Supplementary Information

Cell Membrane Mimetic PVDF Microfiltration Membrane with Enhanced Antifouling and Separation Performance for Oil/Water Mixtures

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Synthesis and characterization of PMEN

The random copolymer PMEN was synthesized by conventional free-radical copolymerization of MPC and NPCEMA, using monomer-starved polymerization technique. The synthetic scheme is shown in **Figure S1.** NPCEMA (1.0 g, 3.4×10^{-3} mol) and MPC (4.0 g, 13.4×10^{-3} mol) were dissolved by ethanol in a 100 mL dropping funnel. The initiator AIBN (0.1 g) was dissolved in 10 mL THF and 2.5 mL of the AIBN solution was added into a 250 mL three-necked flask containing 10 mL absolute ethanol heated to 70 °C. The remaining AIBN solution (7.5 mL) was mixed with the monomer solution and then added dropwise into the flask in 4 h. The

polymerization reaction was performed at 70 °C for 24 h under magnetic stirring and N2 protection. After the reaction, two thirds of the solvent was removed by rotary evaporation, and dialyzed against ethanol first and then phosphate buffer solution (pH 3~4) using a dialysis tube with a molecular weight cutoff (MWCO) of 3 500 Da.

After freeze drying, NMR spectrum of the copolymer PMEN (**Figure S2**) was determined by ^{1}H NMR measurement with a Bruker 400 MHz (AVANCE III, USA). The molar fraction of MPC units in the PMEN polymer was determined to be 89% by ^{1}H NMR spectroscopy, using the signals at 7.55 and 8.22 ppm attributed to protons on benzene skeleton of the NPCEMA units and 3.28 ppm attributed to the $-N^{+}(CH_3)_3$ protons of the MPC units.

The molecular weight of the synthesized PMEN was characterized by a gel permeation chromatograph system (GPC, Dionex Ultimate 3000) with a Shodex RI-101 refractive index detector and a Shodex OHpak SB-803 column (8×300 mm^2). The system was calibrated with narrow molecular-weight poly (ethylene oxide) standards. Aqueous solution of sodium azide (0.02 wt%) was used as the eluent with a flow rate of 1.0 mL·min^{-1} at 40 °C. The PMEN molecular weight (M_w) was 17785 g·mol^{-1} with a of PDI of 2.16.

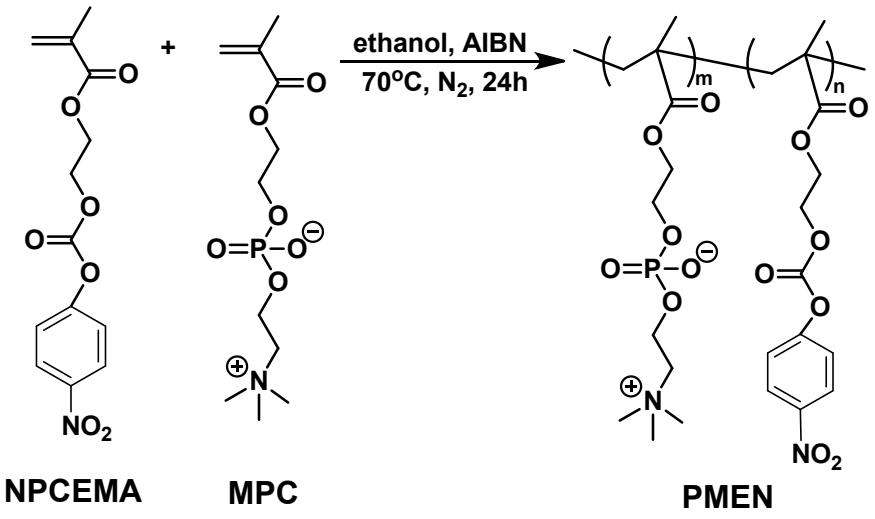

Figure S1. Synthesis route of the random copolymer PMEN.

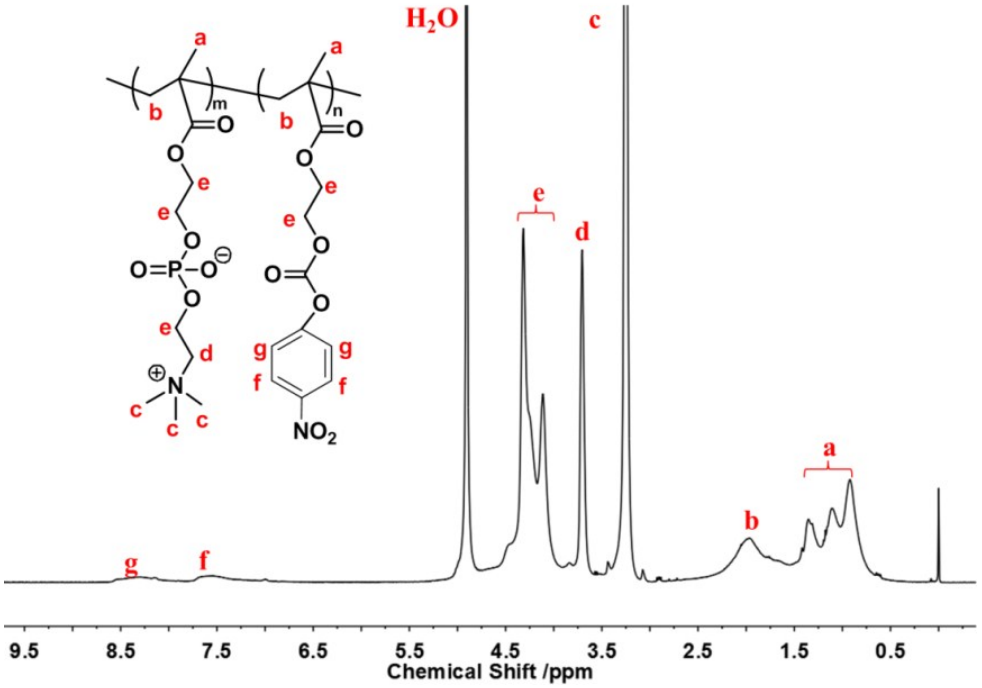

Figure S2. The ^{1}H NMR spectrum of copolymer PMEN in D_2O.

Membrane characterization

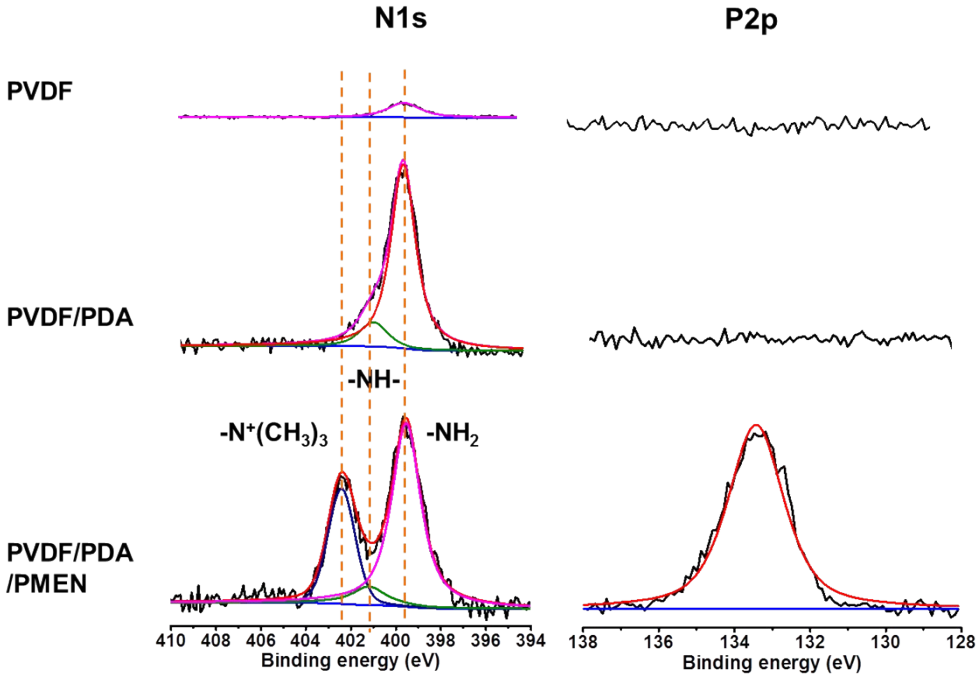

Figure S3. High resolution N1s and P2p XPS spectra of commercial PVDF, PVDF/PDA and PVDF/PDA/PMEN membranes.

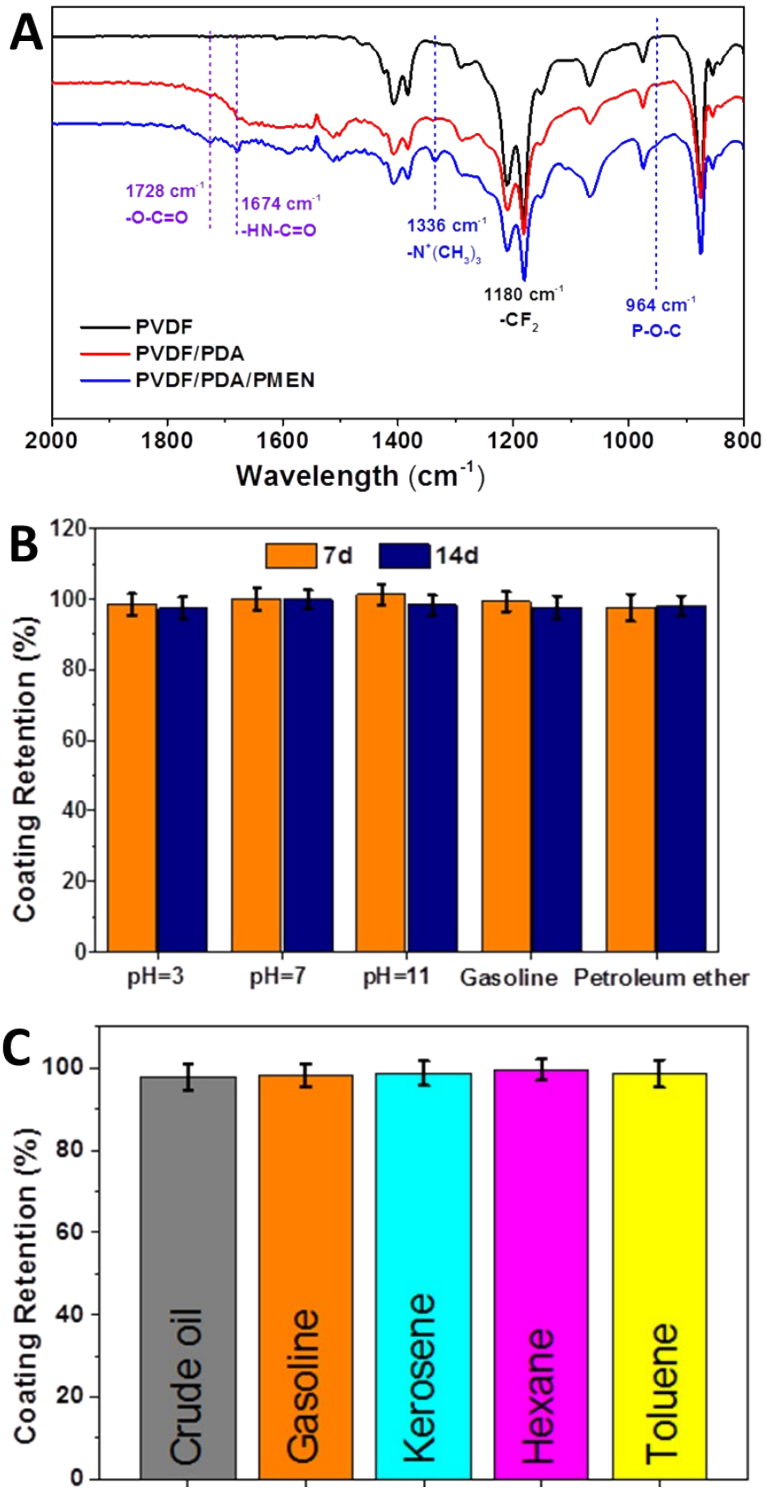

Figure S4. (A) ATR-IR spectra of PVDF, PVDF/PDA, and PVDF/PDA/PMEN membranes. (B) Coating retention of PVDF/PDA/PMEN membrane after immersed in aqueous solutions, gasoline and petroleum ether for 7 and 14 days. (C) Coating retention of PVDF/PDA/PMEN membrane after immersed in oil/water emulsions for 7 days.

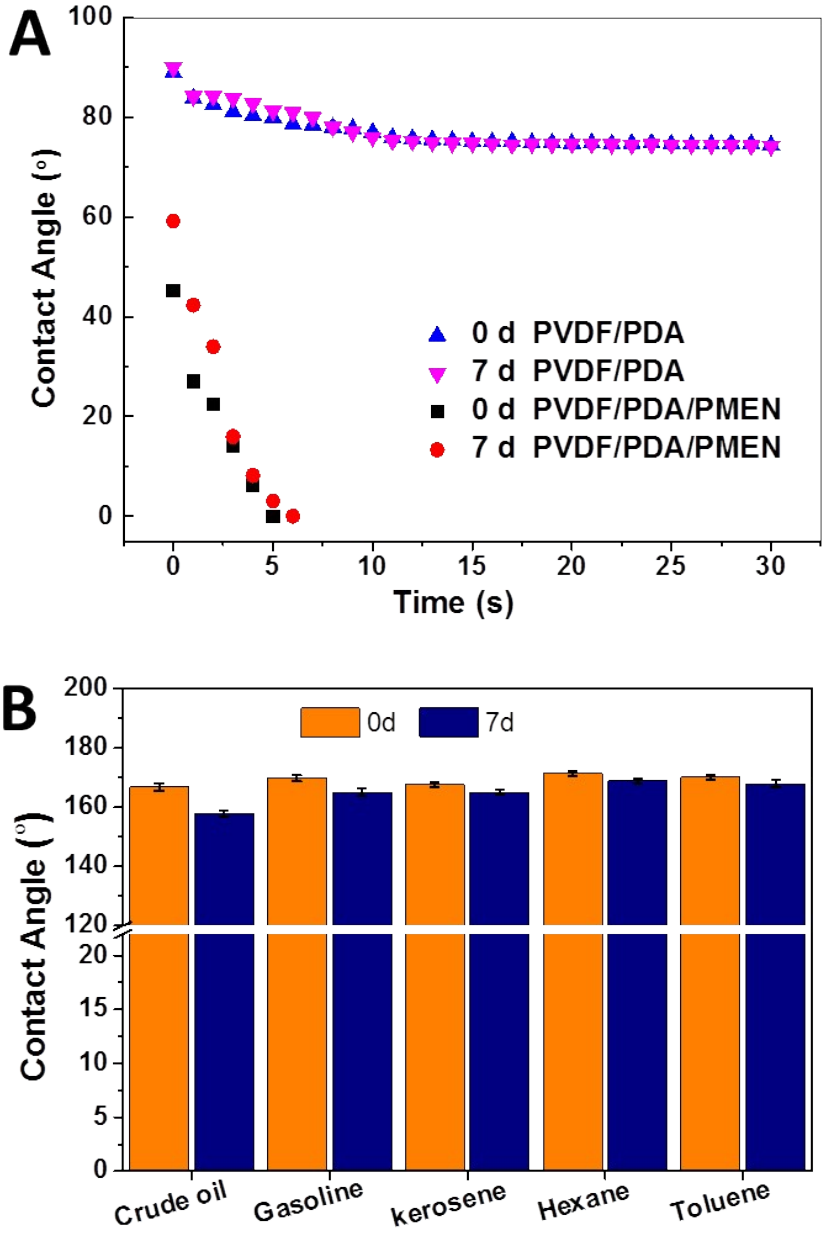

Figure S5. (A) Water contact angle change with time of PVDF/PDA and PVDF/PDA/PMEN surfaces before and after immersed in gasoline/water emulsion for 7-days. (B) Underwater oil contact angles of PVDF/PDA/PMEN surface before (0d) and after treated in the corresponding oil/water emulsion for 7-days.

Oil-in-water emulsion separation

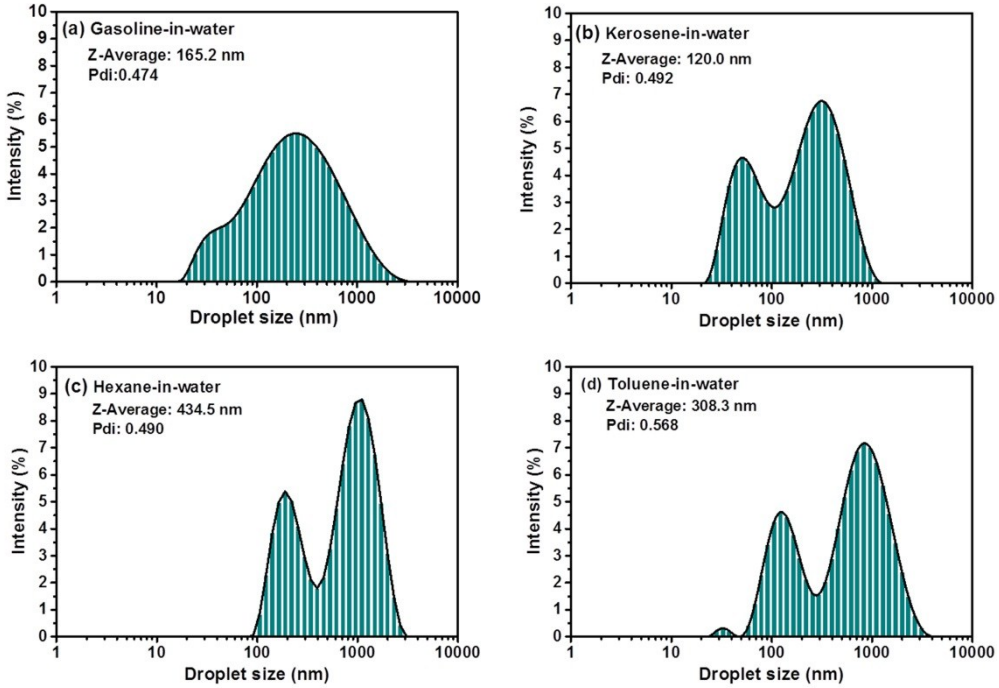

Figure S6. Size distribution of oil-in-water (1:99, v/v) emulsions stabilized by 0.25% SPAN 80 measured by DLS analysis. (a) gasoline–in-water emulsion, (b) kerosene-in-water emulsion, (c) n-hexane-in-water, (d) toluene-in-water emulsion.

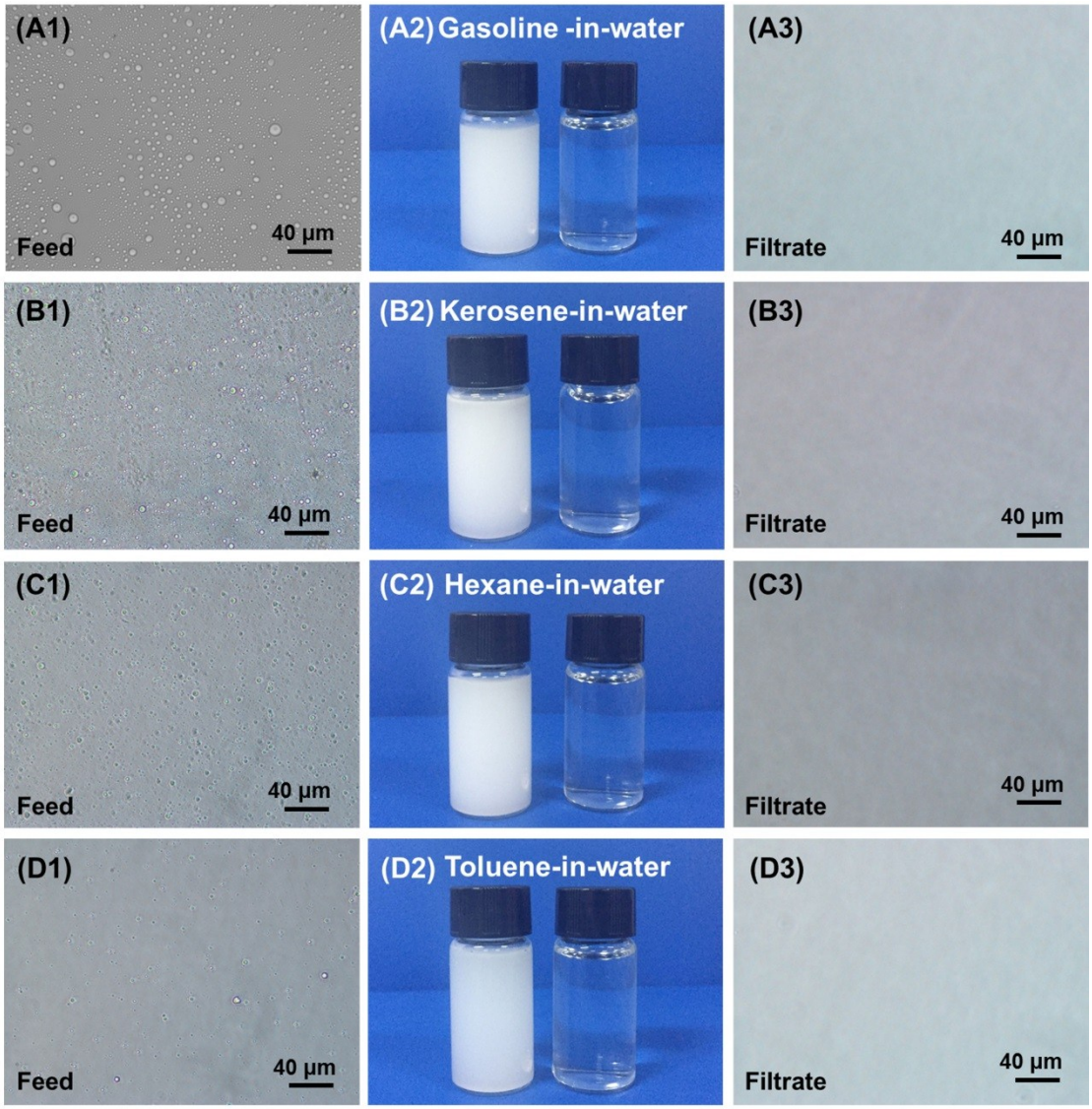

Figure S7. Photographs and microscopic images of different oil-in-water (1:99, v/v) emulsions before and after the filtration separation by PVDF/PDA/PMEN membrane. (A) Gasoline-in-water emulsion, (B) kerosene-in-water emulsion, (C) n-hexane-in-water emulsion, (D) toluene-in-water emulsion. After the separation, all the filtrates become transparent and no oil droplets can be observed by microscope.

Bacterial adhesion

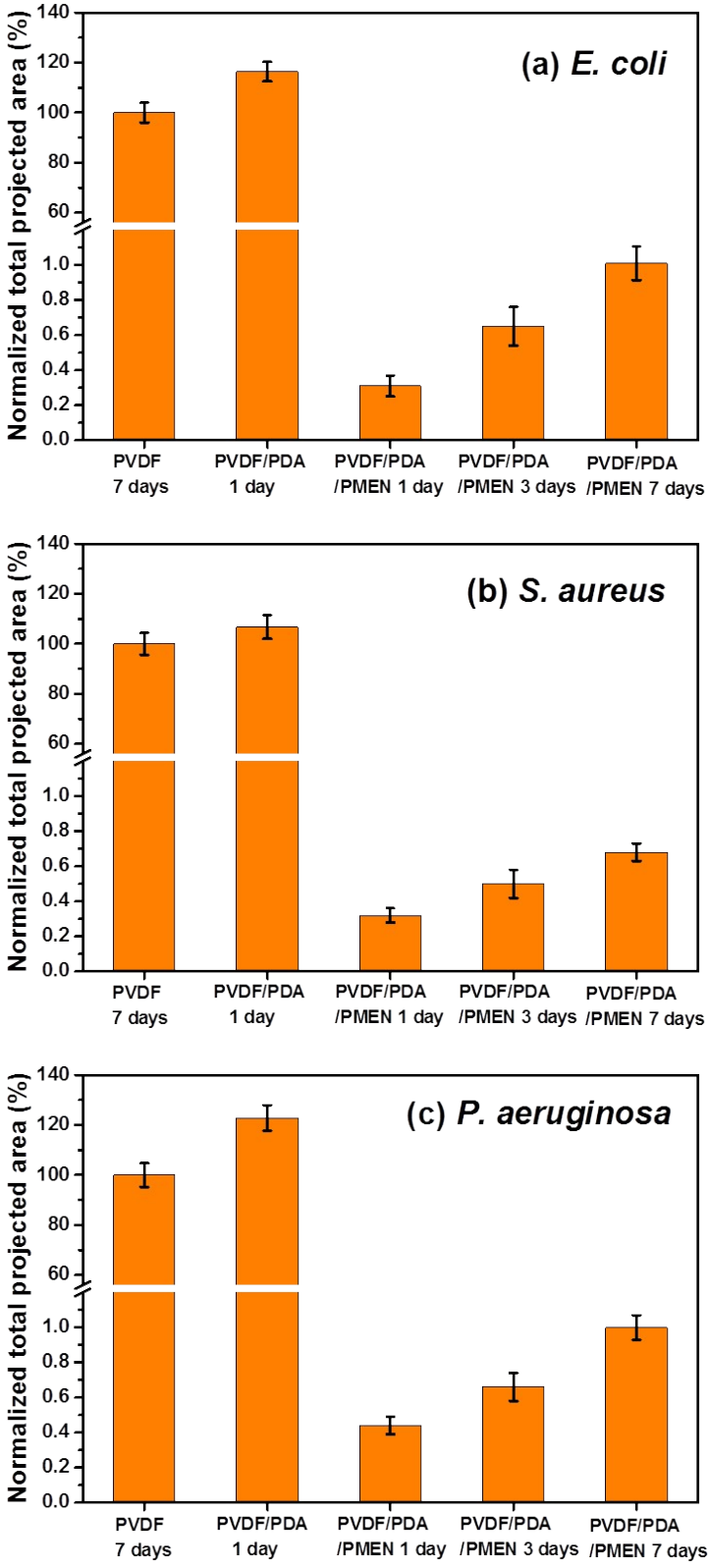

Figure S8. Quantitative results of the attachment of (a) *E. coli*, (b) *S. aureus* and (c) *P. aeruginosa* bacteria on the surfaces of PVDF, PVDF/PDA and PVDF/PDA/PMEN membranes.