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Electronic Supplementary Material

Quantifying functional groups in the active layer of polyamide nanofiltration membranes via the dye adsorption method

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1 R-NH_2 and R-COOH densities

The adsorption behaviors of Orange II and Toluidine Blue O on membrane surfaces are governed by the pK_a values of R-NH_2 and R-COOH on the membrane surfaces. When the pH value of the solution is lower than the pK_a value of R-NH_2 (4–5) on the membrane surface, the protonated amine group (R-NH_3^+) electrostatically adsorbs negatively charged Orange II [1–3]. In contrast, R-NH_3^+ deprotonates and Orange II desorbs from the membrane surface when the solution pH is higher than the pK_a value of R-NH_2 on the membrane surface. Similarly, when the pH value of the solution is higher than the pK_a value of R-COOH (6–9) on the membrane surface, the deprotonated carboxyl group (R-COO^-) electrostatically adsorbs Toluidine Blue O [4]. In contrast, R-COO^- protonates and Toluidine Blue O desorbs from the membrane surface when the pH value of the solution is lower than the pK_a value of R-COOH on the membrane surface. The measured dye adsorption/desorption masses of the membrane surface are supposed to be equivalent to the mass of R-NH_3^+ and the mass of R-COO^-, respectively.

2 Detection and quantification limits

The limit of detection (LOD, μmol·L^{-1}) and the limit of quantification (LOQ, μmol·L^{-1}) were calculated based on Eqs. (S1) and (S2), respectively, which are as follows [5]:

$$D = \frac{VC}{S} \tag{S1}$$

$$\mathrm{LOQ} = \frac{10\delta}{k} \tag{S2}$$

where δ was standard deviation (SD) of the blank solution without Orange II and Toluidine Blue O, and k was the slope of the standard curve of Orange II and Toluidine Blue O. δ was obtained by measuring the absorbance values of the blank solution at 485 and 630 nm using a UV–Vis spectrophotometer, with the measurement repeated six times.

3 UV–Vis spectra and concentration standard curves of Orange II and Toluidine Blue O solution at pH values of 3 and 11

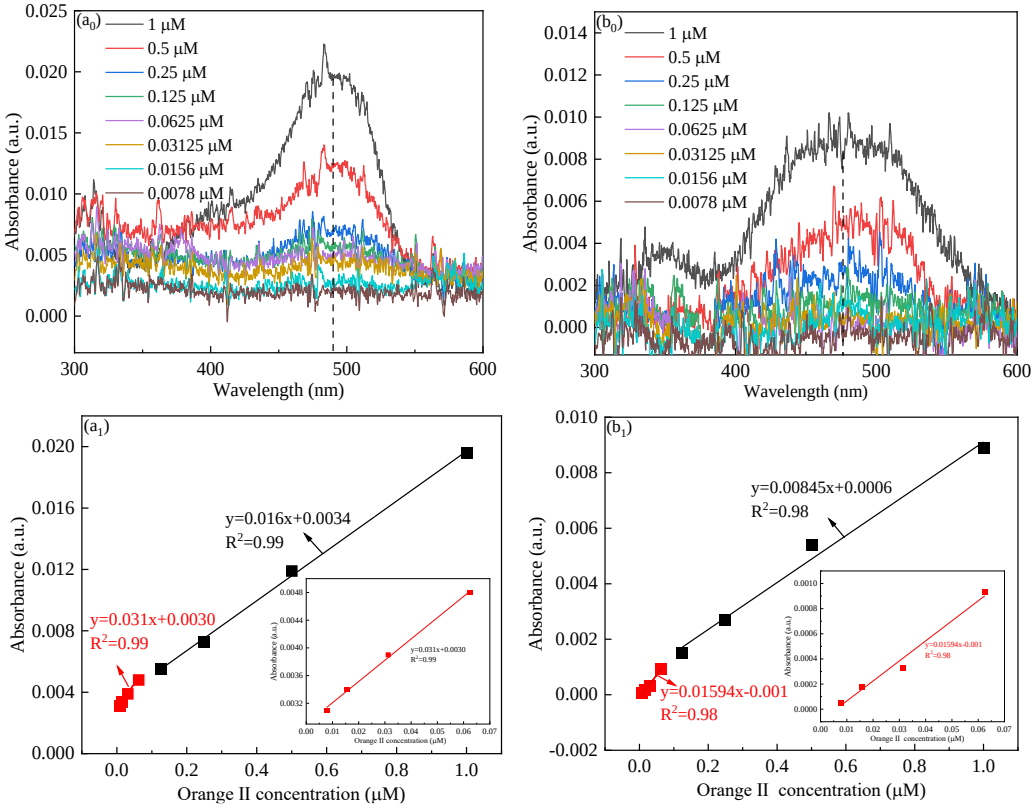

Fig. S1 UV–Vis spectra (upper) and concentration standard curves (lower) of Orange II solutions at **(a)** pH = 3 and **(b)** pH = 11.

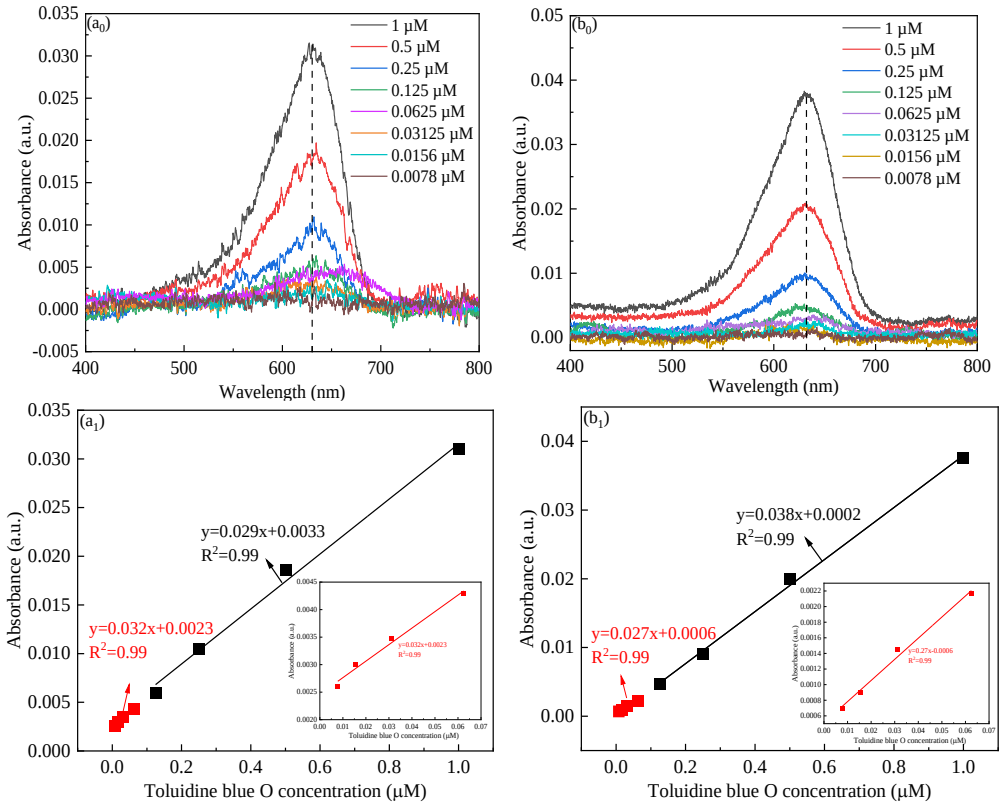

Fig. S2 UV–Vis spectra (upper) and concentration standard curves (lower) of Toluidine Blue O solutions at **(a)** pH = 3 and **(b)** pH = 11.

As determined using a UV–Vis spectrophotometer, values of the maximum absorption wavelength (λ_{max}) for Orange II and Toluidine Blue O were 485 and 630 nm, respectively (Figs. S1 and S2), consistent with those in previous studies [6–7]. A strong linear correlation ($R^2 > 0.98$) was observed between the concentrations of Orange II and Toluidine Blue O and their absorbance within the concentration range of 0.0078–1 μmol·L^{-1} (Figs. S1 and S2). Thus, the concentrations of Orange II and Toluidine Blue O can be quantified using these standard curves. The densities of R-NH_3^+ and R-COO^- could be determined through quantifying the concentrations of bound Orange II and Toluidine Blue O.

4 R-COOH density on the six membranes surfaces measured via the dye desorption method with and without NaCl

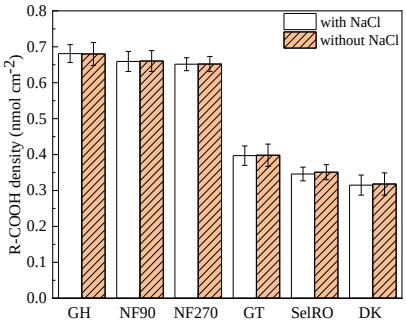

Fig. S3 Densities of R-COOH on surfaces of six membranes measured using the dye desorption method with and without NaCl.

5 The stability of DK, SelRO, GT, NF270, NF90, and GH membranes in solutions with pH values of 3 and 11

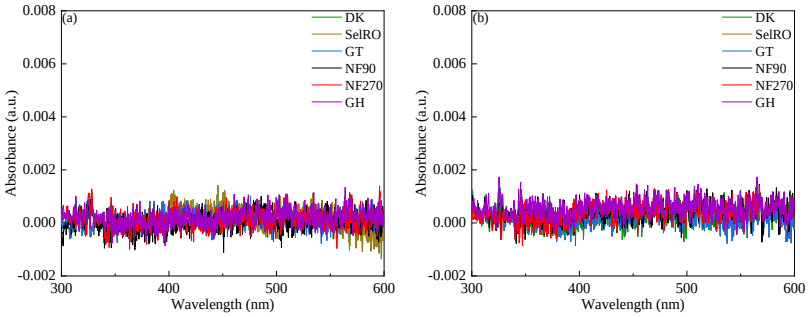

Fig. S4 UV–Vis spectra of untreated DK, SelRO, GT, NF270, NF90, and GH membranes after immersion for 24 h in solutions with pH values of **(a)** 3 and **(b)** 11.

6 Analyses on variance of densities of R-NH_2 and R-COOH measured at 12, 24, and 36 h

Table S1 Analysis results of variance results (*$p < 0.05$)

Functional group	Time/h	p
R-NH_2	12	0.998
	24	
	36	
R-COOH	12	0.927
	24	
	36	

7 Comparison of the dye adsorption method with the dye desorption method

Table S2 Comparison of the dye adsorption method with the dye desorption method for density measurement of R-NH_2 and R-COOH

Functional group	Dye method	SD/(nmol·cm^{-2})	RSD/%	LOD/(μmol·L^{-1})	LOQ/(μmol·L^{-1})
R-NH_2	Adsorption	0.011–0.024	2.25–5.40	0.0087	0.029
	Desorption	0.013–0.032	4.60–7.10	0.0188	0.062
R-COOH	Adsorption	0.007–0.022	2.56–3.58	0.0084	0.028
	Desorption	0.013–0.035	3.17–5.38	0.0110	0.037

Notes: SD, standard deviation; RSD, relative standard deviation; LOD, limit of detection; LOQ, limit of quantification.

References

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