
Supplementary Information

Aminated polystyrene-polymaleic(anhydride) hollow microspheres membrane for fast and efficient dyes and oils filtration from water

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1. Adsorption Isotherm

The experimental details are as follows: 5 mg of PSMM-NH_2 is added into 50 mL of dye solution of different concentrations (30-150 mg·L^{-1}) at pH 3, and the mixture is shaken (200 rpm) at 25°C and 50°C for 12 hours, ensuring the adsorption reaches equilibrium.

Langmuir and Freundlich are applied to describe the equilibrium adsorption performance of AR on the PSMM-NH_2 microspheres. The Langmuir isotherm is based on the assumptions of monolayer and uniform adsorption process, and limited adsorption sites. Freundlich model is used to describe the adsorption interaction on a heterogeneous surface.[1] Langmuir and Freundlich isotherms are expressed as Formula S 1 and S2 respectively:

$$\frac{c_e}{q_e} = \frac{1}{bq_m} + \frac{c_e}{q_m} \quad \text{(S1)}$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln c_e \quad \text{(S2)}$$

where c_e (mg·L^{-1}) represents the equilibrium concentration of AR in the solution, q_e and q_m (mg·g^{-1}) are the equilibrium and monolayer concentration of AR on PSMM-NH_2 microspheres, respectively. b (L·mg^{-1}) represents the Langmuir affinity parameter. K_F (L·mg^{-1}) and n are the Freundlich isotherm constant and the adsorption intensity, respectively.

Moreover, Langmuir isotherm can be expressed by a dimensionless equilibrium parameter R_L:[2]

$$R_L = \frac{1}{1 + bc_o} \quad \text{(S3)}$$

where c_o is the initial concentration of AR in the solution, and the R_L is the type of isotherm, unfavorable (R_L>1), linear (R_L=1), favorable (0<R_L<1) or irreversible (R_L=0).

Fig. S5a shows the relationship between equilibrium concentration and adsorption

capacity. The linear fittings of isotherms according to experimental data are exhibited in Fig. S5b and c, respectively. Obviously, the fits of AR adsorption on PSMM-NH_2 microspheres at different temperature is more in line with the Langmuir isotherm. The corresponding isotherms parameters are summarized in Table S1, and the determination coefficients R^2 of the Langmuir isotherm of PSMM-NH_2 exceed 0.99, which is significantly greater than the Freundlich isotherm, indicating that Langmuir isotherm model can description of the adsorption process well and the adsorption of AR to PSMM-NH_2 microspheres is monolayer in nature and the adsorption sites is homogeneous distribution. In addition, the dimensionless equilibrium parameters R_L are between 0 and 1, demonstrating the adsorption is favorable.

2. Adsorption Kinetic study

In this paper, two widely used adsorption kinetic models, pseudo-first-order and pseudo-second-order are used to study the adsorption of AR to PSMM-NH_2 microspheres. Their linear expressions correspond to Equations S4 and Equations S5 respectively.[3]

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad \text{(S4)}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{(S5)}$$

where q_t (mg·g^{-1}) is the adsorption capacity at time t (min), k_1 and k_2 (g·mg^{-1}·min^{-1}) are the rate constant of the pseudo-first-order and pseudo-second-order models, respectively.

The influence of time on adsorption amount of AR to PSMM-NH_2 microspheres is exhibited in Fig. S5d. PSMM-NH_2 has extremely fast adsorption rate and the adsorption reaches equilibrium within 10 minutes. Linear fittings of the pseudo-first-order and pseudo-second-order kinetic of AR adsorption to PSMM-NH_2 is shown in

Fig. S5e,f respectively, and the kinetic parameters are summarized in Table S2. Obviously, the adsorption of AR to PSMM-NH_2 fits well with the pseudo-second-order kinetic, indicating that the adsorption is controlled by the chemical adsorption mechanism.

3. Supplementary figures

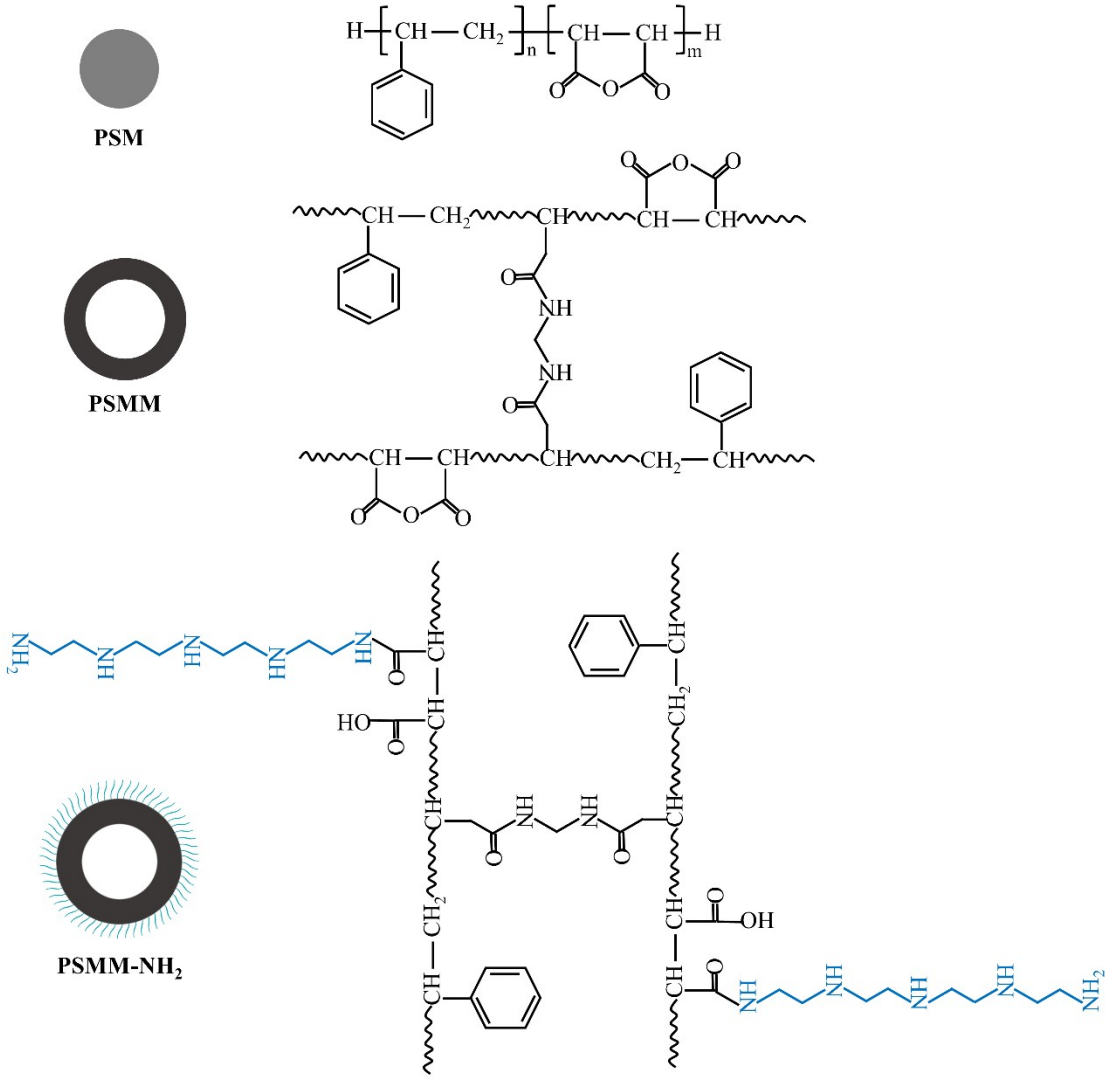

Fig. S1 Chemical structures of PSM, PSMM and PSMM-NH_2

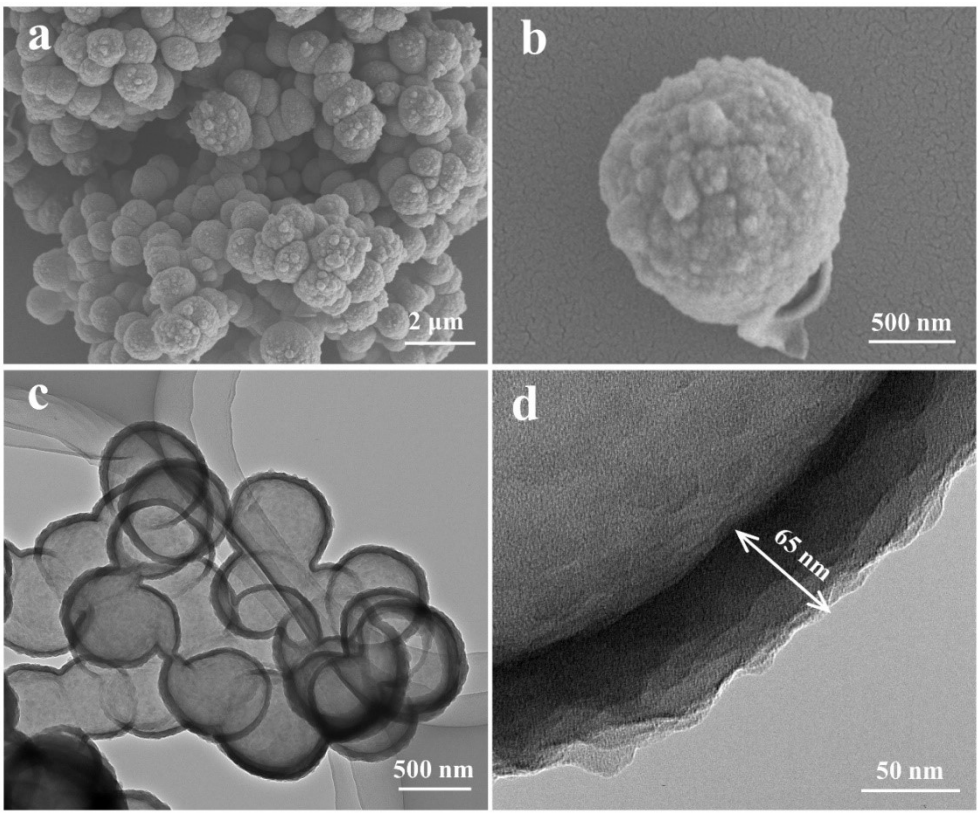

Fig. S2 (a, b) SEM and (c, d) TEM images of PSMM microspheres

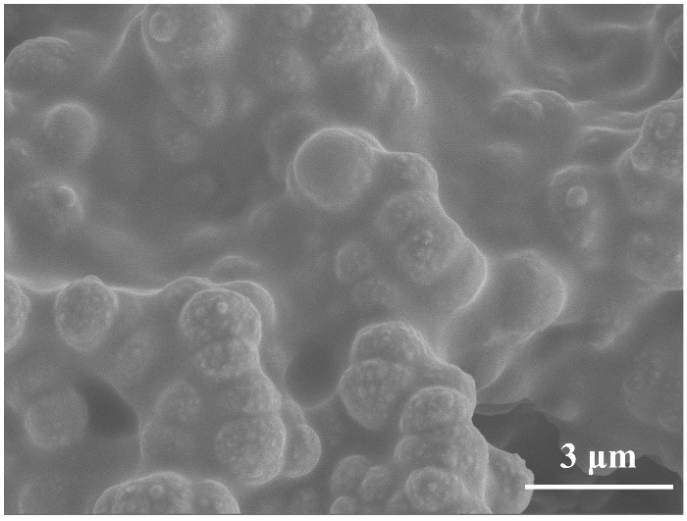

Fig. S3 SEM image of PSMM microspheres grafted with polyethyleneimine

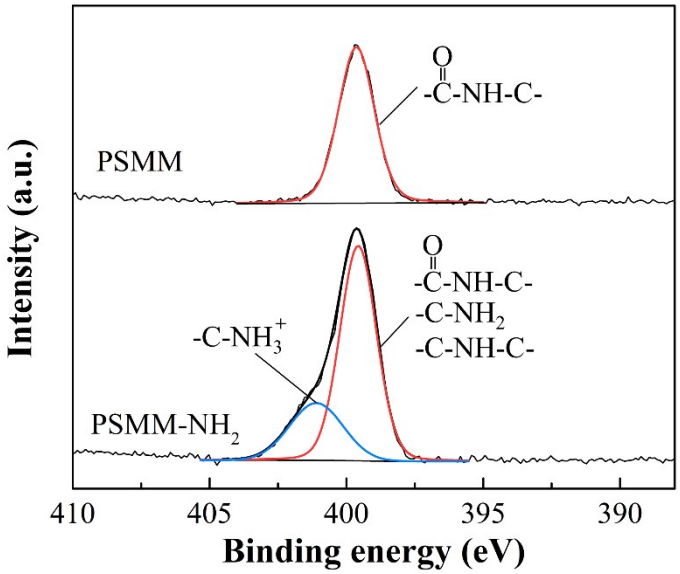

Fig. S4 XPS N1s spectra of PSMM and PSMM-NH_2

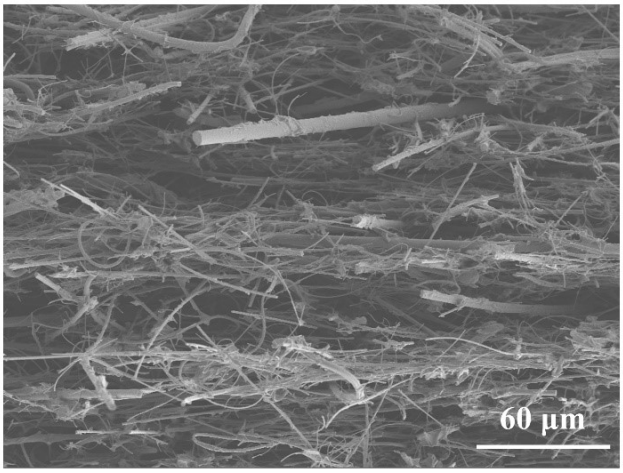

Fig. S5 SEM image of fiberglass membrane

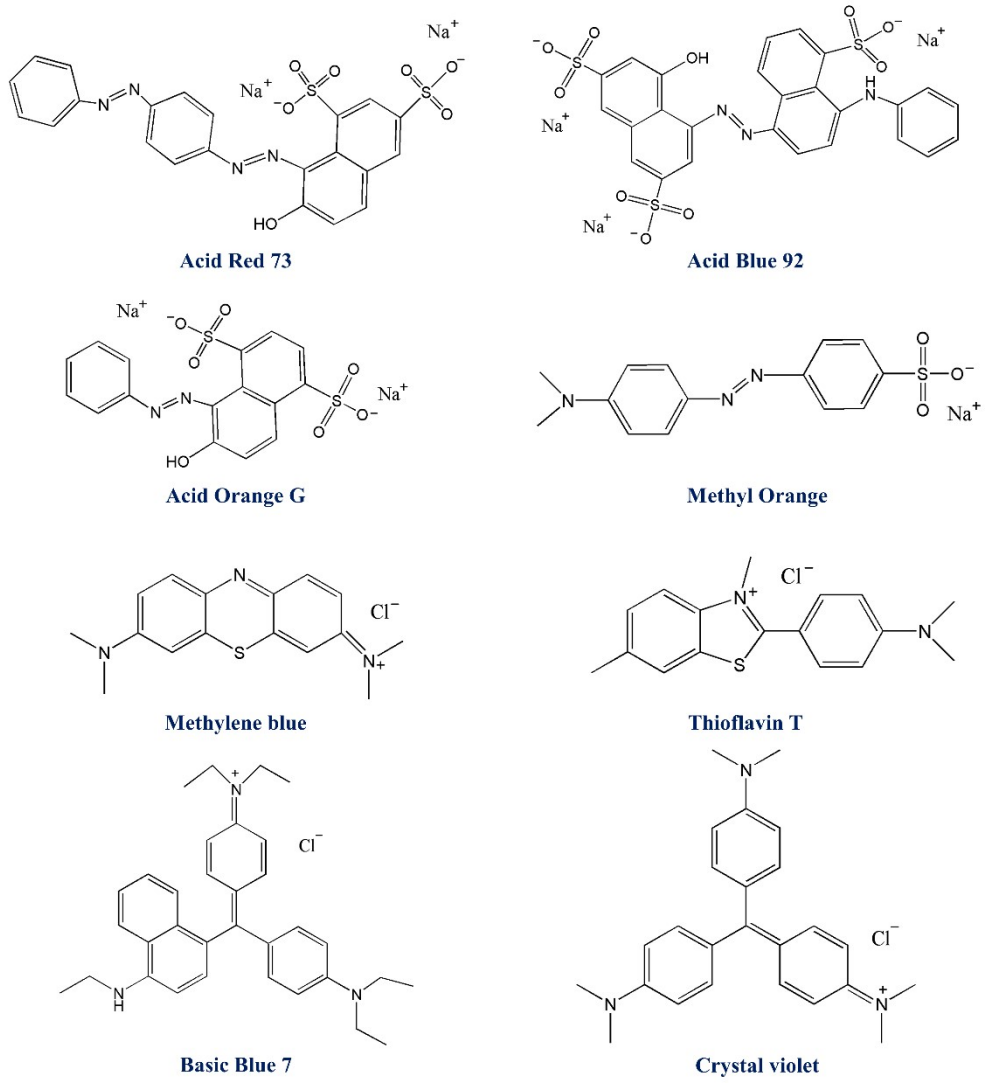

Fig. S6 The molecular structure of dyes used in this paper

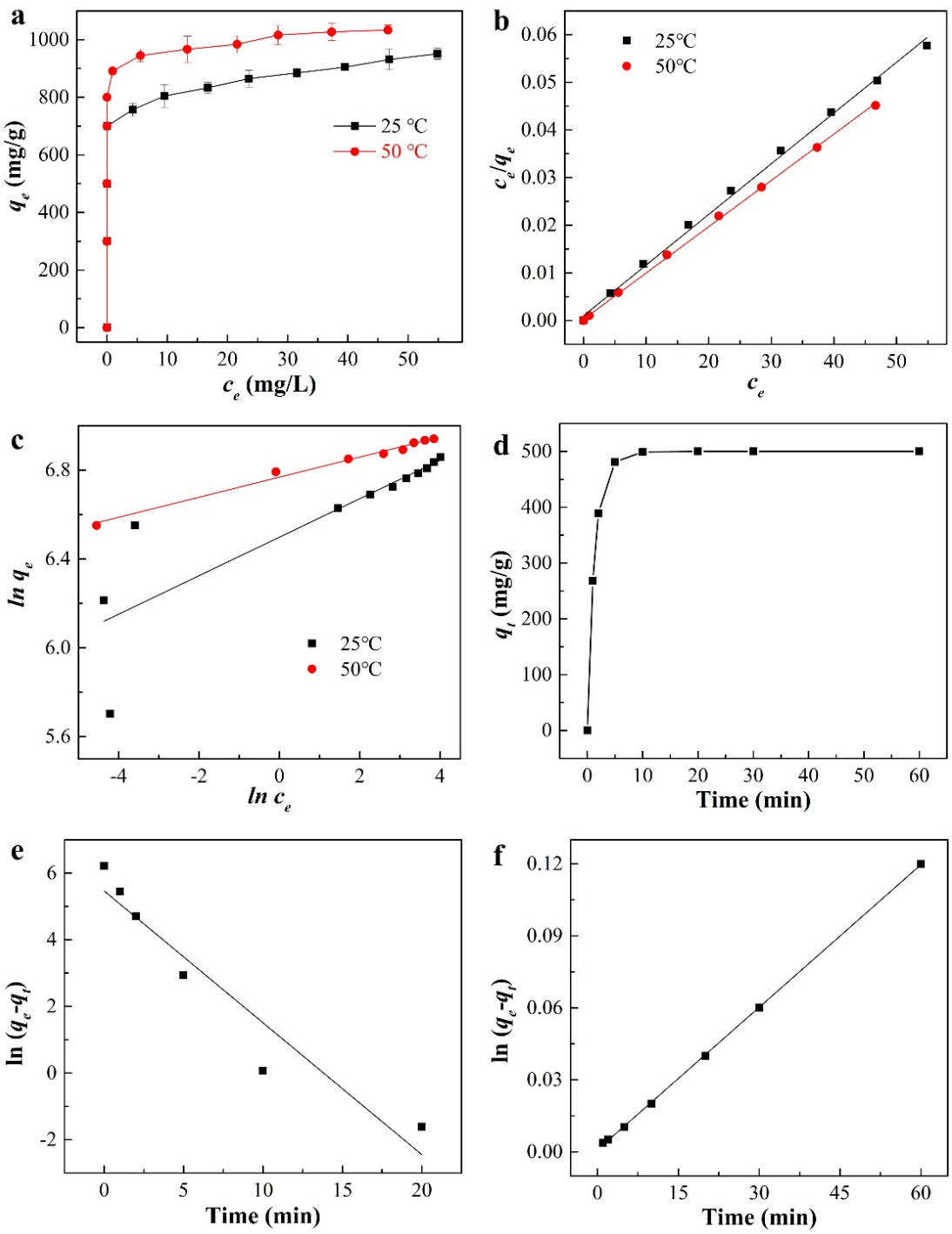

Fig. S7 (a) Equilibrium adsorption experiment of AR on PSMM-NH_2. (b) and (c) are the linear fittings of Langmuir and Freundlich Isotherms respectively. (d) Changes of the adsorption capacity of AR on PSMM-NH_2 with time. (e) Pseudo-first-order model and (f) pseudo-second-order model for AR on PSMM-NH_2.

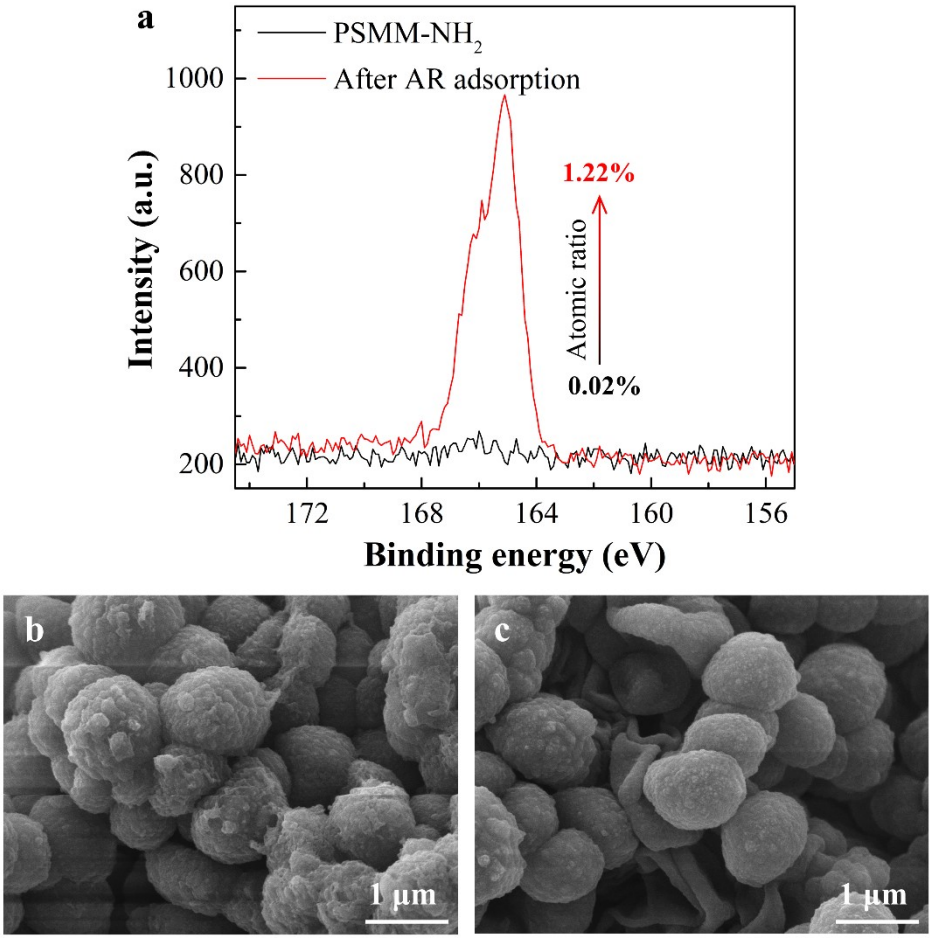

Fig. S8 (a) XPS S_{p2} spectra of PSMM-NH_2 before and after AR adsorption. (b) SEM image of AR adsorbed PSMM-NH_2. (c) SEM image of PSMM-NH2 after five AR adsorption-desorption cycles.

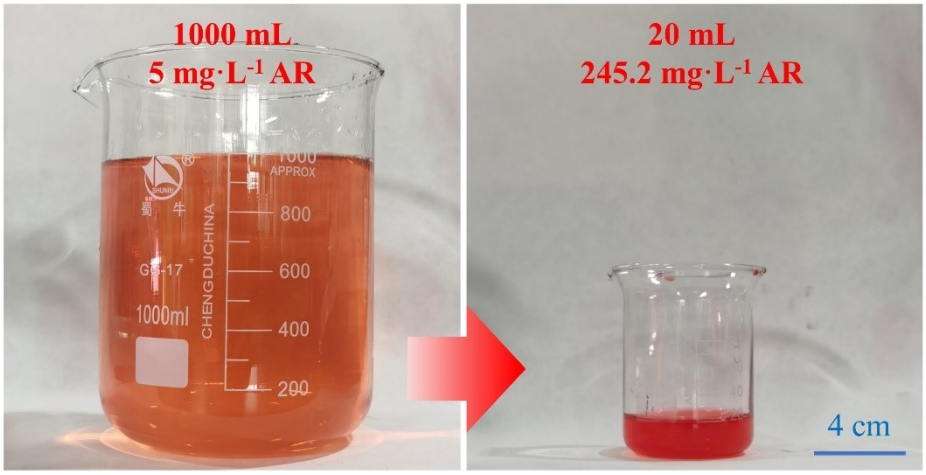

Fig. S9 The adsorption-desorption of PSMM-NH_2 to achieve concentration of AR solution. (Experimental details: 5 mg PSMM-NH_2 is added into 1000 ml AR solution (5 mg·L^{-1}, pH=3). After stirring and adsorbing for 30 min, the solid was collected by pump filtering. The AR adsorbed PSMM-NH_2 was added into 10 ml water (pH=12) and desorbed for 30 minutes. Then the mixture was centrifuged (4000 rpm, 5 min) to collect the solid, and the solid was added into 10 ml pH 12 water to desorbed again. After that, solid and liquid were separated by centrifuging. The two desorbed solutions were mixed to obtain 20 mL of concentrated AR solution.)

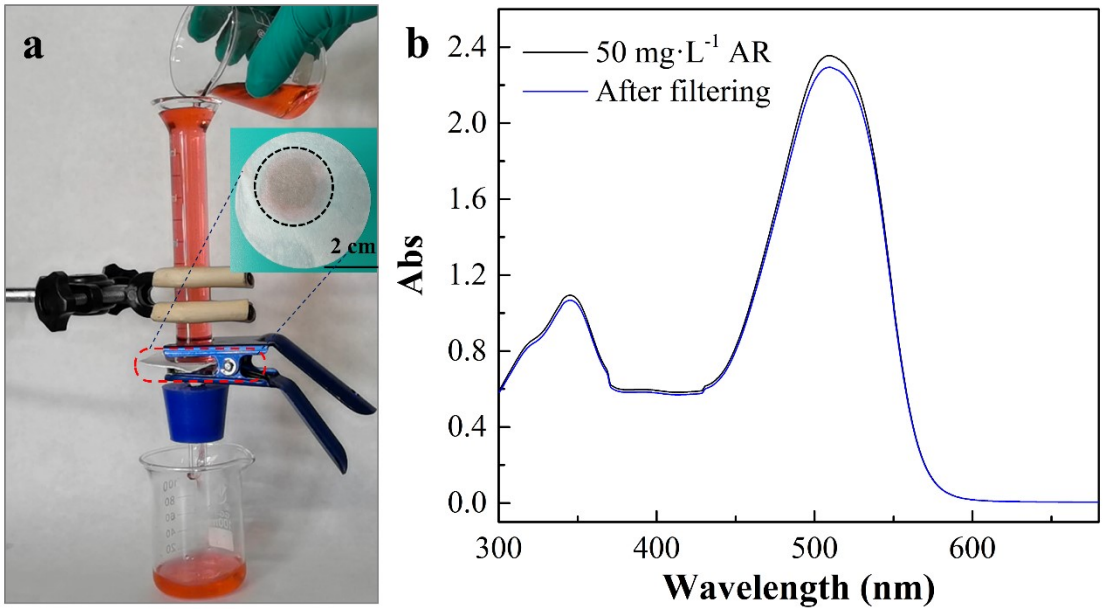

Fig. S10 AR filtration test for fiberglass membrane (pH=3)

Fig. S11 Oil-water separation test of ordinary glass fiber membrane

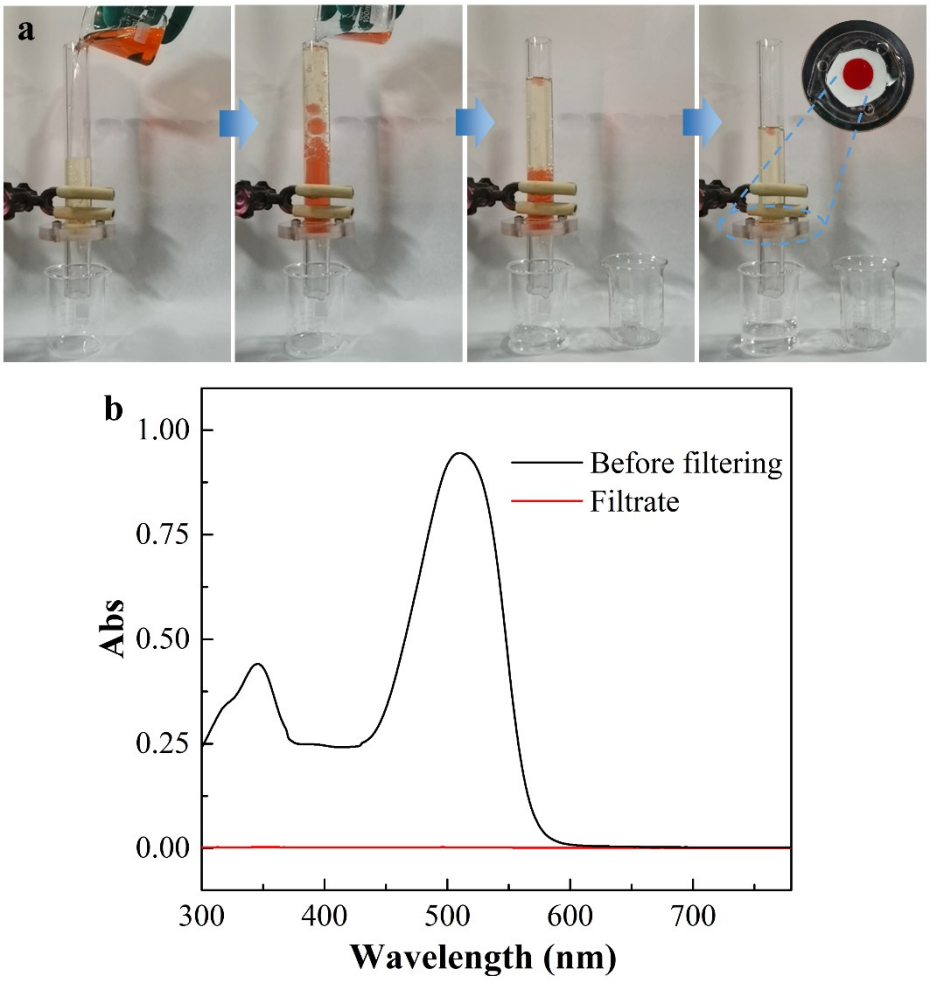

Fig. S12 (a) The dynamic images of separation process of rapeseed oil/AR solution (20 mg·L^{-1}; inset: PSMM-NH_2 membrane after filtration). (b) The UV–vis spectra of AR solution before and after filtration

4. Supplementary tables

Table S1 Isotherm parameters of the AR adsorption on PSMM-NH_2

Temperature	$q_{mx,\ exp}$	Langmuir				Freundlich		
		q_m	b	R_L	R^2	k_F	$1/n$	R^2
25℃	951.1	943.4	1.0836	0.00611-0.0298	0.9973	663.8	0.0867	0.6986
50℃	1033.4	1028.5	4.1532	0.00160-0.00796	0.9994	869.7	0.0452	0.9864

Table S2 Kinetic parameters of the AR adsorption on PSMM-NH_2

$q_{e,\ exp}$	Pseudo-first-order			Pseudo-second-order		
	q_e	k_1	R^2	q_e	k_2	R^2
500.0	236.7	0.3956	0.9037	505.1	4.76×10^{-3}	0.9998

5. Supplementary references

1. R. Xu, G. Zhou, Y. Tang, L. Chu, C. Liu, Z. Zeng and S. Luo, *Chem. Eng. J.*, 2015, **275**, 179.
2. S. Parvin, B. K. Biswas, M. A. Rahman, M. H. Rahman, M. S. Anik and M. R. Uddin, *Chemosphere*, 2019, **236**, 124326.
3. D. Li, Q. Li, N. Bai, H. Dong and D. Mao, *ACS Sustain. Chem. Eng.*, 2017, **5**, 5598.