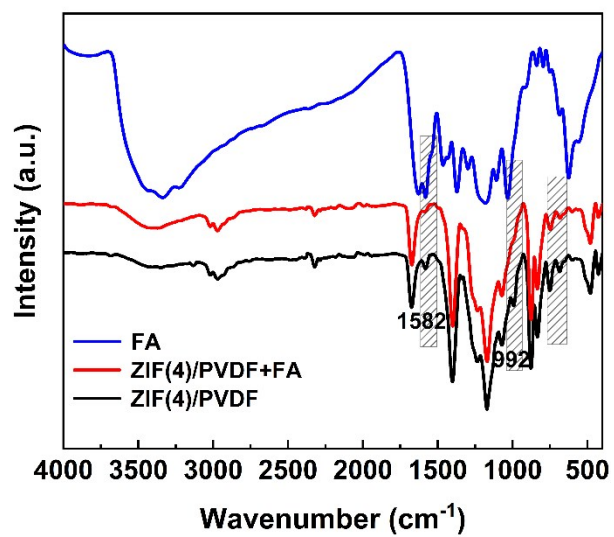
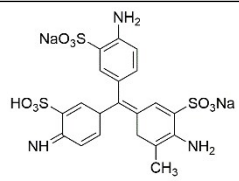
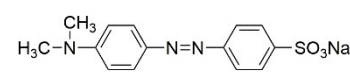
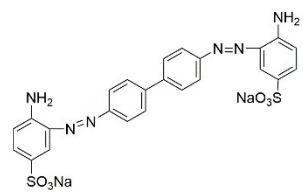
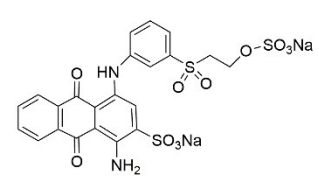
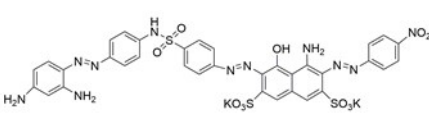
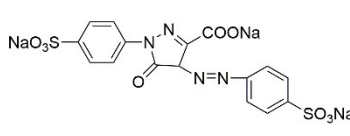
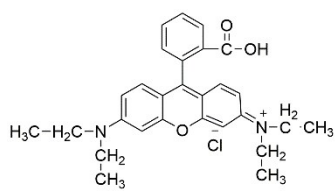
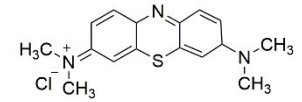
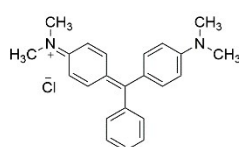


Fig.S5. FTIR spectra of FA, original ZIF (4)/PVDF and FA-adsorbed hybrid membranes.

Table S1. The adsorption performance of MOF/PVDF hybrid matrix membranes in the literature.

PVDF-based membranes	Organics	Adsorption capacities	Ref.
MIL-53/PVDF	MB	264.7 mg/g	[1]
ZIF-8/PVDF	Iodine ions	73.33 mg/g	[2]
UiO-66/PVDF	Arsenate	267 mg/g	[3]
NH ₂ -MIL-101(Cr)/PVDF	CR	645.16 mg/g	[4]
MIL-68/PVDF	PNP	183.49 $\mu\text{g}/\text{cm}^2$	[5]
	MB	74.35 $\mu\text{g}/\text{cm}^2$	
Cu-BTC/PVDF	CR	1157.4 $\mu\text{g}/\text{cm}^2$	[6]
MOF-808/PVDF	Cd ²⁺	42.6 mg/g	[7]
	Zn ²⁺	17.17 mg/g	
PVDF/PEDOT	MO	143.8 mg/g	[8]
Aminated PAN/PVDF	Direct Red23	685.63 mg/g	[9]
HAPNPS/PVDF	CR	10.83 mg/g	[10]
PVDF/GO	MB	621.1 mg/g	[11]
PVDF/PDA	CR	384.6 mg/g	[12]
	MB	370.4 mg/g	
	Cr(VI)	126.7 mg/g	

Table.S2 The molecular weight, ionic nature and molecular structure of nine dyes.

Dyes	Molecular structure	Ion species	Functional groups	Molecular weight
FA		anion	-NH ₂ , -SO ₃	585.4
MO		anion	-SO ₃	327.33
CR		anion	-NH ₂ , -SO ₃	696.68
RB19		anion	-NH ₂ , -SO ₃	626.54
AB210		anion	-NH ₂ , -SO ₃	938.02
AY23		anion	-COOH, -SO ₃	1534.36
RhB		cation	-COOH	479.01
MB		cation		319.85
MG		cation		364.91

References

- [1] Y. Ren, T. Li, W.M. Zhang, S. Wang, M.Q. Shi, C. Shan, W.B. Zhang, X.H. Guan, L. Lv, M. Hua, B.C. Pan, MIL-PVDF blend ultrafiltration membranes with ultrahigh MOF loading for simultaneous adsorption and catalytic oxidation of methylene blue, *J. Hazard. Mater.*, 365 (2019) 312-321. <https://doi.org/10.1016/j.jhazmat.2018.11.013>.
- [2] X. Long, Y.S. Chen, Q. Zheng, X.X. Xie, H. Tang, L.P. Jiang, J.T. Jiang, J.H. Qiu, Removal of iodine from aqueous solution by PVDF/ZIF-8 nanocomposite membranes, *Sep. Purif. Technol.*, 238 (2020) 11. <https://doi.org/10.1016/j.seppur.2019.116488>.
- [3] P. Wan, M.X. Yuan, X.L. Yu, Z. Zhang, B.L. Deng, Arsenate removal by reactive mixed matrix PVDF hollow fiber membranes with UIO-66 metal organic frameworks, *Chem. Eng. J.*, 382 (2020) 9. <https://doi.org/10.1016/j.cej.2019.122921>.
- [4] Y.M. Tan, Z.Q. Sun, H. Meng, Y.D. Han, J.B. Wu, J.L. Xu, Y. Xu, X. Zhang, Aminated metal-organic framework (NH₂-MIL-101(Cr)) incorporated polyvinylidene (PVDF) hybrid membranes: Synthesis and application in efficient removal of Congo red from aqueous solution, *Appl. Organomet. Chem.*, 34 (2020) 13. <https://doi.org/10.1002/aoc.5281>.
- [5] Y.M. Tan, Z.Q. Sun, H. Meng, Y.D. Han, J.B. Wu, J.L. Xu, Y. Xu, X. Zhang, A new MOFs/polymer hybrid membrane: MIL-68(Al)/PVDF, fabrication and application in high-efficient removal of p-nitrophenol and methylene blue, *Sep. Purif. Technol.*, 215 (2019) 217-226. <https://doi.org/10.1016/j.seppur.2019.01.008>.
- [6] C.X. Yu, Y.Y. Liu, X. Zhang, Preparation of Cu-BTC/PVDF Hybrid Membranes Using in situ Doping Method and Their Enhanced Dye Adsorption Properties, *Chem. J. Chin. Univ.-Chin.*, 39 (2018) 1384-1391. <https://doi.org/10.1007/s12221-017-6814-7>.
- [7] J.E. Efome, D. Rana, T. Matsuura, C.Q. Lan, Insight Studies on Metal-Organic Framework Nanofibrous Membrane Adsorption and Activation for Heavy Metal Ions Removal from Aqueous Solution, *ACS Appl. Mater. Interfaces*, 10 (2018) 18619-18629. <https://doi.org/10.1021/acsami.8b01454>.
- [8] R.J. da Silva, L.C. Mojica-Sanchez, F.D.S. Gorza, G.C. Pedro, B.G. Maciel, G.P.

Ratkovski, H.D. da Rocha, K.T.O. do Nascimento, J.C. Medina-Llamas, A.E. Chavez-Guajardo, J.J. Alcaraz-Espinoza, C.P. de Melo, Kinetics and thermodynamic studies of Methyl Orange removal by polyvinylidene fluoride-PEDOT mats, *J. Environ. Sci.*, 100 (2021) 62-73. <https://doi.org/10.1016/j.dyepig.2019.107591>

[9] Z. Mokhtari-Shourijeh, S. Langari, L. Montazerghaem, N.M. Mahmoodi, Synthesis of porous aminated PAN/PVDF composite nanofibers by electrospinning: Characterization and Direct Red 23 removal, *J. Environ. Chem. Eng.*, 8 (2020) 7. <https://doi.org/10.1016/j.jtice.2016.02.008>

[10] J.H. Li, H. Zheng, H.X. Lin, B.X. Zhang, J.B. Wang, T.L. Li, Q.Q. Zhang, Preparation of Three Dimensional Hydroxyapatite Nanoparticles/Poly(vinylidene fluoride) Blend Membranes with Excellent Dye Removal Efficiency and Investigation of Adsorption Mechanism, *Chin. J. Polym. Sci.*, 37 (2019) 1234-1247. <https://doi.org/10.1007/s10118-019-2271-7>

[11] F.F. Ma, D. Zhang, T. Huang, N. Zhang, Y. Wang, Ultrasonication-assisted deposition of graphene oxide on electrospun poly (vinylidene fluoride) membrane and the adsorption behavior, *Chem. Eng. J.*, 358 (2019) 1065-1073. <https://doi.org/10.1016/j.cej.2018.10.121>

[12] F.F. Ma, D. Zhang, N. Zhang, T. Huang, Y. Wang, Polydopamine-assisted deposition of polypyrrole on electrospun poly (vinylidene fluoride) nanofibers for bidirectional removal of cation and anion dyes, *Chem. Eng. J.*, 354 (2018) 432-444. <https://doi.org/10.1016/j.cej.2018.08.048>