

# **Amine grafting and quaternization of thin film composite membrane for osmotic ammonium enrichment and recovery from industrial wastewater**

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## **Abstract:**

Recovery and enrichment of  $\text{NH}_4^+$  from real wastewater was conducted using forward osmosis (FO). FO thin film composite (TFC) membranes were developed via chemical grafting with positively-charged polyethyleneimine (PEI). The TFC membrane surface was first activated using 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) and *n*-hydroxysuccinimide (NHS) to convert the carboxyl groups of polyamide into amine-reactive NHS esters. PEI grafting significantly increased the  $\text{NH}_4^+$  retention in the feed solution. To further improve the  $\text{NH}_4^+$  rejection, quaternization of the amine functional groups of PEI was conducted with iodomethane. Quaternization was found to further increase  $\text{NH}_4^+$  rejection, up to over 98.5%, while maintaining similar water permeability with the PEI-grafted TFC membrane. Fouling control of the pristine and amine-modified TFC membranes were also demonstrated, and the quaternary amine-modified TFC membrane exhibited superior fouling resistance against organic and biological foulants. The amine-modified TFC membranes were evaluated for applicability for dewatering and  $\text{NH}_4^+$  enrichment of real industrial wastewater.  $\text{NH}_4^+$  enrichment using the PEI-grafted membranes was observed following wastewater dewatering, indicating the high  $\text{NH}_4^+$  retention ability of the TFC membranes modified via amine grafting and quaternization. Wastewater dewatering of 90.3 and 92.4% were achieved using TFC-PEI-10 and TFC-qPEI, respectively.

**Keywords:** Forward osmosis; Ammonium enrichment; Thin film composite membrane; Amine grafting; Quaternization