

# Reversing divalent salt and small organics retentions of polyamide nanofiltration membrane by regulating charge distribution

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## Abstract:

A nanofiltration (NF) membrane with high salt permeation and high retention of small organics is appealing for treatment of high-salinity organic wastewater. However, the conventional NF membranes with negatively charged surface show high retention of divalent anions (e.g.,  $\text{SO}_4^{2-}$ ), and the reported positively charged NF membranes normally owns low retention of small organics and high fouling potential. In this work, we proposed a novel “etching-swelling-planting” strategy assisted by interfacial polymerization (IP) using piperazine (PIP) and tannic acid (TA) as aqueous monomers, trimesoyl chloride (TMC) and  $\text{Fe}(\text{acac})_3$  in n-hexane as organic monomers, which could prepare a positively charged NF membrane with both high  $\text{Na}_2\text{SO}_4$  permeation and desirable retention of small organics. The polyester network formed by TA and TMC was hydrolyzed in alkaline polyethyleneimine (PEI) solution (pH 12.4), not only enlarging the pores for reduction of PEI diffusion steric hindrance into the separation layer, but also providing phenolic hydroxyl groups for covalently linking PEI. By XPS depth profiling and pore size distribution analysis, it was found that such strategy could not only deepen the positive charge distribution, but also narrow the pore size. This finely regulated membrane structure reversed the retention of  $\text{Na}_2\text{SO}_4$  and glucose (43% - 71%), meanwhile, due to the high surface hydrophilicity and smoothness as well as the preservation of abundant negatively charged groups (i.e. -OH and -COOH) inside the separation layer, the obtained membrane exhibited excellent antifouling performance, even for the coking wastewater. Our methodology provides a scalable strategy to fabricate highly selective NF membranes for wastewater reclamation.

**Keywords:** nanofiltration; highly selective membrane; desalination; high-salinity wastewater treatment; antifouling performance