

Carbon Dioxide-Mediated Desalination

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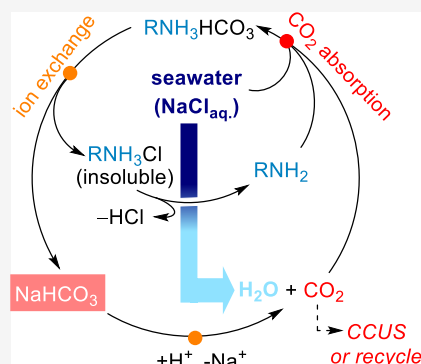


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Supporting Information

ABSTRACT: Conventional desalination membrane technologies, although offer portable drinking water, are still energy-intensive processes. This paper proposes a potentially new approach for performing water desalination and purification by utilizing the reversible interaction of carbon dioxide (CO_2) with nucleophilic amines—reminiscent of the Solvay process. Based on our model studies with small molecules, CO_2 -responsive amphiphilic insoluble diamines were prepared, characterized, and applied in the formation of soda and ammonium chloride upon exposure to ambient CO_2 (1 atm), thus removing chloride ions from model and real seawater. This ion-exchange process and separation of chloride from the aqueous phase are spontaneous in the presence of CO_2 without the need for external energy sources. We demonstrate a flow system to envisage energy-efficient CO_2 -mediated desalination and simultaneous carbon capture and sequestration.



INTRODUCTION

Water is arguably the most important molecule for life on Earth, providing the media in which complex chemical reactions and equilibria create the very essence of life as we know it. However, accelerated global industrialization, among other factors, is leading to unpredictability in secure water supply and is thus threatening the society's sustainable growth.¹ Desalination of seawater or brackish water is a possible approach to secure potable water supply.² Although reverse osmosis implemented with membrane materials can lead to efficient desalination processes, more practical and low-carbon-footprint processes are required and are yet to be developed.³ We propose a potential approach of performing seawater desalination by utilizing the reversible interaction of carbon dioxide (CO_2) and nucleophilic amines. CO_2 -responsive amphiphilic insoluble diamines were prepared, characterized, and applied in the formation of soda and insoluble ammonium chloride upon exposure to CO_2 , thus removing chloride ions from model and real seawater. A treatment with acidic resin and separation afforded desalinated water, without the need for external energy sources, accomplishing conceptual desalination by only using catalytic resources: CO_2 and recyclable diamines, both of which can be regenerated via acid–base chemistry.

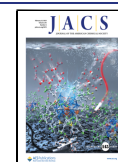
A solution of seawater consists mainly of sodium chloride (85.6% of solubilized ions by weight), which exhibits a positive enthalpy of solution (3.88 kJ/mol). However, the high solvation energy of ions in water hinders the liquid–liquid and solid–liquid extraction of salt—namely, sodium and chloride ions—from water.⁴ To circumvent the use of heat and electrical energy in a desalination process, we envisaged that recognition of sodium and chloride ions will be critical for the

success of desalination. Chloride ions in aqueous systems pose a significant environmental and agricultural threat because of the excessive use of the water softener.^{5,6} Various chloride ion recognition and sequestration processes in aqueous solutions have been reported, mainly in the realm of supramolecular host–guest chemistry with sophisticated receptors, which require strenuous synthetic procedures.^{7–12} Recently, polymeric variants of host–guest chemistry showed a promising performance in chloride ion capture, an approach that may lead to a whole new path for desalination processes.^{13–15}

Although carbon dioxide is one of the most problematic greenhouse gases, its low toxicity and accessibility prompted us to apply it in water purification and desalination processes. Sequestration of heavy metal ions from aqueous media has been achieved by harnessing the reactivity of amines with CO_2 , with insoluble oligomeric amines providing heterogeneous environments to form separable complexes.^{16–18} Another such example is the Solvay process (Figure 1A)—a process for industrial production of soda ash from seawater, CO_2 , and ammonia—which operates based on CO_2 –amine chemistry, by providing an ion-exchange system that precipitates out sodium bicarbonate from the basic solution.¹⁹ In the process, the water-soluble ammonium chloride is treated with a base, namely, CaO , to regenerate the “catalytic” amine and CO_2 .

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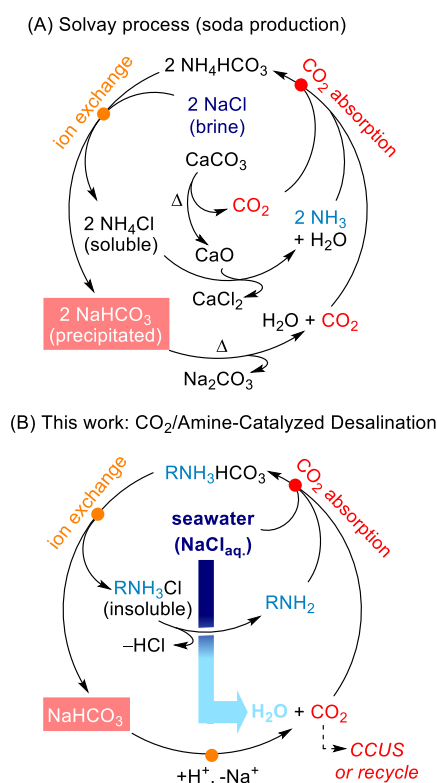


Figure 1. Schematic representation of the (A) Solvay process and (B) desalination mediated by CO_2 and insoluble diamines (R-NH_2) and their regeneration.

Various organic amines can reversibly form complexes with carbon dioxide, resulting in the thermally labile carbamate and bicarbonate/carbonate salts.^{20,21} Under reduced pressure or mild heat, dissociation of CO_2 from the diamines occurs, and the parent diamines can be regenerated. This reversible carbon dioxide capture process has been applied in carbon capture processes,²² switchable solvents,¹⁶ and heavy metal extraction.^{17,23} CO_2 -responsive autonomous aggregation (or precipitation) is controlled by polarity alteration of the monomeric entity, which is key to induce this dynamic behavior.²⁴ An example of the spontaneous self-assembly of nanomaterials was demonstrated by decorating gold nanoparticles with diamines, upon which the materials self-aggregate, driven by the surface polarity changes in nanoparticles on CO_2 exposure.²⁵

Given the above discussed precedents, and as a working hypothesis, we envisioned that reversible CO_2 -responsive formation of ammonium bicarbonate could induce spontaneous ion exchange with anions from a feeding solution (Figure 1B).²⁶ The sodium ions could then be removed from seawater via the formation of bicarbonate using the so-called dual alkali approach, which mimics the Solvay process.^{27,28} However, to achieve complete desalination, it would still be necessary to remove water-soluble ammonium chloride (NH_4Cl). We hypothesized that this process could be controlled by insoluble diamines or polymeric CO_2 -responsive materials, thus controlling the solubility of ammonium chloride salt, RNH_3Cl .^{27,28} The insoluble alkyl ammonium chloride could then be collected, regenerated, and recycled via stoichiometric base treatment, thus providing a more energy-efficient catalytic desalination than the traditional thermal and reverse osmosis processes.

RESULTS AND DISCUSSION

Model Seawater Desalination Using Small-Molecule Diamines. To accelerate the screening of the functional groups of CO_2 -responsive organic materials to be used in the proposed desalination application, we evaluated the performance of diamines in terms of conductivity, a measure that can provide information on the mobilities of ions, viscosity, and CO_2 responsiveness. Conductivity was thought to be an important metric to facilitate amine structure screening. According to our hypothesis, it is critical to equip the process with highly active amine absorbents which can mediate ion exchange while remaining insoluble during the whole process for fast recovery of the ammonium chloride. Conductivity measurements give a fast real-time response from CO_2 bubbling and the formation of insoluble structures. Therefore, we performed the screening experiments using a model seawater solution (20 mL, NaCl 35 g/L) with an organic compound (10 wt %, approximately 10 equiv based on NaCl) and CO_2 (99.6% purity, >50 mL/min). We extensively tested several nitrogen-based compounds. Most of the conventional diamines, amino alcohols, and their derivatives resulted in a homogeneous solution and, therefore, mostly increased the conductivity of the solution upon CO_2 bubbling. This can be ascribed to the increased concentration of ammonium carbonate and bicarbonate ions in the solution, without phase separation. Alkylated diamines (Figure 2A; also see Figure S2), however, showed a significant conductivity reduction, potentially because of spontaneous and reversible hydrogel formation. Further optimization revealed that both tertiary and secondary amines are important. *N,N*-dimethyl-1,3-propanediamine (P) showed the highest observed reduction of conductivity (92% within 2–10 min) when alkylated with a C12 (dodecyl) unit (C12P, Figure 2B). We evaluated some critical molecular functional groups—long alkyl chain (>C10) and diamine groups with a secondary and a tertiary amine.

Next, we quickly verified that the chain length of the alkylated diamines plays a significant role in the CO_2 absorption and conductivity reduction and, therefore, should heavily affect performance (Figure 2C). It became clear that the chain length C11–C12 is optimal, with longer chain lengths (C13–C16) being detrimental because of their insolubility in water, both with and without CO_2 . The optimal diamine (C12P) showed critical micelle formation concentration (CMC) at around 0.3 M at room temperature (Figure 2D). The presence of CMC indicates the importance of the self-aggregation feature, which is sensitive toward pH: disaggregation was observed after continuously injecting CO_2 . An acidic medium was formed after 10 min of continuous CO_2 bubbling, reaching pH 4, when the formation of micelles was reversed based on the measurement of viscosity and dynamic light scattering (DLS, Figures S5 and S6). A higher conductivity reduction was obtained at higher temperatures, even though a full recovery of the conductivity was detected after 10 min (Figure 2E). We postulated that the hydrophobicity of C12P was increased at higher temperatures, leading to a more significant conductivity reduction, induced by the formation of micelles with random size distribution.²⁹

Further investigation in larger-scale experiments (1 L of model seawater with C12P) was conducted under a continuous measurement of pH and conductivity (Figure S7). We confirmed that the turbidity and solubility of the

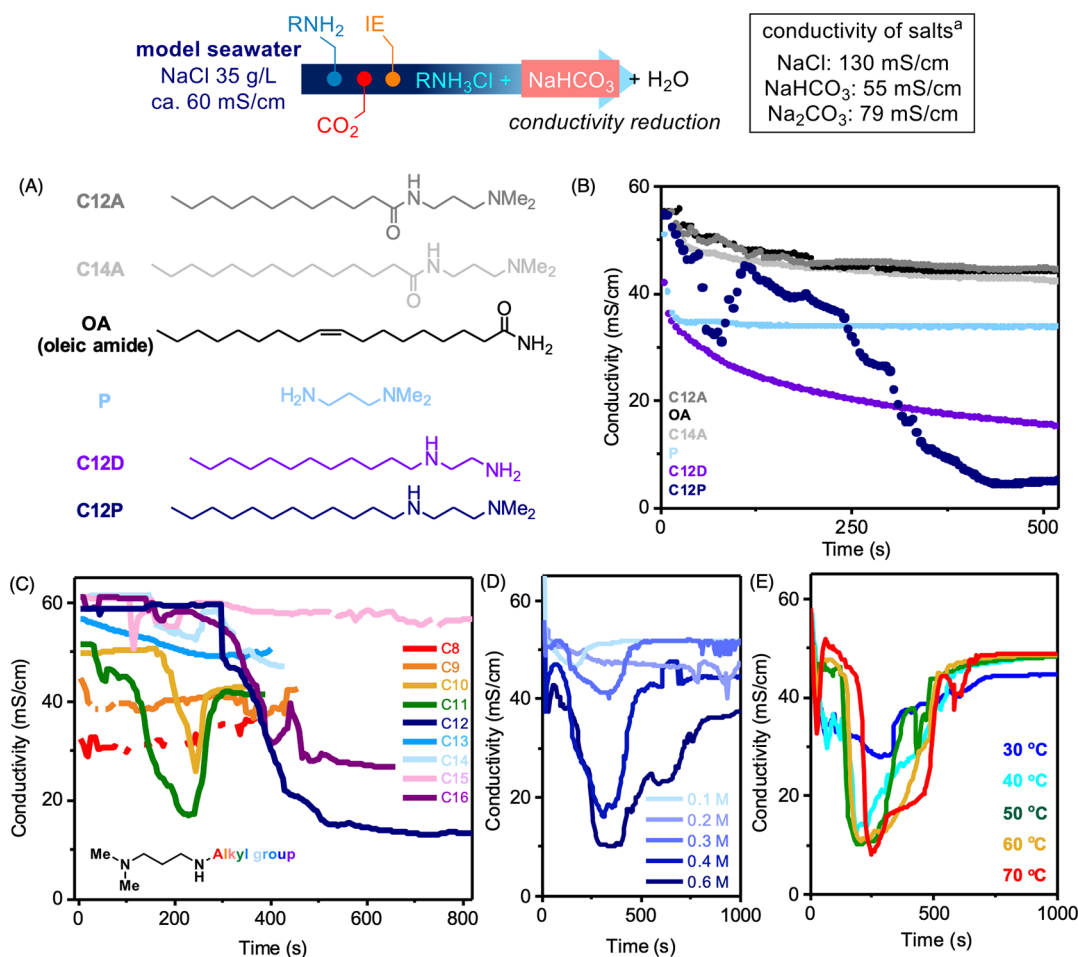


Figure 2. Conductivity measurements of model seawater using small-molecule diamines. (A) Chemical structures of representative amines. Conductivity measurements with continuous CO₂ injection (99.9%, 15 mL/min, open system) into diamine-containing saline solutions at room temperature. Effects of (B) different CO₂-responsive molecules and (C) chain length of the diamine. Alkyl group (C_n): linear C_nH_{2n+1}, (D) different concentrations of diamine C12P, and (E) different temperatures. ^aConductivity of 10% (w/w) in brine at 25 °C.³⁰

diamines were directly correlated with the observed pH, which can be controlled by the amount of CO₂ injected to form carbonic acid, bicarbonate, and carbonate ions. By measuring the gas feed at the inlet and outlet, we determined that approximately 0.33 equiv of CO₂ was needed to reach minimum conductivity (Figure S8), presumably by forming mostly ammonium bicarbonate salts (Figure S9). During the process, the pH of the solution increased to 10.5 after the addition of C12P but afterward dropped dramatically, buffering at 8–9 (pK_a of alkylammonium chloride = ca. 9–10 and carbonic acid = 6), the point where the lowest conductivity was observed. It is important to note that the measured conductivity is not correlated with the salinity of the solution, given that the mixture of diamine and CO₂ in NaCl solutions forms a turbid mixture with unidentifiable aggregates. DLS measurements suggest the formation of aggregated particles (ca. 700 nm), albeit with a random and broad distribution of particle sizes (Figure S6). A mathematical analysis based on the theoretical molar conductivity of Na⁺, Cl[−], HCO₃[−], H⁺, and hydroxide confirmed a 23% conductivity reduction when a quantitative anion exchange occurs with ca. 0.3 equiv of bicarbonate from CO₂. Therefore, the extra reduction of conductivity in our experiments can be attributed to the formation of aggregates, which affects the viscosity of the solution and the mobility of ions in the solution.

To verify the applicability of our method toward removal of chloride from sea water, we used broad-range ²³Na and ^{35/37}Cl NMR spectroscopy to determine the concentrations of sodium and chloride ions in the solution before and after the CO₂–diamine process (Table S1). The solution with a treatment of only diamine or only CO₂ showed no significant difference from the non-treated water sample (entries 1 and 2). We observed a reduction of chloride ions of up to 27% after membrane (cutoff range 10 kDa) and filter paper filtration (entries 3 and 4). This experiment manifested the formation of insoluble particles containing chloride ions, with the sodium ions still being retained in the solution with bicarbonate counteranions. An argentometry (Mohr method) and high-pressure ion chromatography (HPIC) analysis further confirmed the sequestration of chloride from the aqueous phase, while the analysis of organic and inorganic carbon showed a quantitative yield of bicarbonate ions, which is in accordance (in terms of mass balance) with the anion-exchange process.

Modification of Polymeric Diamines for Desalination of Model and Real Seawater. We then addressed the difficulties associated with the separation and regeneration of small organic compounds by preparing polymeric and resin-bound materials, an approach that should enable a more efficient recovery of the diamine and minimize the risk of

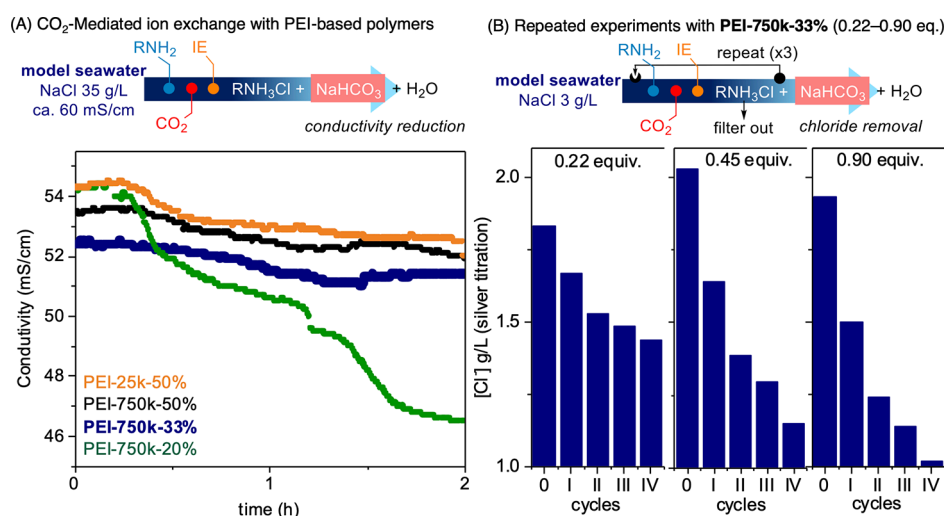


Figure 3. Influence of alkylation degree and molar ratio on chloride reduction using hydrophobic PEIs. (A) Desalination using PEI-based polymers with 35 g/L NaCl model seawater solution. (B) Effect of molar ratio between PEI-polymers (PEI-750k-33%) and NaCl for 3 g/L NaCl model seawater for repeated chloride removal.

potential contamination of the purified water with excess solubilized diamines. Polyethyleneimines (PEI)—amine-based polymers³¹—were initially chosen to optimize the functional groups by their varying branching degrees, hydrophobicity, and molecular weight, parameters that can control the compatibility of polymers in water.³² Chemical functionalization of commercially available PEI was performed, and alkyl chain-modified PEIs with different alkyl chain lengths (C8–C16) were generated. We also varied the stoichiometry of the alkyl halide reagents to control the amphiphilicity of the modified PEIs. Among these, for example, C16-alkyl chain-modified PEI (with an average molecular weight of 750,000 g·mol^{−1}), upon exposure to CO₂ in saline water (35 g/L NaCl), presented a higher ion-exchange capacity than others. We observed up to 7 g/L chloride ions captured in the polymer, providing >99% of recovered water (0.99 L, Table S1, entry 5) after simply filtering the mixture with conventional filter paper. We then evaluated the effect of the alkylation degree (20–50%, when compared to the number of nitrogens; Figure 3A). PEI-750k-20% at a lower alkylation degree afforded a gel-state morphology, while a higher than 30% alkylation resulted in a powder form. The molar ratio of PEI-750k-33% compared to NaCl was important to maintain optimal performance of chloride removal: we found that a 0.9 equimolar ratio of the polymer showed the highest chloride removal performance (Table S3). Based on our NMR analysis, silver titration, conductivity measurement, and HPIC analysis, >50% of chloride ions were removed after five cycle periods starting from a 3 g/L NaCl model seawater solution (Figure 3B). It is noteworthy that the solution became basic after the fifth cycle, due to the generation of NaHCO₃ via CO₂ capture, and, therefore, the conductivity measurement alone was not reliable as a proxy to analyze chloride concentration.

Complete Desalination of Regenerated Polymeric Diamines for Real Seawater. The polymer was easily recyclable after washing it with a hydroxide solution, affording quantitative recovery yields of the polymers. The polymers were then used for further cycles, exhibiting compatible ion-exchange capacity under CO₂ conditions for up to six cycles. The chemical and physical behavior and stability of the optimal polymer PEI-750k-33% were investigated by ¹H NMR

spectroscopy, thermogravimetric analysis (Figures S10–S17), and titration (Figure S18), thus confirming the regeneration of the free amines under our regeneration conditions. In addition, the analysis of the filtrate water showed no detectable diamine or PEI units, indicating that the PEIs were stable under both the CO₂ conditions and the regeneration process. With recyclable polymer PEI-750k-20%, a preliminary test with real seawater samples (salinity: 18 g/L, obtained from the Copenhagen canal in August 2021, Figure 4A–E) showed a CO₂ effect on chloride ion removal, manifesting the robust ion-exchange mechanism in the presence of an ammonium bicarbonate/carbonate system (Figure 4B; also see Figures S19 and S20 for the effect of the molar ratio between polymers and NaCl). A silver titration and HPIC analysis of the remaining seawater confirmed efficient chloride ion removal, over 20% of chloride ions, by simply bubbling the solution of seawater with CO₂ in the presence of the polymer (Figure 4C). The in situ-generated NaHCO₃ from real seawater (Figure 4D) was conveniently removed by treating the filtrate solution with a commercially available sulfonic acid-based resin (marked with stars, after third, fifth, and sixth cycles; Figure 4E), decomposing NaHCO₃ to CO₂ and water while sequestering sodium ions as sulfate on the polymer. This process overall completes the removal of sodium and chloride ions from real seawater without an external energy input besides the chemical potential of acids and bases used for regeneration (Figure 4F). Considering that CO₂ had been utilized as a regenerant for cation-exchange resins, we believe that the CO₂ can be the sole input in complete desalination, at least, from low-salinity brine solutions, while capturing gaseous CO₂ in the solution.^{33,34}

Use of Diamine-Functionalized Resin in the Continuous Flow Process. To provide conceptual feasibility of our desalination system, we synthesized a diamine-modified resin (Figure 5A) for the continuous ion-exchange process in a 1 L column (Figure 5B). A resin without the diamine modification also showed no activity toward CO₂ in chloride ion removal (see Supporting Information, Figure S21). We performed a set of breakthrough experiments showing a high chloride ion removal rate (up to 80% from 0.08 M [NaCl], 1.5 L/h) after purging the amine-packed column with pure CO₂ until saturation (Figure 5C). Importantly, no ion-exchange

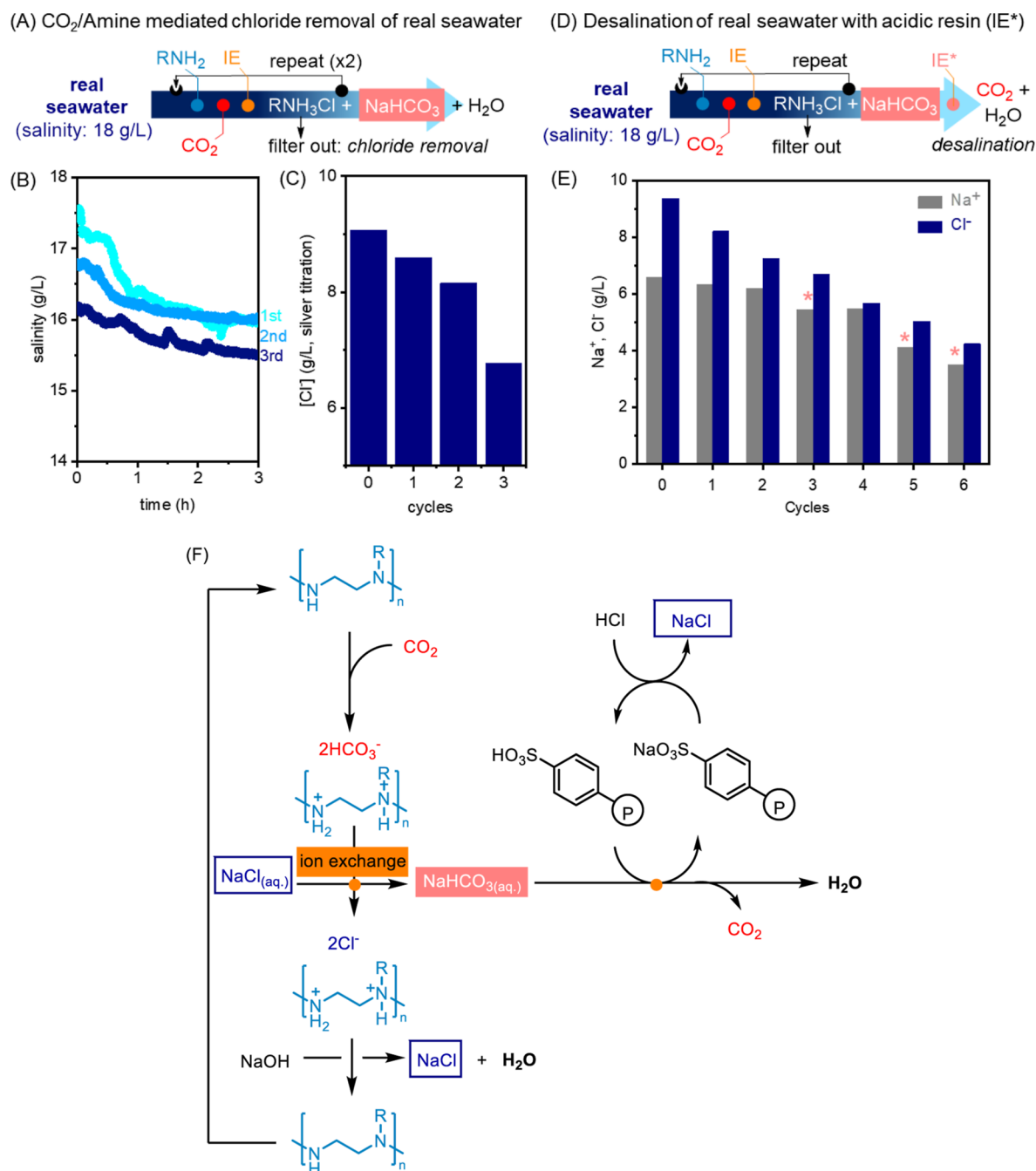


Figure 4. (A) Real seawater chloride removal using PEI-750k-20%, 0.30 molar ratio, at 15 °C. (B) In situ salinity measurements using a conductivity meter. (C) Silver titration of solution after each cycle. (D) Desalination of real seawater using PEI-750-20% (0.3 molar ratio compared to NaCl, 15 °C). (E) Observed Na⁺ and Cl⁻ ion concentration (g/L) over cycles. *indicates polystyrene sulfonic acid treatment (0.5 molar ratio, 1 h, room temp.) for Na⁺/H⁺ exchange and sodium ion removal. (F) Overall reaction pathway for Cl⁻ and Na⁺ removal from seawater using CO₂, diamines, cation-exchange resin, and acid-base.

activity was observed without CO₂, implying that the ion-exchange process only occurs after in situ formation of ammonium bicarbonate after the activation of the resin-charged column with CO₂. The captured chloride ions were quantitatively recovered after treating the column with a basic KOH or NaOH solution (0.1 N) without using excess amounts of bases in continuous experiments (Figure S5D). It is important to note here that the regenerated resin showed no sign of degradation after more than 30 experiments with model and real seawater samples (Figure S22). Furthermore, our process provides mildly basic bicarbonate solution at the efflux,

thus potentially applicable for controlling chloride concentrations in providing soft water and desalinating low-concentration brine feed where RO membranes exhibit a lower performance. A dual-alkali process can be applied to precipitate and remove sodium carbonate/bicarbonate, thus completing the desalination with modified resin, polymers, and monomers.

CONCLUSIONS

The cost and energy input, with the current setup, are solely associated with resin regeneration which requires stoichio-

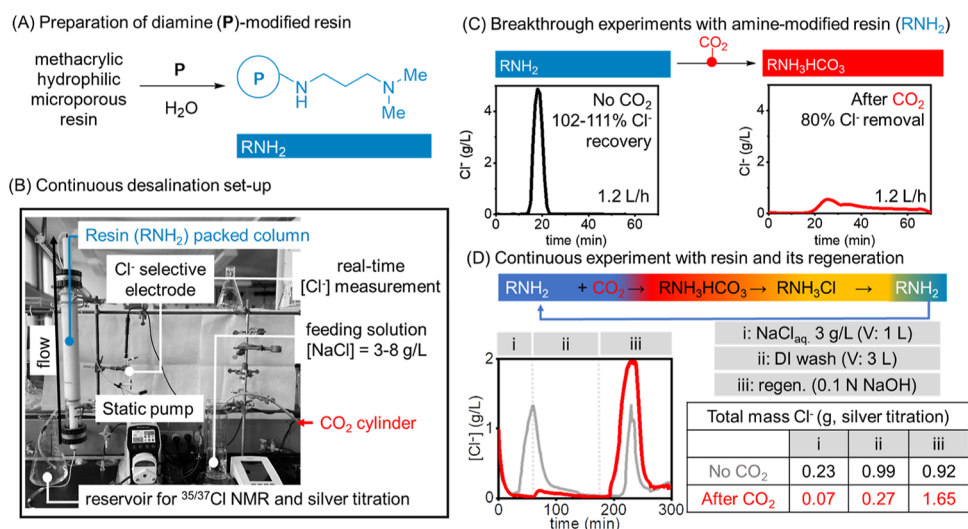


Figure 5. Diamine-modified resin for continuous desalination. (A) Scheme for preparation of diamine-modified resin, (B) desalination setup, (C) chloride ion breakthrough experiment, and (D) continuous chloride removal and resin regeneration (rate: 1.5 L/h) measured by a chloride-selective electrode and total mass of chloride in each phase: (i) saline water injection, (ii) DI water wash, and (iii) regeneration of resin using 0.1 N NaOH solution until no chloride ion was detected by the chloride ion-selective electrode.

metric amounts of NaOH for ammonium chloride salt of PEI and HCl for sodium salt of sulfonate resin (see Supporting Information, Figure S24). Without sophisticated modeling, the energy consumption for the production of HCl and NaOH based on the chloralkali process (brine electrolysis) can be translated for the regeneration cost, approximately 4–18 kWh/ m^3 desalinated water at 3–15 g/L salinity based on the energy consumption of the chloralkali process.³⁵ Therefore, further developments in desalination in continuous flow reactors and their combination with CO_2 capture³⁶ and sequestration processes are foreseeable by coupling with electrochemical pH swing for efficient column regeneration.^{37,38} This is to improve the efficiency of the regeneration step, which is the only step that requires an energy input. Further developments in advanced polymers, resins, and porous materials with high amine loadings that allow facile diffusion of ions and their exchange are expected to overcome the current limitations associated with the slow “ CO_2 -treatment” step, in order to utilize ambient CO_2 sources, for example, from flue gas or even directly from air.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.2c11880>.

Materials, methods, salinity reduction measured by conductivity, silver titration, benchtop ^{23}Na and $^{35}/^{37}\text{Cl}$ NMR, and HPIC, calibration of salinity meter and influence of continuous CO_2 bubbling, screening of various organic amines, conductivity measurements over time at room temperature, comparison of viscosity and pH over time, dynamic light scattering measurements, large-scale conductivity measurement, stoichiometry of required CO_2 , NMR spectra, TGA analysis, pH measurements, chloride removal from real seawater, effect of molar ratio between PEI-polymers and NaCl, chloride ion breakthrough experiments, continuous chloride removal experiments, experimental setup for testing of the ion exchange capacity toward chloride,

chloride mass balance, comparison of performance in terms of chloride ion removal per nitrogen atoms, and energy consumption comparison (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare the following competing financial interest(s): JWL declare the existence of a financial/non-financial competing interest based on the filed patent applications (PA201870726, PCT/EP2019/080221).

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