



Poly(vinylidene fluoride)/Poly(acrylic acid)/Calcium Carbonate Composite Membranes via Biomineralization

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Poly(vinylidene fluoride) (PVDF) is one of the most extensively used materials for membranes. However, its hydrophobic nature, has become a conspicuous drawback for its application. Much attention has been paid to organic–inorganic composite PVDF membranes which are fabricated through blending PVDF with inorganic nanoparticles. However, the commonly employed blending method usually fails to improve the membrane hydrophilicity. Compared with the organic–inorganic composites generated via biomineralization in nature, it is questionable about the stability of the inorganic particles on the hydrophobic surface of PVDF membrane. Therefore, we aimed to develop PVDF/CaCO₃ composite membranes by depositing CaCO₃ particles both on the membrane surfaces and in the membrane pores via blending and then mineralization.

Formation of CaCO₃ particles in/on the PVDF/PAA blend membrane

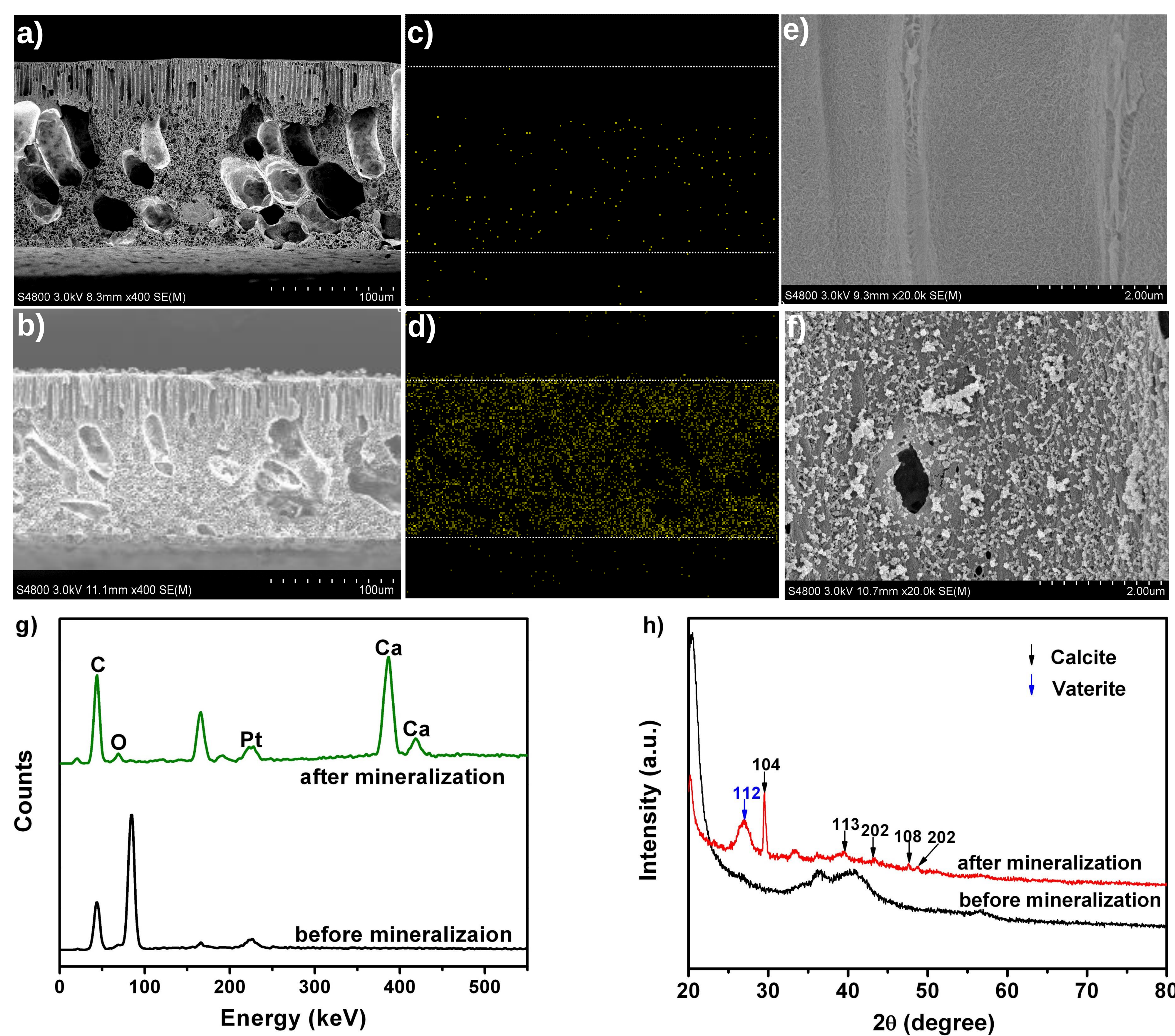


Figure 1. FESEM images (a, b) and EDX maps (c, d) of the PVDF/PAA blend membrane cross-section without (a, c) and after (b, d) mineralization. EDX curves (e) and XRD diffraction patterns (f) of PVDF/PAA blend membrane with 2 wt.% PAA.

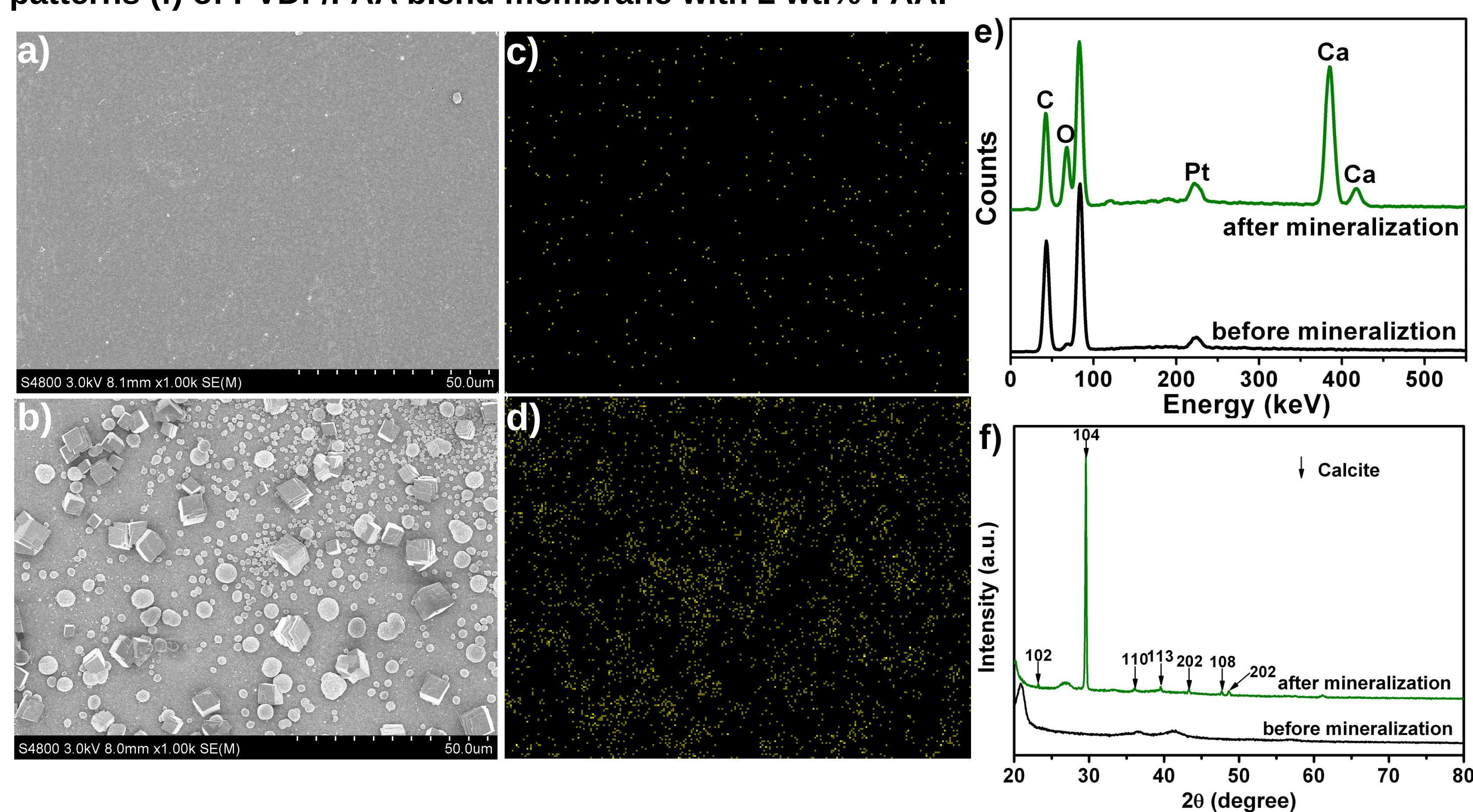
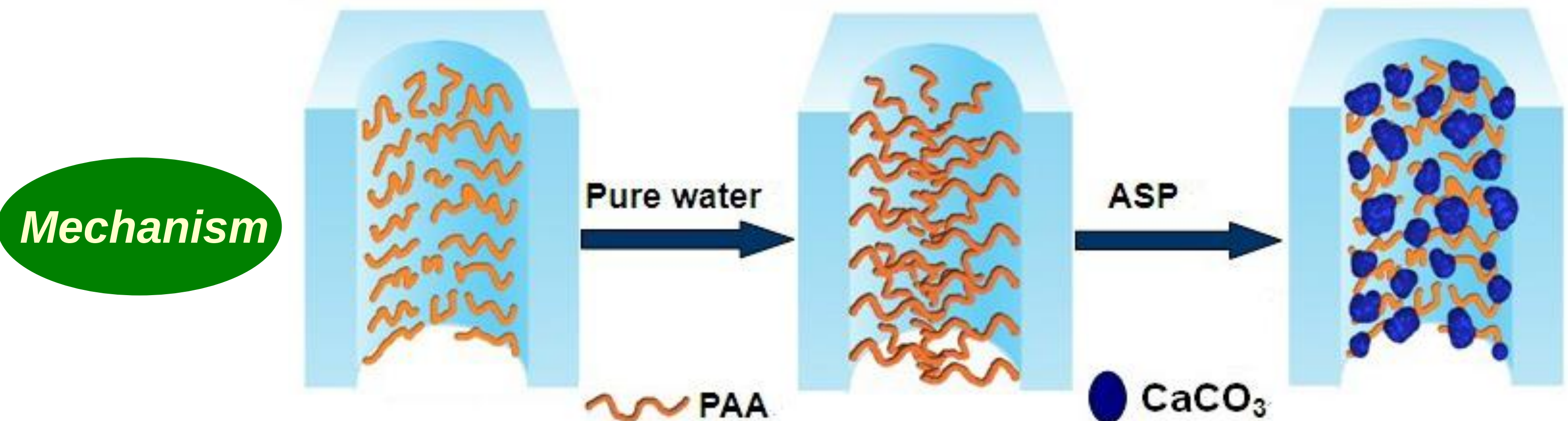


Figure 2. FESEM images (a, b) and EDX maps (c, d) of the membrane top surface without (a, c) and after (b, d) mineralization. EDX curves (e) and XRD diffraction patterns (f) of PVDF/PAA membrane with 2 wt.% PAA.



Effects of mineralization on membrane properties

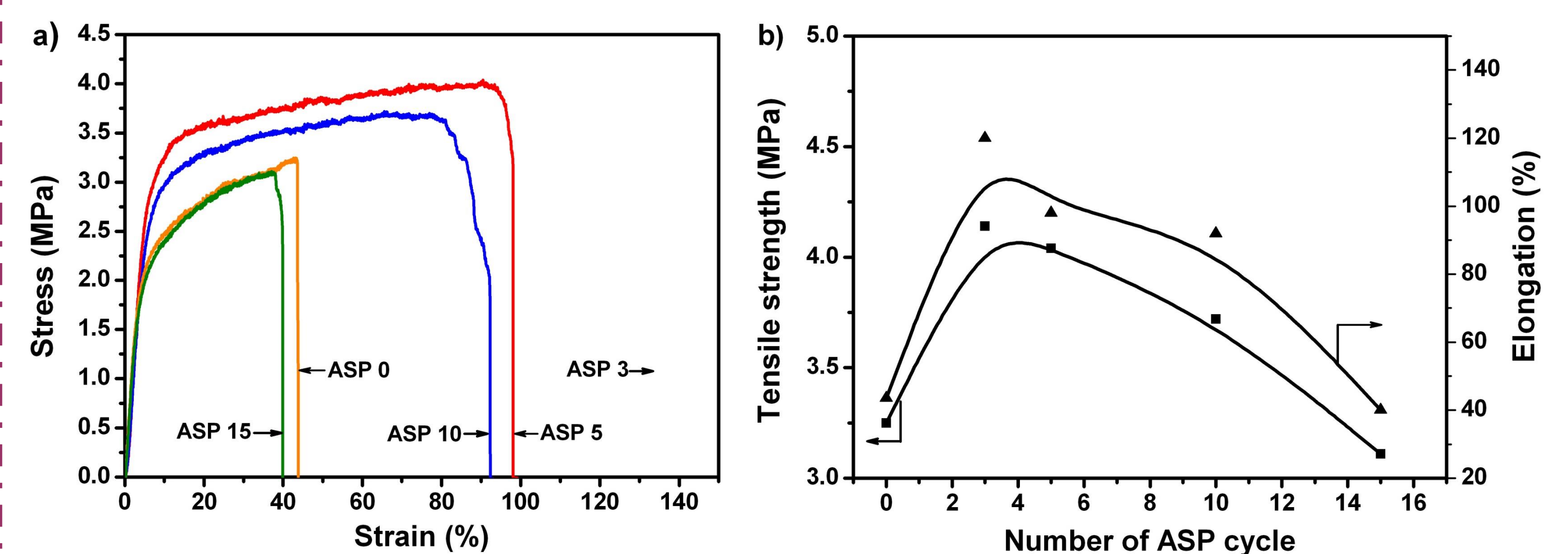


Figure 3. Stress-strain curve (a) and corresponding tensile strength and elongation (b) for the mineralized PVDF/PAA blend membrane containing 2 wt.% PAA prepared by different ASP cycles in 200 mM CaCl₂/Na₂CO₃ solution.

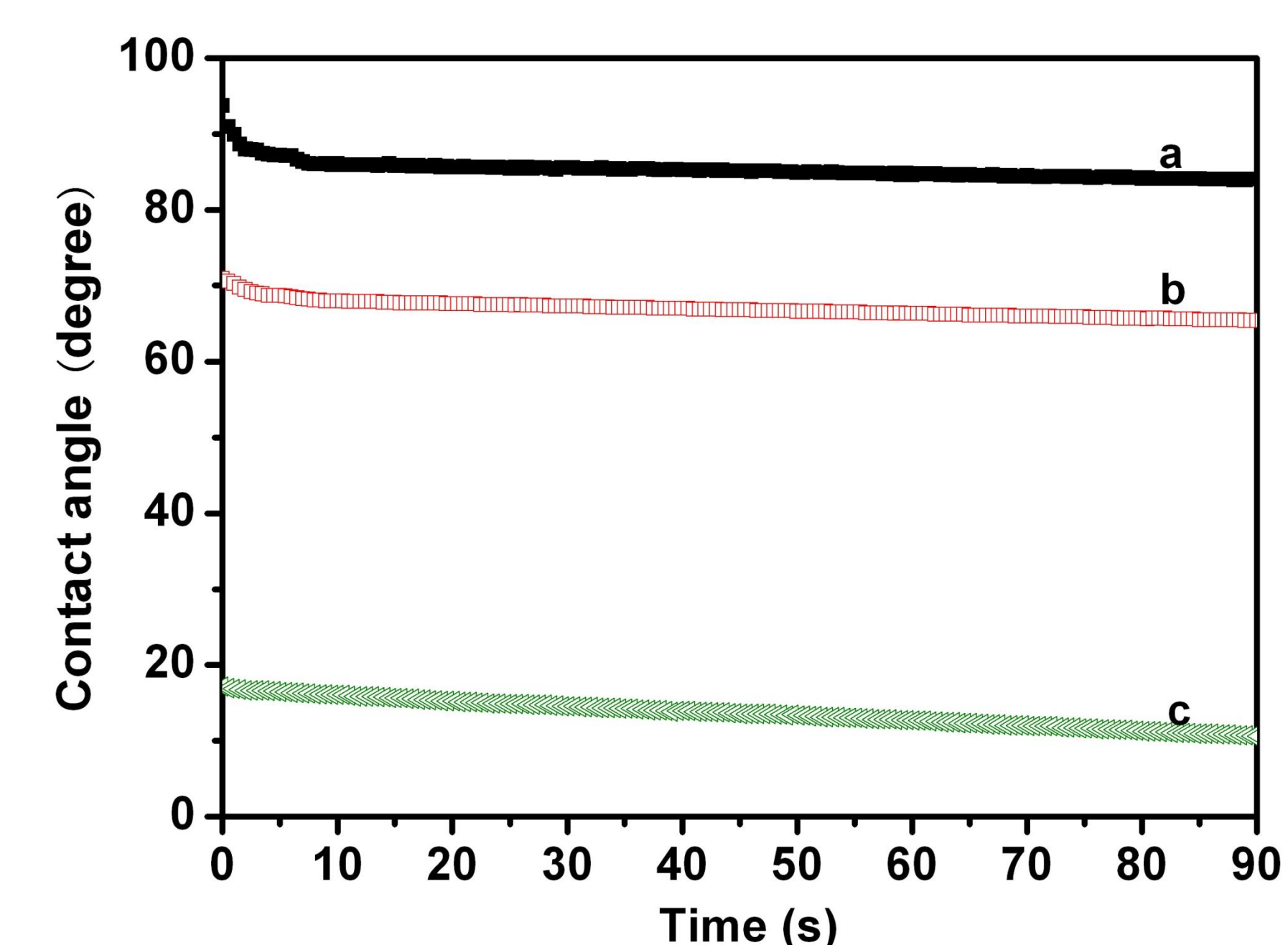


Figure 4. Water contact angle of PVDF membrane (a), PVDF/PAA membrane with 2 wt.% PAA (b) and corresponding mineralized PVDF/PAA membrane (c).

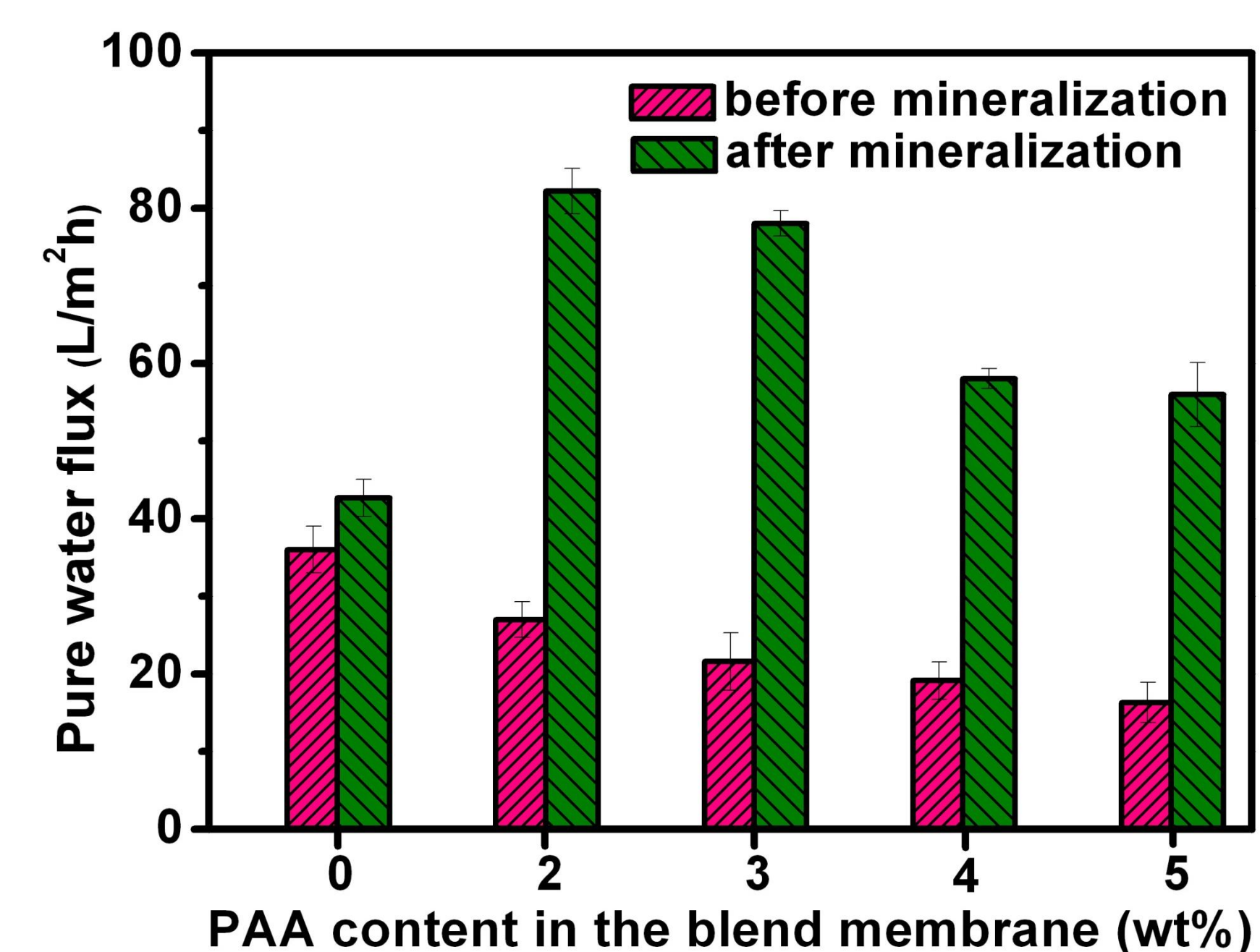


Figure 5. Pure water fluxes of the PVDF/PAA blend membranes before and after mineralization.

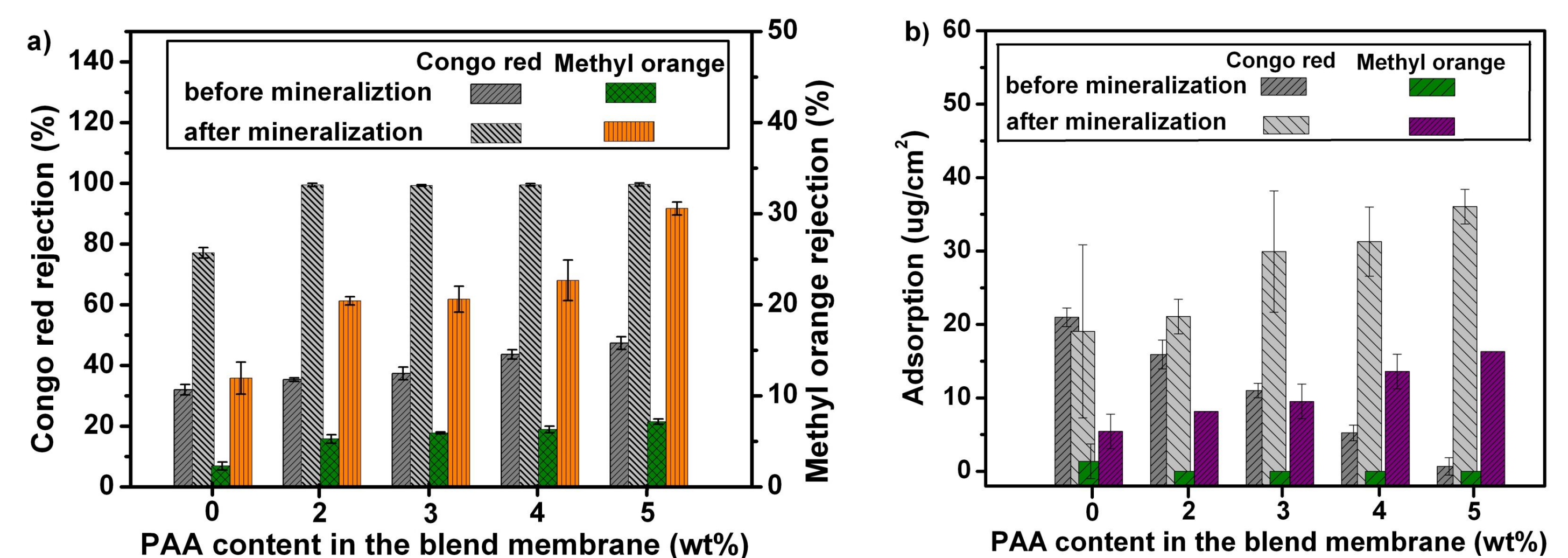


Figure 6. Rejection (a) and adsorption (b) to Congo red and Methyl orange for the PVDF/PAA blend membranes before and after mineralization.

Conclusions

PVDF/PAA/CaCO₃ composite membranes were fabricated by the immersion precipitation method followed with the deposition of CaCO₃ particles on the membrane surface and in the membrane cross-section via an alternate soaking process. The pure water flux of PVDF/PAA blend membrane decreases with PAA content, which is owing to the stretching and swelling of PAA chains. In contrast, the pure water flux is improved to about three times for all mineralized membranes owing to the collapse of PAA chains and the introduction of hydrophilic CaCO₃ particles. The membranes after mineralization even show a high rejection of Congo red up to 99.85%. ASP method is a promising modification approach to advanced hydrophilic organic–inorganic composite membranes.

Acknowledgements

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