

ENHANCING COPPER REMOVAL THROUGH INTEGRATED CAPACITIVE DEIONIZATION WITH HETEROGENEOUS CATION EXCHANGE MEMBRANE

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Abstract

Capacitive deionization (CDI) is a novel technique to eliminate ions present in the solution. This study was designed to evaluate the impact of cation exchange resin loading on the membrane using the nonsolvent-induced phase inversion method. After optimizing the resin loading on the membrane, the prepared membrane was employed for the membrane capacitive deionization (MCDI). A concentration of 500 mg.L⁻¹ Cu²⁺ was used as a test contaminant in the CDI system to study Cu²⁺ removal and recovery at different voltages. Results showed that resin loading substantially influenced the membrane structure and enhanced the Cu²⁺ removal by the CDI technique. The presence of cation exchange resin on the membrane was found by the appearance of a peak at 1,007 cm⁻¹, 1,035 cm⁻¹, and 1,128 cm⁻¹ in the FTIR spectra of the –SO₃ group, which became more significant as the amount of resin increased. The prepared membrane's water uptake and ion exchange capacity increased as the quantity of resins loaded onto the membrane increased. When monitoring a current-time graph during CDI tests, an adsorption amount of 6.9 mg.g⁻¹ of Cu²⁺ and recovery efficiency of 51.7 % at the 10th cycle in the MCDI cell was observed for M20 (20% by wt resin). Using the prepared membrane in the CDI system has the potential to remove Cu²⁺ from the solution selectively.

Keywords: Copper; Capacitive deionization; Cation exchange membrane; Heavy metal

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Introduction

Heavy metals are defined as elements with specific gravity exceeding 5 g/cm³ and atomic weights ranging from 63.5 g/g.mol to 200.6 g/g.mol (Srivastava and Majumder, 2008). Some heavy metals, including copper, manganese, selenium, and zinc, are widely recognized as essential micronutrients for humans and other organisms (Fairbrother *et al.*, 2007). In contrast, heavy metals such as arsenic, cadmium, chromium, lead, mercury, and nickel have no evidence of nutritional benefits (Fairbrother *et al.*, 2007). They are known to cause harmful effects. The risk for exposure and toxicity from these metals is not readily preventable, so action must be required to reduce human exposure to the lowest. Furthermore, heavy metal removal from water sources has been recognized as an important goal, aligning with the United Nations' Sustainable Development Goals. Various methods, including adsorption, ion exchange, chemical precipitation, and membrane separation, have been extensively researched for removing heavy metals from effluent (Fu and Wang, 2011; Qasem *et al.*, 2021). Although these methods have demonstrated promising results in metal removal, they also pose certain environmental challenges (Fu and Wang, 2011). Therefore, it is essential to explore cost-effective techniques for wastewater treatment, with limited generation of the secondary product and the potential regeneration of resources during the treatment process.

Capacitive deionization (CDI) has emerged as a promising desalination technique since its introduction in 1996 (McNair *et al.*, 2021). Although it has been thoroughly examined in the setting of desalination, studies regarding its applicability for removing heavy metals are still underway (Tan and Babel, 2023). Numerous studies have focused on enhancing CDI performance by improving electrode material properties. However, despite their extraordinary desalination capabilities, the modified electrode materials have certain drawbacks (Cheng *et al.*, 2019). Conventional CDI exhibits significantly lower energy efficiency than intended, primarily due to co-ion expulsion (Nguyen Tan *et al.*, 2024). This phenomenon arises as ions with the same charge undergo continuous adsorption and desorption on the surface of the electrode material, leading to a decline in the number of extractable counter-ion from the solution (Hosseini *et al.*, 2014; McNair *et al.*, 2021). To address these challenges and enhance operational efficacy, the CDI system has been reconfigured to incorporate both an anion exchange membrane and a cation exchange membrane. By placing ion exchange membranes

in front of the pair of electrodes, ion removal efficiency is improved as co-ions are inhibited, and ion storage within the electrodes increases (Luo *et al.*, 2020). Ion exchange membranes exhibit exceptional selectivity towards specific ions, enabling efficient ion removal with minimal energy input. Therefore, utilizing ion exchange membranes has emerged as a viable strategy to enhance CDI performance.

Based on the structure of membranes, homogeneous and heterogeneous ion exchange membranes are two types commonly investigated in the membrane technique. Each type exhibits a distinctive set of characteristics in the context of the CDI technique. Utilizing homogeneous ion exchange membranes in CDI systems demonstrates high selectivity towards specific ions, enabling efficient ion removal and low energy consumption compared to CDI systems (Luo *et al.*, 2020; Zhang *et al.*, 2020). However, the primary concern associated with homogeneous ion exchange membranes lies in their high cost, which necessitates consideration when developing and implementing long-term strategies. On the other hand, despite having inferior electrochemical properties compared to homogeneous ion exchange membranes, heterogeneous ion exchange membranes are widely utilized due to their straightforward fabrication method and lower processing costs (McNair *et al.*, 2021). The cost-effectiveness and convenience of manufacturing are driving factors behind the broad acceptance of heterogeneous ion exchange membranes (Khoiruddin *et al.*, 2017). Normally, heterogeneous ion exchange membranes can be generated using the solvent evaporation method. However, this method is more likely to result in the macrophase separation of the blend elements because of the solvent evaporation procedure (Zare and Kargari, 2018). Nonsolvent-induced phase inversion is a promising technology with the potential to improve the results of macrophase separation on a membrane (Mondal *et al.*, 2018). In this process, a polymer mixture is poured onto a support material; after that, it is put into a non-solvent solution, which changes the phase of the material (Mondal *et al.*, 2018; Zare and Kargari, 2018). However, this process has yet to be fully utilized for its application in the CDI technique.

This study aims to find an approach for the fabrication of a cation exchange membrane based on polyvinylidene fluoride through the addition of polyethylene glycol and different quantities of cation exchange resins into the dope solution. Firstly, the effect of the amount of cation exchange

resins on the morphological properties of the membrane was evaluated. Secondly, the prepared membrane's water uptake and ion exchange capacity were examined, providing valuable insight into the membrane's ability in ion exchange. After obtaining an in-depth knowledge of the properties of cation exchange membrane, its performance in a CDI system for removing Cu^{2+} was assessed to determine the membranes' suitability and efficiency.

Materials and Methods

Analytical grade cupric nitrate trihydrate, hydrochloric acid, sodium chloride, N, N-Dimethylacetamide (DMAc) were ordered from Loba (India); polyvinylidene fluoride (PVDF), and sodium hydroxide were acquired from Merck (Germany); Polyethylene Glycol (PEG) was obtained from Tokyo Chemical Industry Co., Ltd (Japan). No extra purity procedures have been used on any of the chemicals before their use in the experiment.

Before being used, the electrode material, activated carbon cloth (ACC), was treated with 5% hydrochloric acid to eliminate traces of pollutants on the ACC. The anion exchange membrane (AMI-7001S) from Membranes International Inc. (USA) was immersed in deionized water and a 5% sodium chloride solution for membrane hydration. Cation exchange resins (Purolite C100) from Purolite Co., (USA) were treated with each 5% hydrochloric acid and 5% sodium hydroxide. Afterward, they were cleaned and dried at 60°C, ground, and sieved to obtain resin particles with a size no bigger than 53 μm .

Five membranes were fabricated and identified as membranes M0, M5, M10, M15, and M20, following their respective compositions. These labels correspond to the weight of cation exchange resins in the casting solution, indicating 5%, 10%, 15%, and 20% by weight of the resin and membrane M0 (without resins) in the casting solution. 0.25 g of PVDF and 0.1 g of PEG were added to each flask to produce the polymer solution for membrane casting. Different amounts of DMAc (4.65 g, 4.4 g, 4.15 g, 3.9 g, and 3.65 g) were added to the respective flasks. These mixtures were stirred at 60°C. After 4 hours of mixing, various amounts of cation exchange resins (0.25 g, 0.5 g, 0.75 g, and 1.0 g) were introduced to their respective mixed solutions (M5, M10, M15, and M20), while the solution for M0 was prepared without the addition of resins. It was continuously mixed at 60°C for 2 h. The dope solution was poured over the polyester fabric, and then a casting tool with a height setting of 400 μm was used to produce the membrane. After

the membrane casting process, the fabricated membrane was submerged in a deionized water tank for at least 30 min before its use.

The prepared materials were examined using characterization techniques. To see functional groups that exist on the surface of the membranes, Fourier transform infrared spectroscopy (FTIR) measurements were conducted within the scanning range of 4,000-400 cm^{-1} using the NicoletTM iS50 analyzer (Thermo Fisher Scientific, USA). The morphology of membranes was analyzed using a Field Emission Scanning Electron Microscope (FE-SEM) (Jeol JSM7800F, Japan).

The water uptake is the volume of water that holds the membrane channels, influencing the hydrophilicity of the membrane's surface and the porosity of its bulk. The water uptake of the prepared membranes was determined by calculating the difference in weight between dried and wet membranes. After drying at 60°C for 2 h in a vacuum oven, the mass of membrane with dimensions of 4 cm $\times$ 4 cm was measured. Subsequently, the cation exchange membrane was submerged in deionized water for 24 h. Upon completion of this immersion period, any remaining DI water on the surface of the membrane was removed, and the mass of the ion exchange membranes was measured again. The water uptake percentage was established using Equation (1):

$$\text{Water uptake (\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \quad (1)$$

where W_{wet} (g) is the mass of the wet membrane and W_{dry} (g) is the mass of the dry membrane.

An acid-base titration method was employed to determine the prepared membrane's ion exchange capacity. Initially, the prepared membrane with 4 cm $\times$ 4 cm size was weighed after drying at 60°C in a vacuum oven for 2 h. The membrane was then kept in 100 mL of 1 M HCl solution for 24 h to convert any salt forms of sulfonate groups to the $-\text{SO}_3\text{H}$ group, followed by thorough washing with deionized water. Subsequently, the membrane was submerged in 10 mL of 0.1 M NaOH solution for 24 h. The supernatant was collected, and three drops of phenolphthalein were added. Titration was then performed using a 0.1 N HCl solution to observe the color change, which was recorded. The ion exchange capacity (IEC) of the prepared membrane was calculated using Equation (2):

$$\text{IEC (meq. g}^{-1}\text{)} = \frac{(V_{\text{NaOH}} \times C_{\text{NaOH}}) - (V_{\text{HCl}} \times C_{\text{HCl}})}{W_{\text{dry}}} \quad (2)$$

where (V_{NaOH} and V_{HCl} are volumes of NaOH and HCl, respectively, and C_{NaOH} and C_{HCl} are the

concentrations of NaOH and HCl, respectively and W_{dry} is the mass of the dried membrane.

This study uses two configurations of CDI systems, including CDI and MCDI. In Figure 1(a), the CDI cell comprises two symmetrical square-shaped ACC electrodes, each with a 14.44 cm² geometrical surface area. A graphite sheet was attached to the outer side of each electrode, which was connected to the current collector. A DC power supply was used to provide a potential to the current collectors, while a data logger (ADC-20, Pico Technology, The United Kingdom) was utilized for monitoring the reactor's current profile during the experiment. To avoid short-circuit and facilitate the feed passage, a spacer was inserted between two electrodes. Nuts and bolts were used for securely connecting a polyacrylic sheet to the framework structure of the reactor. The configuration of the MCDI cell was constructed in a manner like the CDI cell, with the incorporation of two membranes. Figure 1(b) depicted the positioning of an anion exchange membrane (AMI-7001S) in front of the anode, while the cation exchange membrane, which had been prepared beforehand, was placed in front of the cathode.

The adsorption amount (q) in mg.g⁻¹ was defined by Equation (3):

$$q = \frac{(C_o - C_t) \cdot V}{M} \quad (3)$$

where C_o is a concentration at the initial time (t_o), C_t is the concentration after time t of Cu²⁺ (mg.L⁻¹), V is a volume of Cu²⁺ solution (mL), and M is a weight of the material (g), respectively.

This study conducted electrosorption experiments at various applied potentials to gain in-depth knowledge of the membrane's functionality in the CDI system. A peristaltic pump was employed to provide 100 mL of a Cu²⁺ solution, characterized by a concentration of 500 mg.L⁻¹, into the CDI system, maintaining a regulated flow rate of 10 mL.min⁻¹. After ending its passage in the cell, the solution was put back into the feed tank. The total time of the entire experiment was 150 min, which included 10 cycles. Each cycle consisted of three stages: a 10-min charging mode, a 3-min negative voltage mode, and a 2-min short-circuiting mode. The concentration of Cu²⁺ in the solution was conducted through Inductively Coupled Plasma-Optical Emission Spectrometry (Avio 200, PerkinElmer, USA).

Results and Discussion

The IR spectra depicted in Figure 2 provided valuable insight into functional groups on the prepared membrane. Five membranes displayed distinct peaks at wavelengths 3,024 and 2,982 cm⁻¹, representing asymmetric and symmetrical vibrations of the C-H band, respectively. In addition, these membranes had peaks at wavenumbers 1,400 cm⁻¹, 1,180 cm⁻¹, 875 cm⁻¹, and 840 cm⁻¹, which were assigned to C-H vibration, C=C band, asymmetric CCC, and vibration of C-F stretch, respectively.

The distinctive peaks detected at wavenumbers 1,007 cm⁻¹ and 1,035 cm⁻¹ correspond to the symmetric stretching vibrations, while the peak at 1,128 cm⁻¹ indicates the asymmetric stretching vibrations. These characteristics are indicative of

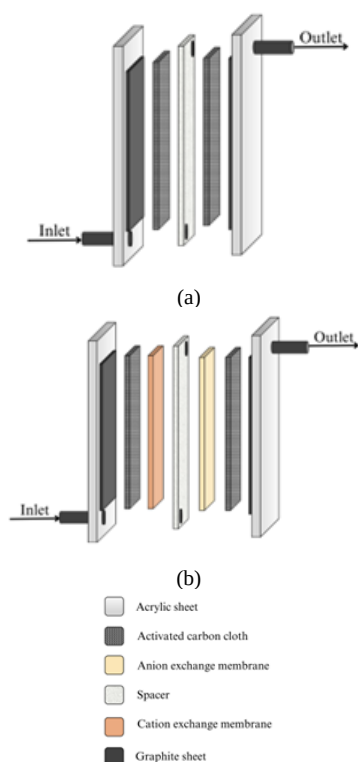


Figure 1. Components of a) CDI cell, b) MCDI cell

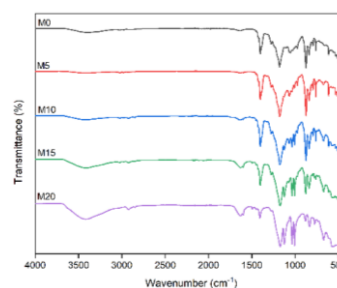


Figure 2. IR spectra of the membrane M0, M5, M10, M15, and M20

the vibrational modes associated with the O=S=O bond. The observed intensity at the peaks of membranes M5, M10, M15, and M20 provided strong evidence for the presence of the resins containing $\text{-SO}_3\text{H}$ groups within the membrane. Notably, the intensity of these peaks increased proportionally with the quantity of resin applied to the membrane, establishing a clear correlation.

The Scanning Electron Microscopy (SEM) technique was used to explore the surface features of the prepared membrane, providing detailed knowledge about its morphology. Figure 3 presents the SEM images of membranes M0, M5, M10, M15, and M20 with various resin contents.

Figure 3(a) depicts the surface properties of the pristine membrane (M0), revealing a heterogeneous spatial distribution of surface membrane pores (black holes). As illustrated in Figure 3(b-e), the resin addition induced significant alterations in the surface membrane. The resin content on the membrane gradually increased (from 5% to 20% by wt resin), and the empty spaces were effectively filled, resulting in a surface with enhanced uniformity and equality. Incorporating cation exchange resins into the dope solution yielded dual advantages, as evidenced by the study's findings. Firstly, this mixing method improved the chemical properties of the membrane by increasing the abundance of functional groups, specifically $\text{-SO}_3\text{H}$ groups within the membrane. Secondly, it contributed to the homogeneity of the membrane by facilitating the formation of a more uniform membrane structure than the pristine membrane (M0).

The water uptake of the prepared membranes was investigated with an emphasis on finding the impact of resin loading on the membrane. Figure 4(a)

presents the prepared membranes' water uptake. Incorporating PEG into the casting solution produced macro voids, voids, and vacant regions inside the membrane (Hosseini *et al.*, 2014). These macrovoids allowed the membrane to retain additional water molecules. Furthermore, introducing cation exchange resins particles into the membrane matrix introduced irregularities in the polymer structure, resulting in extra water pockets (Kumar *et al.*, 2014). Initially, the membranes' relatively low water uptake value of 40.3% indicated the inherent hydrophobic nature of the PVDF membrane. Subsequently, as the resin concentration increased, the water uptake of cation exchange membranes gradually rose from 59.0 % (M5) to 76.6 % (M20). The observation made was consistent with the expected results. Due to the presence of functional groups, specifically the $\text{-SO}_3\text{H}$ group in cation exchange resins, which can interact with water molecules, the hydrophilic properties of the membrane tend to increase as the resin content rises.

The ionic conductivity of the prepared membranes can be measured using an index called ion exchange capacity. Figure 4(b) presents ion exchange capacity measurements of the prepared membrane. As shown in Figure 4(b), the ion exchange capacity rose approximately in proportion to the available resin on the prepared membrane.

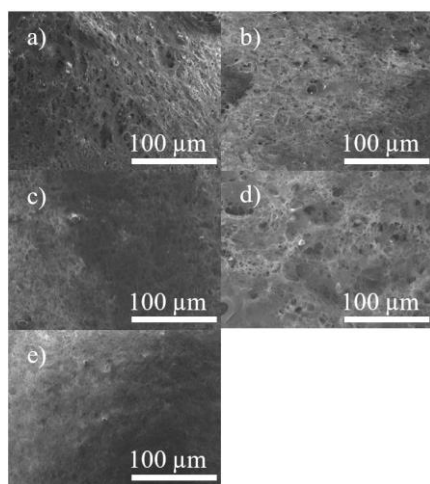


Figure 3. SEM images of the prepared membrane a) M0, b) M5, c) M10, d) M15, and e) M20

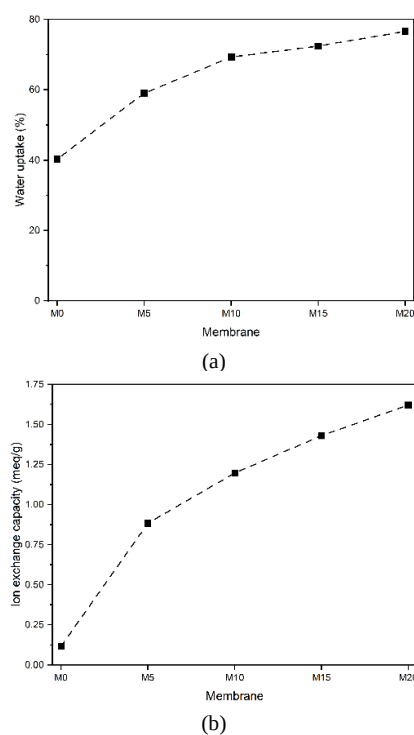


Figure 4. a) Water uptake of the prepared membrane; b) Ion exchange capacity of the prepared membranes

The initial ion exchange capacity value of the pristine membrane (M0) was 0.12 meq.g^{-1} . The ion exchange capacity value increased from 0.88 to 1.62 meq.g^{-1} as the quantity of resins in ion exchange membranes risen from 5% to 20% by weight of resin. As stated previously, when the ratio of resins increases, the density of ionic functional groups also increases. The presence of the $-\text{SO}_3\text{H}$ group improved polar-polar interactions between the surface of cation exchange membrane and the solution (Zhang *et al.*, 2015). This enhanced the ion exchange capacity, making it easier for ions to migrate through the membrane.

The electrosorption experiment comprised 10 cycles, during which the performance of the CDI cell and MCDI cell in the membrane M20 was compared in the presence of Cu^{2+} at a concentration of 500 mg.L^{-1} . Figure 5 illustrates the adsorption capacity and recovery efficiency of Cu^{2+} at different voltages in CDI and MCDI cells.

In Figure 5(a), the adsorption amount of Cu^{2+} in the CDI cell was determined to be 6.2 mg.g^{-1} , while the MCDI cell equipped with membrane M20 achieved an adsorption amount of 6.9 mg.g^{-1} after the 10th cycle at the voltage of 1.2 V. Throughout this investigation, MCDI consistently demonstrated greater adsorption capacities for Cu^{2+} than CDI. In addition, the increased applied voltage from 0.4 V to 1.2 V increases the adsorption amount and recovery rate of Cu^{2+} in both CDI systems. This

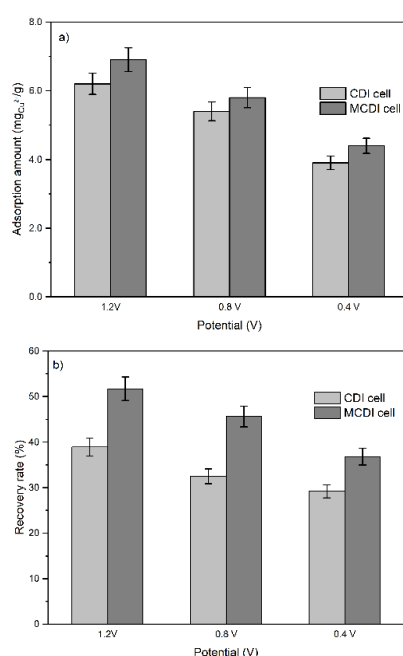


Figure 5. The value of a) adsorption amount and b) recovery rate of Cu^{2+} in both CDI cell and MCDI cell at various voltages of the 10th cycle

increase is attributable to the improved electrostatic interaction between electrodes, which influenced the overall efficiency of Cu^{2+} removal. Regarding recovery rates, it is important to note that the performance of MCDI outperformed CDI. This observation suggests that using ion exchange membranes by cation exchange resins increases the recovery rate of Cu^{2+} from solution. MCDI obtained a remarkable recovery rate of 51.7%, whereas CDI reached a maximum recovery rate of 33.9% at 1.2 V, as revealed in Figure 5(b).

Incorporating heterogeneous cation exchange membrane in the CDI system has substantially enhanced the adsorption capacity and recovery rate. This improvement is attributable to the design of heterogeneous membranes, which integrate multiple layers with varying pore sizes. These distinctive membrane characteristics permit increased ion removal from the input stream while minimizing ion losses during regeneration.

Figure 6 depicts the current profiles in both CDI systems of the adsorption and desorption processes at the 10th cycle. The MCDI cell displayed a significantly higher current reading during the charging phase than the CDI cell, indicating a faster ion adsorption rate. This revealed that the Cu^{2+} adsorption capacity of the CDI cell was measured at 6.2 mg.g^{-1} , while the MCDI cell displayed a higher adsorption capacity of 6.9 mg.g^{-1} . Figure 6 also shows that the MCDI cell's discharge phase exhibited a delayed saturation rate compared to the CDI cell, leading to an improved ion adsorption capacity for the MCDI cell compared to the CDI cell.

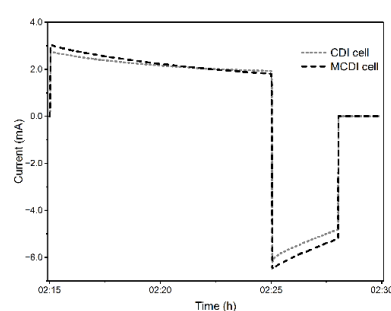


Figure 6. Comparison of the current profile of CDI cell and MCDI cell at the 10th cycle

Conclusions

Heterogeneous membranes were successfully produced by incorporating cation exchange resins onto the membrane surface via the nonsolvent-induced phase inversion process. The resin loading

on the membrane had an evident impact on the membrane structure and significantly enhanced the capability to remove Cu^{2+} . The presence of sulfonic acid groups (evidenced by distinct peaks at $1,007\text{ cm}^{-1}$, $1,035\text{ cm}^{-1}$, and $1,128\text{ cm}^{-1}$) indicated that cation exchange resins were successfully incorporated into a pristine membrane (M0). Consequently, the holes on the membrane surface were effectively filled, resulting in a more uniform and homogeneous surface. In addition, both water uptake and ion exchange capacity exhibited an upward trend as resin loading improved. By employing a membrane containing 20% resin by weight (M20) in MCDI cell, notable electrosorption was attained, resulting in an increase in the Cu^{2+} adsorption capacity from 6.2 mg.g^{-1} (CDI cell) to 6.9 mg.g^{-1} (MCDI) at 1.2 V at the 10^{th} cycle. This study indicated that incorporating additional resins into heterogeneous membranes is a viable strategy for improving the efficiency of Cu^{2+} removal in CDI systems. Future research should investigate the effects of various resins to widen the options of targeted ion selection in solution. To obtain an in-depth overview of the membrane properties, a cross-section SEM picture, the loading capacity of the membrane, and the influential role of water uptake capacity from the membrane on the MCDI system should be analyzed to provide visibility into the membrane's structure.

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