

Fig. S1 Appearance of PVDF membrane and PVDF composite membranes.

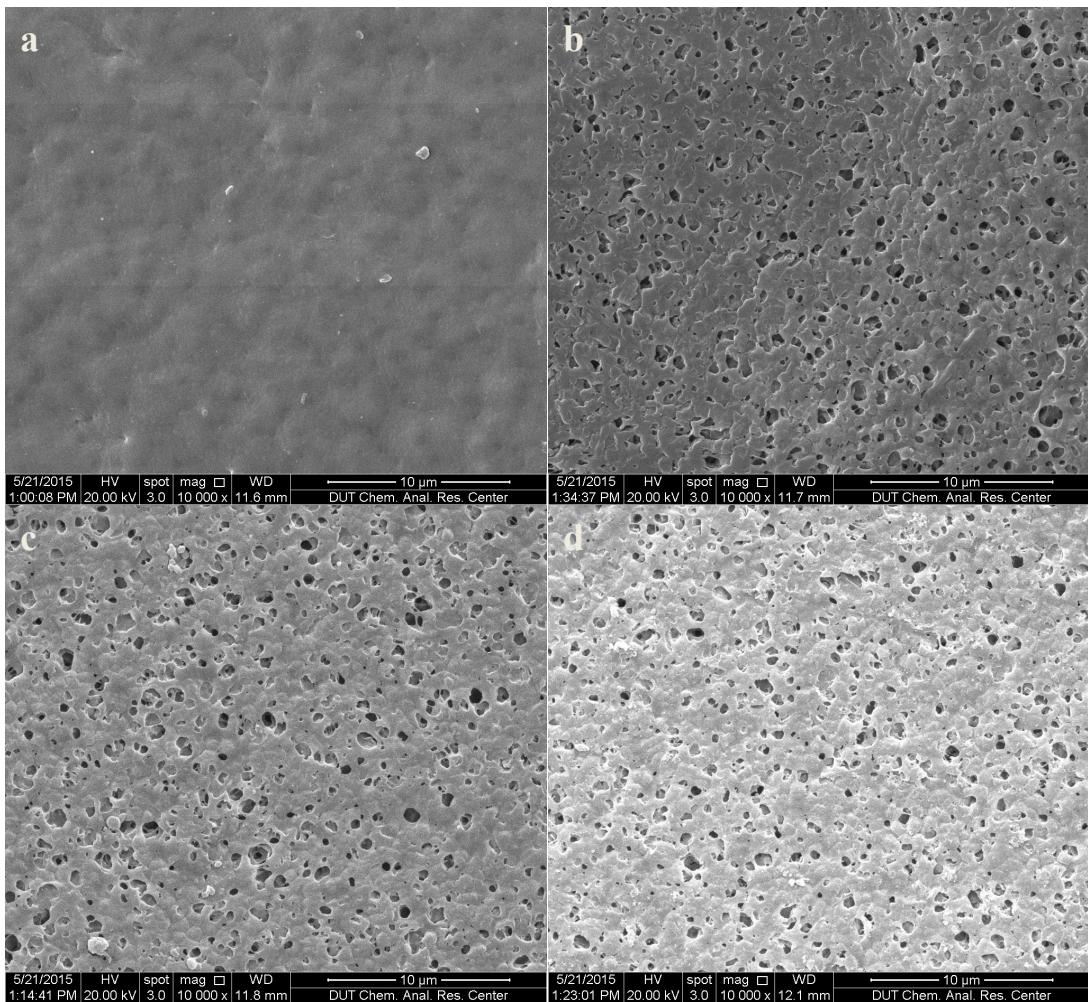


Figure S2 Bottom surface SEM images of (a) PVDF, (b) PVDF/GO, (c) PVDF/RGO and (d) PVDF/MnO<sub>2</sub>.

**Table S1** Porous structure parameters of PVDF and PVDF composite membranes.

Membrane	BET surface area (m <sup>2</sup> ·g <sup>-1</sup> )	BJH desorption average pore diameter (nm)	BJH desorption Cumulative volume of pores (cc/g)
PVDF	2.82 ± 0.18	0.06 ± 0.01	0.004 ± 0.001
PVDF/GO	13.85 ± 0.94	1.38 ± 0.08	0.028 ± 0.001
PVDF/RGO	15.55 ± 0.68	1.39 ± 0.08	0.034 ± 0.002
PVDF/MnO <sub>2</sub>	14.21 ± 0.58	1.37 ± 0.09	0.032 ± 0.002

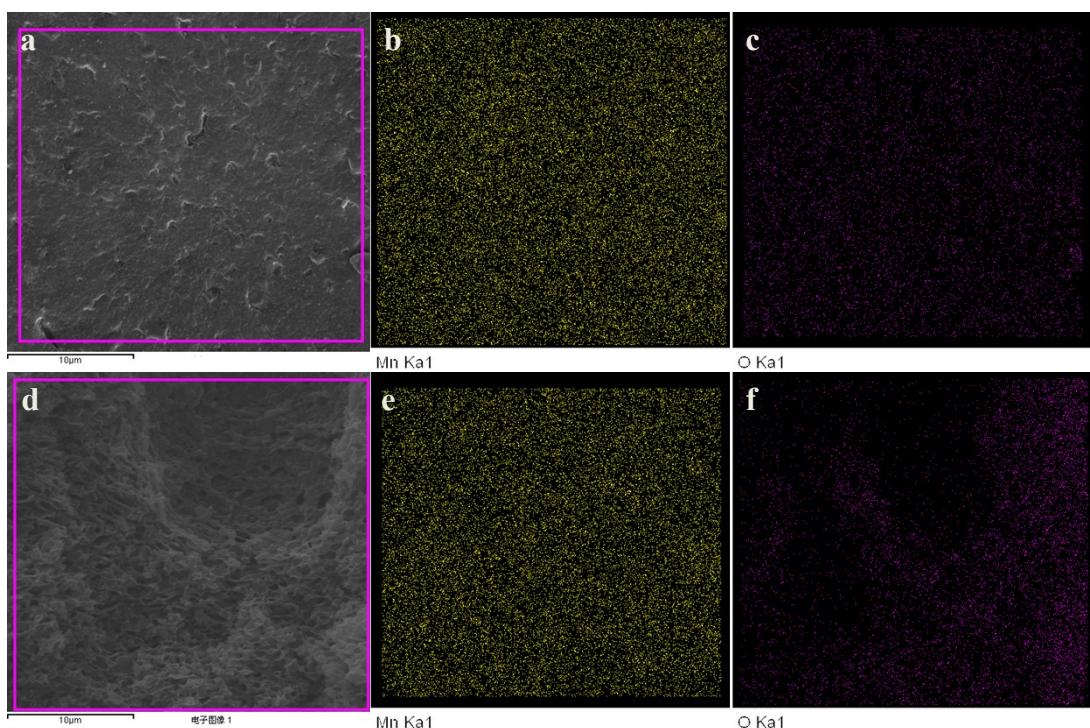


Figure S3 Upper surface of PVDF/MnO<sub>2</sub>: (a) SEM image, (b) manganese mapping and (c) oxygen mapping and cross-section of PVDF/MnO<sub>2</sub>: (d) SEM image, (e) manganese mapping and (f) oxygen mapping.

Table S2 Elemental analysis of PVDF membrane and PVDF composite membranes.

Membrane	Location	Atomic percent (%)			
		C	F	O	Mn
PVDF		53.06	46.94		
PVDF/GO-4		52.64	45.35	2.01	
PVDF/RGO-4		53.52	44.99	1.49	
PVDF/MnO <sub>2</sub> -1	upper surface	48.80	49.09	1.64	0.47
PVDF/MnO <sub>2</sub> -2		49.33	47.38	2.40	0.89
PVDF/MnO <sub>2</sub> -4		50.09	44.31	3.96	1.64
PVDF/MnO <sub>2</sub> -4	cross-section	50.53	44.65	3.75	1.07

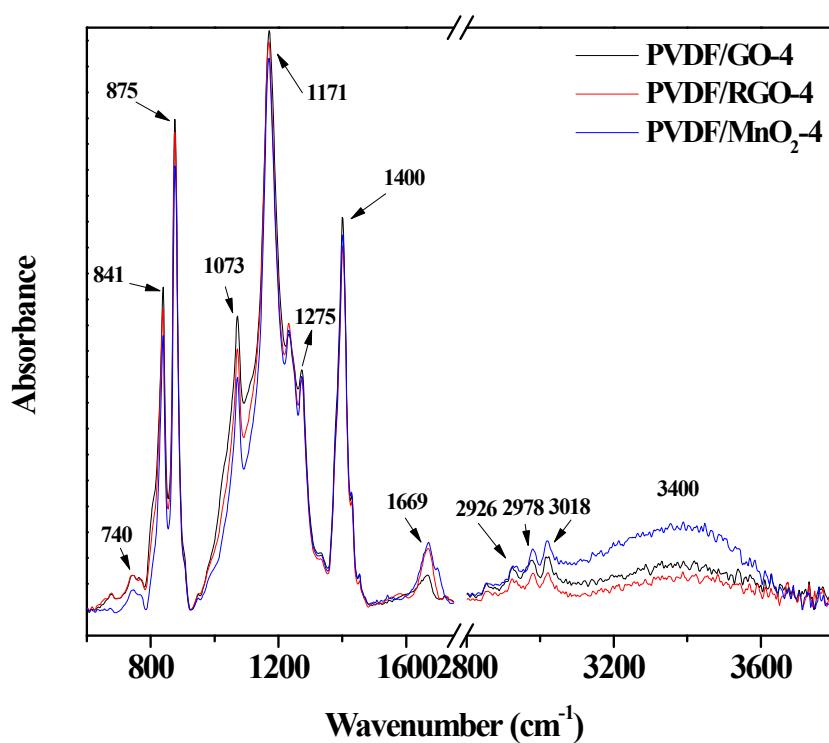


Figure S4 ATR-FTIR spectra of PVDF composite membranes.

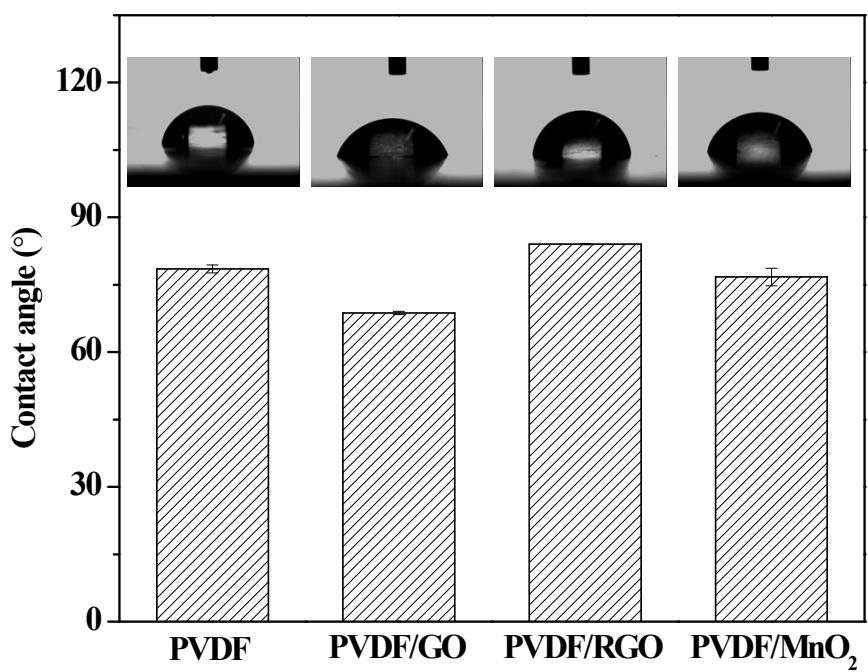


Figure S5 Contact angle comparison of PVDF, PVDF/GO, PVDF/RGO and PVDF/MnO<sub>2</sub> membranes.

**Table S3** Value of thermodynamic parameters for adsorption of Ni(II) on PVDF/MnO<sub>2</sub>-4 membrane.

Thermodynamic parameters	Temperature (K)		
	298	308	318
$K_0$	22.88	29.78	34.80
$\Delta G^\circ$ (kJ·mol <sup>-1</sup> )	-7.76	-8.69	-9.38
$\Delta H^\circ$ (J·mol <sup>-1</sup> ·L <sup>-1</sup> )	81.48	81.48	81.48
$\Delta S^\circ$ (kJ·mol <sup>-1</sup> )	16.49	16.49	16.49

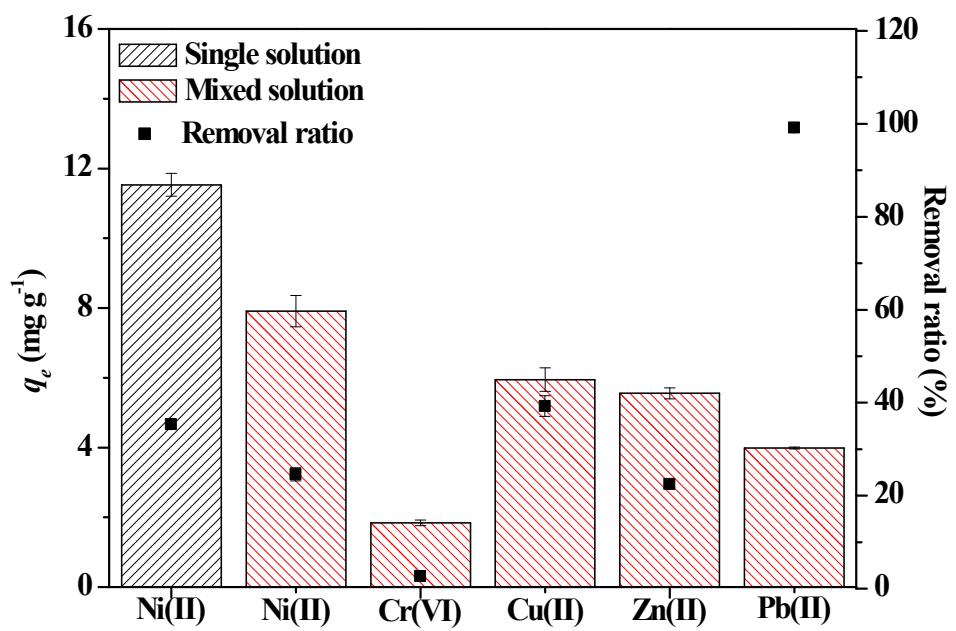


Figure S6 Adsorption of various heavy metal ions by PVDF/MnO<sub>2</sub> composite membrane from a simulated wastewater sample.

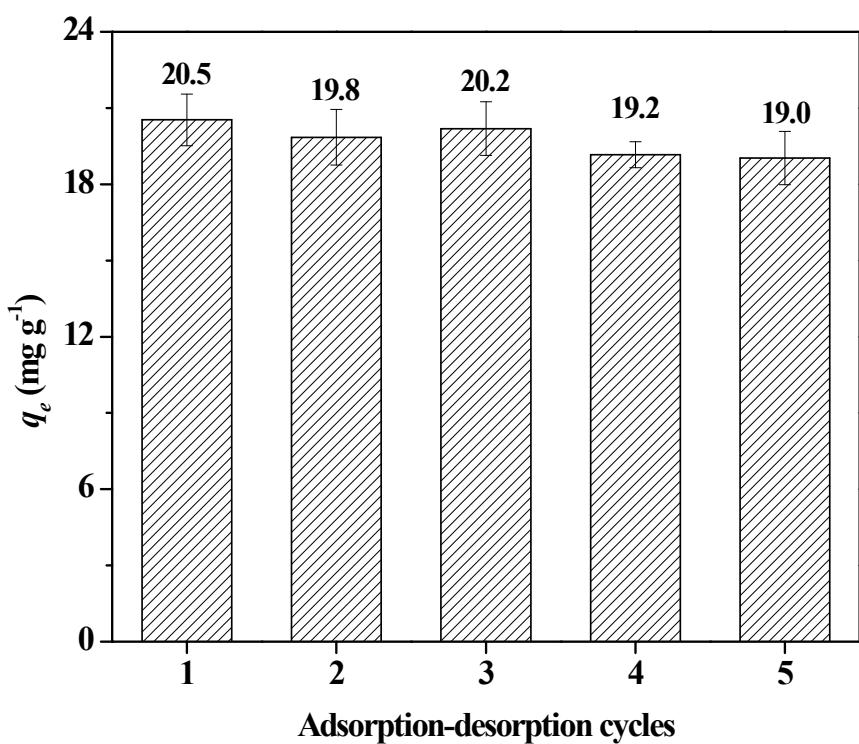


Figure S7 Desorption of Ni(II) from metal loaded PVDF/MnO<sub>2</sub> membrane using 0.1 M HNO<sub>3</sub> solution.

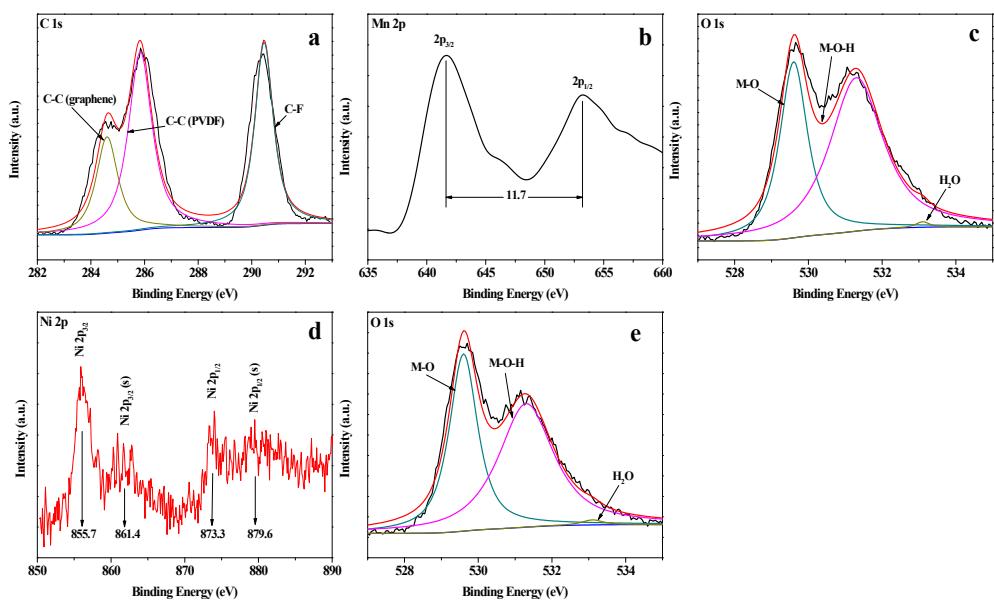


Figure S8 XPS spectra of PVDF/MnO<sub>2</sub> before and after adsorption of Ni(II): (a) C 1s, (b) Mn 2p, (c) O 1s of PVDF/MnO<sub>2</sub> before adsorption, (d) Ni 2p of PVDF/MnO<sub>2</sub> after adsorption and (e) O 1s of PVDF/MnO<sub>2</sub> after adsorption.