

Supplementary Information

Membrane fouling in integrated adsorption-UF system: Effects of NOM and adsorbent properties

Kai Li ^{a,b*}, Shu Li ^{a,b}, Ce Sun ^{a,b}, Tinglin Huang ^{a,b**}, Guibai Li ^c, Heng Liang ^c

^a *Key Laboratory of Northwest Water Resource, Environment and Ecology, MOE, Xi'an University of Architecture and Technology, Xi'an, 710055, PR China*

^b *Shaanxi Key Laboratory of Environmental Engineering, Xi'an University of Architecture and Technology, Xi'an, 710055, PR China*

^c *State Key Laboratory of Urban Water Resource and Environment (SKLUWRE), Harbin Institute of Technology, Harbin 150090, PR China*

The particle size, surface area, pore size distribution, and amount of surface groups of MAR and PAC are presented in Table S1. It can be seen that the average particle size of MAR was smaller than that of PAC, but the difference (25.2 versus 32.1 μm) was not remarkable. The BET surface area of MAR was much smaller than that of PAC, and the pore size distribution of the two adsorbents varied significantly. Mesopores with widths in the range of 10~50 nm accounted for 78% of the pores of MAR, whereas PAC was abundant in micropores and pores larger 10 nm only took up 14%. The average pore size of MAR was much larger than that of PAC (16.4 versus 2.2 μm). The amounts of surface functional groups were quantified by Boehm titration ^{1, 2}. The

amount of phenol on the surface of MAR was similar with that on PAC, but there were much less other functional groups on MAR. The surface groups of MAR were supposed to be formed during the dissolution of polyethersulfone in organic solvent (N-methyl pyrrolidone) and its precipitation in water, while the abundant surface groups of PAC were mainly formed during the carbonization and activation process ³.

Table S1 Physical and chemical properties of MAR and PAC.

Parameter		MAR ¹	PAC ¹
Average particle size (d_{50} , μm)		25.2 ± 0.8	32.1 ± 0.7
Zeta potential (mV) ²		-22.4 ± 1.0	-23.9 ± 0.9
BET surface area (m^2/g)		108 ± 9	1219 ± 13
Average pore size (nm)		16.4 ± 0.5	2.2 ± 0.1
Pore volumes (cm^3/g)	Micropore ($w < 2 \text{ nm}$)	0.031 ± 0.003	0.244 ± 0.013
	Small mesopore ($2 < w < 10 \text{ nm}$)	0.021 ± 0.003	0.075 ± 0.004
	Large mesopore ($10 < w < 50 \text{ nm}$)	0.215 ± 0.015	0.037 ± 0.003
	Macropore ($w > 50 \text{ nm}$)	0.010 ± 0.002	0.016 ± 0.002
Surface group amount based on	Phenol	0.11 ± 0.02	0.10 ± 0.01
	Carboxyl	0.01 ± 0.01	0.52 ± 0.08
Boehm titration (mmol/g)	Lactone	0.01 ± 0.01	0.07 ± 0.01
	Basic	0.09 ± 0.01	1.15 ± 0.02

Note:

1. Values represent average $\pm$ standard deviation, $n=3$.
2. Zeta potentials of MAR and PAC were measured at the pH of 7.0 ± 0.1 .

FTIR spectra of MAR and PAC are shown in Figure S1. For MAR, many strong peaks can be attributed to functional groups of the polyethersulfone molecule: peaks at 1323, 1299, 1150, 1105 and 560 cm^{-1} were related to sulfone groups; bands located at 3000, 1582, 1485, 870, and 835 cm^{-1} were attributed to the presence of aromatic rings; a strong peak at 1241 cm^{-1} was due to the aromatic ether structure ^{4,5}. Meanwhile, peaks at $3660\text{-}3500 \text{ cm}^{-1}$ and 1040 cm^{-1} indicated the presence of O-H and C-O bonds, respectively, suggesting the formation of some surface groups during preparation. With

respect to PAC, the peaks were mainly due to surface functional groups. The peak around 3640 cm^{-1} was assigned to stretching vibration of O-H, while the strong peak at 1040 cm^{-1} could be attributed to stretching vibration of C-O⁶. The presence of C=O and aromatic rings was confirmed by the presence of peaks around 1650 and 1460 cm^{-1} , respectively⁷.

Based on Boehm titration and FTIR analysis, the surface chemistry of PAC used in this study was similar with those reported in literature^{3,7}. Compared with PAC, there was less oxygen surface groups on MAR, but the sulfone, ether and aromatic rings in the structure of polyethersulfone molecules can also act as reactive functional groups. Therefore, apart from the hydrophobic interaction, it was possible that some NOM molecules were adsorbed due to specific interactions, such as hydrogen bonds.

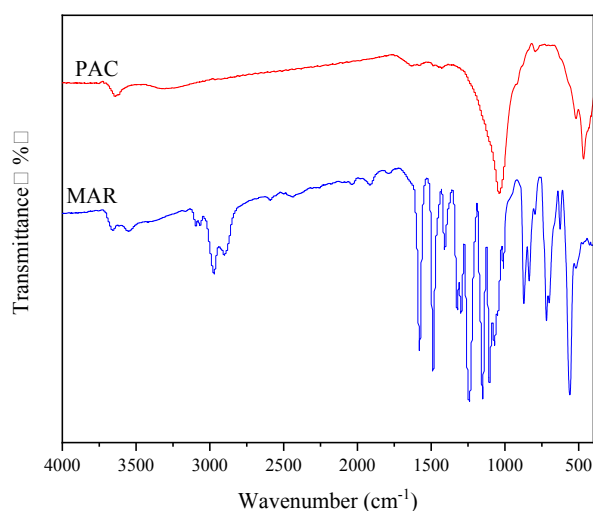


Figure S1. FTIR spectra of MAR and PAC.

DOC concentrations in permeate of UF, MAR/UF and PAC/UF are shown in Figure S2. The addition of PAC resulted in obvious improvement of permeate quality, but the addition of MAR only slightly decreased DOC in permeate compared with UF alone. The results were consistent with the much lower specific surface area and

adsorption capacity of MAR compared with PAC.

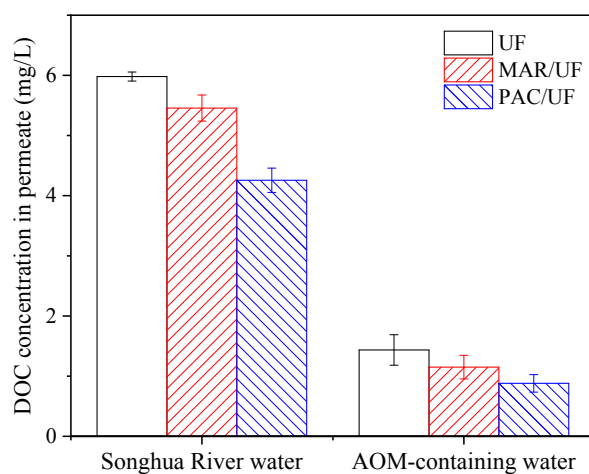


Figure S2. Effects of MAR and PAC addition on DOC concentration in membrane permeate

References

1. S. L. Goertzen, K. D. Thériault, A. M. Oickle, A. C. Tarasuk and H. A. Andreas, Standardization of the Boehm titration. Part I. CO₂ expulsion and endpoint determination, *Carbon*, 2010, **48**, 1252-1261.
2. A. M. Oickle, S. L. Goertzen, K. R. Hopper, Y. O. Abdalla and H. A. Andreas, Standardization of the Boehm titration: Part II. Method of agitation, effect of filtering and dilute titrant, *Carbon*, 2010, **48**, 3313-3322.
3. L. Li, P. A. Quinlivan and D. R. U. Knappe, Effects of activated carbon surface chemistry and pore structure on the adsorption of organic contaminants from aqueous solution, *Carbon*, 2002, **40**, 2085-2100.
4. L. C. Koh, W.-Y. Ahn and M. M. Clark, Selective adsorption of natural organic foulants by polysulfone colloids: Effect on ultrafiltration fouling, *J. Membr. Sci.*, 2006, **281**, 472-479.

5. Z. Zhou, G. Huang, Y. Xiong, M. Zhou, S. Zhang, C. Y. Tang and F. Meng, Unveiling the Susceptibility of Functional Groups of Poly(ether sulfone)/Polyvinylpyrrolidone Membranes to NaOCl: A Two-Dimensional Correlation Spectroscopic Study, *Environ. Sci. Technol.*, 2017, **51**, 14342-14351.
6. M. Forouzesh, A. Ebadi, A. Aghaeinejad-Meybodi and R. Khoshbouy, Transformation of persulfate to free sulfate radical over granular activated carbon: Effect of acidic oxygen functional groups, *Chem. Eng. J.*, 2019, **374**, 965-974.
7. E. K. Putra, R. Pranowo, J. Sunarso, N. Indraswati and S. Ismadji, Performance of activated carbon and bentonite for adsorption of amoxicillin from wastewater: Mechanisms, isotherms and kinetics, *Water Res.*, 2009, **43**, 2419-2430.