

Leveraging Electrodialysis for Ion Removal

Amrinder Bhuller

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Escalating demand for clean and accessible water across the globe has resulted in an urgent need for advanced water purification technologies. A substantial (over 65%) portion of the world population faces clean water scarcity due to contamination and inadequate sanitation.¹⁻⁴ Current freshwater sources are limited, resulting in a need to purify water from alternative sources. However, nontraditional water sources suffer from high salt concentration and the presence of trace toxic ions. Alternatively, these sources contain high-value ions that, in principle, could be retrieved during desalination.⁵ Desalination is the process of removing salt and contaminants from water sources. Multiple desalination technologies, such as reverse osmosis and electrodialysis, have emerged, but face challenges for large-scale application. Current technologies face high energy consumption, high costs, and suffer from membrane fouling.^{1,4-5} Thus, the development of robust, cost-effective, and energy-efficient water separation technologies is needed to meet demand.

One separation technique that is gaining popularity for water purification is electrodialysis (ED) due to its continuous operation, simplicity, and various applications.⁶ ED is an electrochemical process that allows for selective ion transport upon the application of an electric field. This allows for the separation of selective ions through ion-exchange membranes. A typical electrodialysis setup (**Figure 1**) consists of alternating anion-exchange membranes (AEM) and cation-exchange membranes (CEM) between a pair of electrodes. These membranes serve as selective barriers, only allowing certain charged ions to pass through. A feed solution consisting of a mixture of ions is introduced to the system and an electric potential is applied. This results in the cations to migrate through the CEM towards the cathode and anions to migrate to the anode via AEM. The selective interaction of moving ions with charged functional groups of the ion-exchange membranes allows for the facilitation of ion transport. This results in ions to accumulate in a certain compartment denoted as the concentrated compartment, while the compartments containing minimized ion concentrations are known as the dilute compartments. Thus, electrodialysis allows for desired purification and separation through compartmentalization. This allows electrodialysis to serve as a versatile continuous operation for water purification. However, limitations such as membrane fouling, scaling, cost, and electrical energy requirement affect the overall sustainability and wide-scale application of electrodialysis.⁶

Conventional electrodialysis has fallen short for the efficient fractionation of organic-rich waste waters due to prominent membrane fouling.⁸ Nanofiltration is the most common separation technology for these solutions but falls short for large-scale application due to high-pressure requirements and the large consumption of pure water. Recently, Lin et al. have proposed a strategy to combine the advantages of nanofiltration (usage of nanoporous membranes) and electrodialysis (no pressure requirements) for highly efficient fractionation.⁸ An anion-conductive thin-film composite nanoporous membrane was synthesized via the co-deposition of polyethyleneimine and

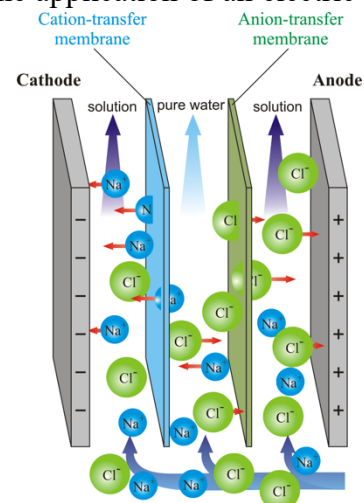


Figure 1. Simplified schematic diagram of electrodialysis. Taken from reference 7.

dopamine on a polyamide membrane substrate to replace anion-exchange membranes in electrodialysis. The most promising coated membrane was labeled as NPM-6.

NPM-6 was exposed to antibiotic/NaCl solutions to examine the fractionation efficacy. A desalination efficiency of approximately 99.3% and recovery efficiency of roughly 99.1% was observed for all mixed solutions, outperforming pressure-driven filtration processes using NPM-6.⁸ The proposed mechanism of enhanced anion transfer involving the NPM-6 membrane during fractionation of the mixed salt solutions can be found in **Figure 2**. It is believed that the small pore size of the NPM-6 results in the retention of organics, prohibiting the penetration of organic ions through the inner pores structure of the membrane. Furthermore, the enhanced fast ion transfer of the inorganic anions is due to a shorter ion diffusion length and reduced negative charge density, intensifying the shielding effect.⁸

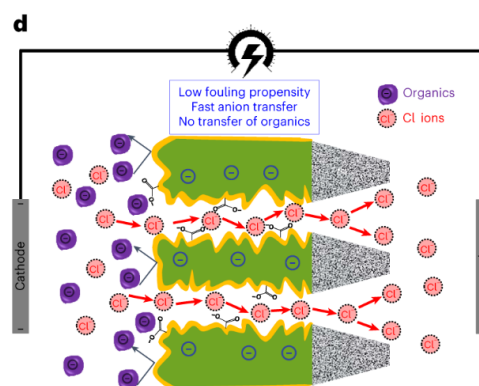


Figure 2. Schematic drawing of ion transport using NPM-6. Taken from reference 8.

Conventional separation technologies lack the selectivity for capturing high-value ions in contaminated water sources. In 2021, Uliana et al. presented a remarkable study involving the desalination and detoxification of nontraditional water sources with simultaneous capturing of target ions

(e.g. Hg^{2+}) through a one-step process denoted as ion-capture electrodialysis.⁵ They synthesized a multifunctional adsorptive membrane through the incorporation of porous aromatic framework (PAF) nanoparticles onto ion-exchange membranes. The prepared adsorptive membranes involved the embedment of PAF-1-SH onto a sulfonated polysulfone (sPSF) cation exchange matrix. The best performing membrane exhibited a 20 wt% of PAF-1-SH onto sPSF, which was denoted as 20 wt% PAF-1-SH. 20 wt% PAF-1-SH demonstrated excellent stability (only 8% capacity loss) over 10 adsorption-desorption cycles and minimal swelling was achieved. **Figure 3** represents the ion-capture electrodialysis curves for various water samples and the breakthrough experiment results.⁵ As observed in figures A-C, 20 wt% PAF-1-SH exhibited excellent capture of various 5ppm Hg^{2+} solutions with ranging desalination efficiency of 97-99%. Inductively coupled plasma optical emission spectrometry exhibited no Hg^{2+} concentration and negligible amounts of competing cations (insets of A-C) in the receiving solutions. Breakthrough experiments revealed that 10 and 20 wt% PAF-1-SH achieved 96% of theoretical capacity prior to observing Hg^{2+} in the receiving solution. Calculations revealed that approximately 34,500 liters of 5 ppm Hg^{2+} contaminated water could be treated with 1kg of the 20 wt% PAF-1-SH before regeneration is required. Furthermore, the research group developed various PAF-1 nanoparticles for the selective capture of Cu^{2+} , Fe^{3+} , and $\text{B}(\text{OH})_3$. Thus,

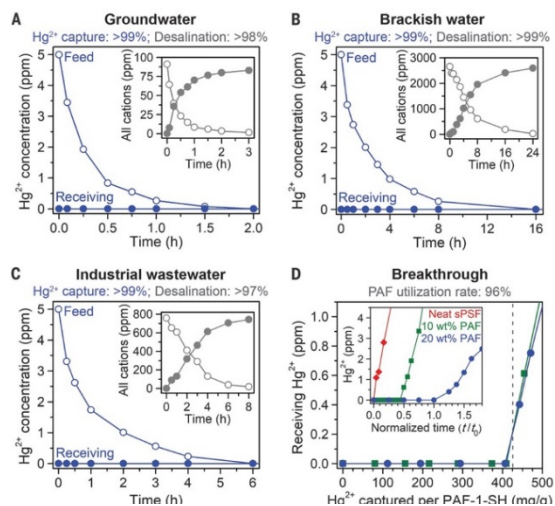


Figure 3. Ion-capture electrodialysis curves for synthetic A) groundwater, B) brackish water, and C) industrial wastewater solutions. D) Breakthrough data. Taken from reference 5.

this study has described a generalized approach for the fabrication of tunable adsorptive membranes through PAF nanoparticles for efficient one-step ion capture electro dialysis.⁵

Recently, Yu et al. proposed a novel hybrid process involving the utilization of membrane-based electrochemical precipitation (MEP) and electro dialysis (ED) for the removal of hardness and conventional ions present in cooling water.⁹ Although ED has been proposed for the treatment of cooling water, it suffers limitations in efficiency due to membrane scaling. MEP has been shown to remove hardness ions but lacks the separation of other ions present.¹⁰ This new hybrid process was labeled as membrane deposition electro dialysis (MDED), which allows for the removal of hardness ions via MEP and electro-migration of conventional ions via ED.⁹ Furthermore, a bi-pair electrode system is adapted to overcome common electrode stability issues observed with the use of polarity reversal to detach scales deposited on membranes in MEP.

Figure 4 demonstrates a schematic diagram of the experimental apparatus during the desalination and scale detachment stage.⁹ The dilute compartment was sandwiched between two AEMs to facilitate hardness deposition. A solution is passed upwards, and a direct current is supplied between electrode pair 1 during the desalination stage. After this, the direct current supply was altered to electrode pair 2, and a cooling water solution is continuously poured downward, allowing for detachment of the scale.⁹

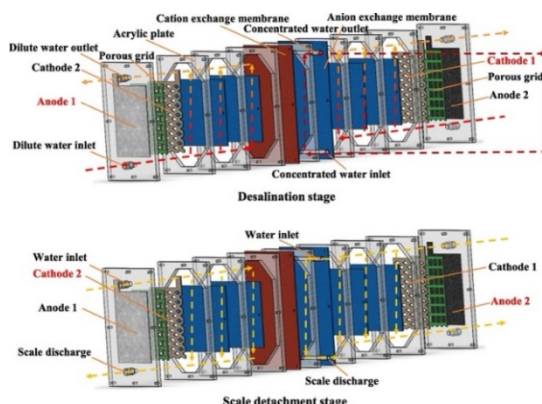


Figure 4. Schematic diagram of MDED apparatus. Taken from reference 9.

Desalination experiments revealed an initial rapid decrease in the effluent conductivity followed by a gradual increase to a final conductivity value of 1017.8 $\mu\text{S}/\text{cm}$.⁹ Compared to ED, MDED exhibited less concentration of Ca^{2+} , Mg^{2+} , and HCO_3^- and more of Na^+ and Cl^- . Furthermore, MDED exhibited a concentration selectivity of 2.3 (0.5 for ED). In MDED, the pre-deposition of hardness ions resulted in a decreased penetration competition between them and other ions (e.g., Na^+), resulting in more Na^+ and Cl^- ions to electro-migrate into the concentrate compartment, increasing concentration selectivity. Thus, MDED allows for ion step removal processes in which the hardness ions may be removed first through membrane deposition and the remaining ions through electro-migration. Furthermore, accelerated life experiments were conducted to test electrode and membrane stability. The service life for electrodes involving polarity reversal was roughly 211 h, whereas the bi-pair electrode switching mechanism exhibited a steady voltage for up to 1800 h. The service life for AEM and CEM was 999 h and 1660h, respectively. Lastly, an operational stability test of MDED was conducted for 30 days. Stable detachment efficiency and good reproducibility was observed, with minimized corrosion problems. The synergy between membrane deposition and electro-migration has expressed great stability and efficient ion step removal for enhanced treatment of cooling water.⁹

In conclusion, recent works have demonstrated the usage of electro dialysis for enhanced desalination for various water sources.^{5,8-9} These research studies exhibit the future trend of separation technologies: combining the technical merits of various separation methods with electro dialysis. Modification of the ion-exchange membranes and decreasing membrane fouling propensity are key challenges that need to be overcome for practical applications. Current technologies still lack in terms of robust, cost-effective, and energy-efficient methods for water purification, but changes to the conventional electro dialysis system are promising for long-term application.

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