Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B. This journal is © The Royal Society of Chemistry 2024

## Enhancing Biofouling Resistance in Microfiltration Membranes through Capsaicin-Derivative

## **Functionalization – Supporting Information**

Saitao Yan<sup>1</sup>, Qisheng Ye<sup>1</sup>, Jiayi Wu,<sup>1</sup> Wangli Yao<sup>1</sup>, Baoliang Chen<sup>1, 2</sup> and Xiaoying Zhu<sup>\*1, 2</sup>

1. Department of Environmental Science, Zhejiang University, Hangzhou, Zhejiang 310058, China.

2. Innovation Center of Yangztze River Delta, Zhejiang University, Jiaxing, Zhejiang 314100, China

\*Corresponding author email:

Dr. Xiaoying Zhu: zhux@zju.edu.cn

Tel: +86-571-88982651

Fax: +86-571-88982651

Co-author email:

Saitao Yan: <u>yansaitao@zju.edu.cn</u>

Qisheng Ye: qsye@zju.edu.cn

Jiayi Wu: wujiayi0212@zju.edu.cn

Wangli Yao: 22114034@zju.edu.cn

Baoliang Chen: blchen@zju.edu.cn

## Text S1 Synthesis of P(VDF-CTFE)-g-PMAA

The synthesis of P(VDF-CTFE)-g-PMAA was carried out in two stages, as previously described in our study [1]. In the first stage, the carbon chloride bond on the P(VDF-CTFE) backbone was grafted with tert-butyl methacrylate (tBMA) through atom transfer radical polymerization (ATRP), followed by hydrolysis to obtain P(VDF-CTFE)-g-PMAA with carboxyl functional groups.To initiate this process, P(VDF-CTFE) with a chlorine content of 2.4 mmol (1.5 g) and CuCl (238 mg, 2.4 mmol) were placed in a 100 mL Schlenk flask under a nitrogen atmosphere. The flask was subjected to three cycles of vacuum extraction and nitrogen refilling, followed by the addition of 25 mL of N-methyl-2-pyrrolidone (NMP) which was dissolved by magnetic stirring. A mixture of tertbutyl methacrylate (96 mmol, 15.27 mL) and NMP (5 mL) containing PMDETA (0.24 mmol, 0.5 mL) was then added. The system was heated to 80 °C in an oil bath under a nitrogen atmosphere and allowed to proceed for 20 h before being quenched by exposing the system to air at room temperature. The resulting product was diluted with 5 mL of acetone and purified by adding it dropwise into a mixed solution of water and methanol (volume ratio of 1:2, 1.2 L). The (P(VDF-CTFE)-g-PtBMA) product was then washed with pure water until the filtrate was colorless and subsequently freeze-dried for further use.

In the second stage, the tert-butyl methacrylate on the backbone was hydrolyzed. Specifically, 2.5 g of P(VDF-CTFE)-g-PtBMA was added to a 250 mL round-bottomed flask containing 50 mL of toluene, followed by the addition of p-toluenesulfonic acid (TSA, 4.0 g). The mixture was heated to 85 °C for 8 h to hydrolyze the tert-butyl ester groups in the PtBMA units. The resulting P(VDF-CTFE)-g-PMAA product was washed by a mixed solution of water and ethanol (volume ratio of 1:2) and recovered by vacuum filtration. After drying under vacuum, P(VDF-CTFE)-g-PMAA was stored

for further use.



Figure S1. <sup>1</sup>*H* NMR spectra of (a) CD, (b) P (VDF-CTFE) and (c) P (VDF-CTFE)-g-PtBMA.



Figure S2. FTIR spectra of the (a) CD, (b) P (VDF-CTFE) and (c) P (VDF-CTFE)-g-PtBMA.



Figure S3. Zone of inhibition experiment without (b,e) and with (c,f) capsaicin derivatives CD.



Figure S4. XPS of (a) CD, (b) P (VDF-CTFE) and (c) P (VDF-CTFE)-g-PtBMA.



Figure S5. Water contact angle of the membranes. (a) M0, (b) M1, and (c) MA.



Figure S6. Pore size distribution of the M1 (a) and MA (b) membranes. (Note: determined by

mercury intrusion porosimeter.)



Figure S7. Growth of E. coli detached from M0 (a), M1 (b), and MA (c) on LB plates.



Figure S8. SEM image of M0 (a), M1 (b), and MA (c) fixed with glutaraldehyde after soaking in the *B. subtilis* suspension; the growth of *B. subtilis* detached from M0 (d), M1 (e), and MA (f) on LB plates.



Figure S9. Fluorescence microscope images of *B. subtilis* on the M0 (a and d), M1(b and e) and MA (c and f) stained with SYTO 9 and PI, respectively. Note: the scale bar is 100 μm.

Materials	C%	F%	O%	N%
CD	75.34	0	14.93	9.15
P (VDF-CTFE)	48.13	50.97	0	0
P (VDF-CTFE)-g-PtBMA	53.93	41.04	4.51	0
P (VDF-CTFE)-g-PMAA	49.71	47.99	1.77	0
МА	64.05	22.51	8.31	5.01

Table S1. Composition of elements (C, F, O, N) in the prepared materials.

Note: Estimated from the XPS spectra.

Table S2. Relative flux decay (RFD) and relative flux recovery (RFR) of M1 and MA during filtration (transmembrane pressure: 0.01 MPa).

Cycle number		JO	J1	J2	RFD	RFR
		$(L/m^2h)$	$(L/m^2h)$	$(L/m^2h)$	(%)	(%)
1	M1	41.38	21.04	28.66	49.15	69.26
	MA	62.07	43.62	57.52	29.72	92.67
2	M1		16.79	22.54	59.42	54.47
	MA		39.56	56.24	36.27	90.61
3	M1		9.92	19.26	76.03	46.54
	MA		36.62	52.73	41.00	84.95

Table S3. Comparison the performance of MA with the other antibacterial membranes.

Membrane matrix	Antibacterial material	Modification reaction	Permeability ( $Lm^{-2}h^{-1}/Bar$ )	Relative Flux recovery (% )	Reference
PES	Capsaicin derivative	UV-grafting	120.0	92.3	1
PSF	Capsaicin derivative	UV- grafting	700.0	45.0	2
CA	Quaternary ammonium	Etherification	308.0	80.3	3
PVDF	$Ag^+$	Blend	671.0	61.6	4
P(VDF-CTFE) grafted with capsaicin derivative (PD)	Capsaicin derivative	Esterification	620.7	85.0	This Work

## **References:**

1. J. Wang, X. Gao, Q. Wang, H. Sun, X. Wang and C. Gao, *Applied Surface Science*, 2015, **356**, 467-474.

2. G. Xueli, W. Haizeng, W. Jian, H. Xing and G. Congjie, *Journal of Membrane Science*, 2013, 445.

3. Y. Zhou, Y. Jiang, Y. Zhang and L. Tan, *ACS Applied Materials & Interfaces*, 2022, **14**, 38358-38369.

4. C. Liao, P. Yu, J. Zhao, L. Wang and Y. Luo, *Desalination*, 2011, **272**, 59-65.