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Technical, Economic, Energetic, and Environmental Evaluation of Pretreatment Strategies for Scaling Control in Brackish Water Desalination Brine Treatment

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Abstract: Effective pretreatment is essential for achieving long-term stable operation and high water recovery during the desalination of alternative waters. This study developed a process modeling approach for technical, economic, energetic, and environmental assessments of pretreatment technologies to identify the impacts of each technology treating brackish water desalination brine with high scaling propensity. The model simulations evaluated individual pretreatment technologies, including chemical softening (CS), chemical coagulation (CC), electrocoagulation (EC), and ion exchange (IX). In addition, combinations of these pretreatment technologies aiming at the effective reduction of key scaling constituents such as hardness and silica were investigated. The three evaluation parameters in this assessment consist of levelized cost of water (LCOW, $/m^3), specific energy consumption and cumulative energy demand (SEC|CED, kWh/m^3), and carbon dioxide emissions (CO_2, kg $CO_{2\text{-eq}}$/m^3). The case study evaluated in this work was the desalination brine from the Kay Bailey Hutchison Desalination Plant (KBHDP) with a total dissolved solids (TDS) concentration of 11,000 mg/L and rich in hardness and silica. The evaluation of individual pretreatment units from the highest to lowest LCOW, SEC|CED, and CO_2 emissions in the KBHDP brine was IX > CS > EC > CC, CS > IX > EC > CC, and CC > CS > EC > IX, respectively. In the case of pretreatment combinations for the KBHDP, the EC + IX treatment combination was shown to be the best in terms of the LCOW and CO_2 emissions. The modeling and evaluation of these pretreatment units provide valuable guidance on the selection of cost-effective, energy-efficient, and environmentally sustainable pretreatment technologies tailored to desalination brine applications for minimal- or zero-liquid discharge.

Keywords: process modeling; pretreatment technology; desalination brine treatment; technoeconomic analysis; carbon emissions; specific energy consumption

Academic Editor: José Luis Sánchez-Lizaso

Received: 28 January 2025
Revised: 15 February 2025
Accepted: 17 February 2025
Published: 28 February 2025

Citation: Lugo, A.; Mejía-Saucedo, C.; Senanayake, P.S.; Stoll, Z.; Sitterley, K.; Wang, H.; Kota, K.; Kuravi, S.; Fthenakis, V.; Kurup, P.; et al. Technical, Economic, Energetic, and Environmental Evaluation of Pretreatment Strategies for Scaling Control in Brackish Water Desalination Brine Treatment. *Water* **2025**, *17*, 708. https://doi.org/10.3390/w17050708

1. Introduction

Water is essential for human life, economic development, and environmental sustainability through its efficient use and reuse. Ninety-seven percent of the water on Earth is saline or hypersaline, making desalination a critical treatment technology that can help augment freshwater supplies. Desalination of seawater, brackish water, and industrial/municipal wastewater has been increasingly utilized to provide a viable option to meet the global freshwater demand, which is expected to double in the future, driven mainly by population growth and rising industrial water uses [1,2]. The implementation of desalination systems inevitably needs to address the management and disposal of desalination brine (also known as reject or concentrate) with total dissolved solids (TDS) concentrations between 5000 and 300,000 milligrams per liter (mg/L).

Brine is a concentrated saline water generated from desalination processes. The annual global brine production from desalination facilities was estimated at 51.7 billion cubic meters (m^3) in 2019, which is 50% greater than the average volume of desalinated water, indicating the magnitude of brine that can be produced in the future associated with increasing desalination capacities [3–5]. The disposal of the generated brine can have potential environmental impacts due to its high salinity, temperature, pH, and the potentially harmful chemicals it may contain [6,7]. Most seawater desalination facilities dispose of the generated brine in a nearby marine environment. Facility operators and planners must account for the vulnerability of the marine environment to minimize the environmental implications of the brine salinity and consider blending with lower salinity water to reduce its salinity impact [8,9]. Potential negative effects on the environment include disruption of the osmotic balance of marine species and accumulation of harmful treatment chemicals (e.g., antiscalants) in the discharge area if the marine environment is not suitable for brine disposal [7,8,10,11].

Inland desalination has been the center of attention in many applications since it accounts for the desalination of alternative waters such as brackish water, agricultural, power plant, oil and gas, and municipal/industrial wastewater [12,13]. Inland desalination brine can be disposed of through several methods, such as sewer discharge, deep-well injection, evaporation ponds, surface water discharge, or land application on salt-tolerant plants. Some of the common adverse environmental impacts of inland brine disposal methods involve the inhibition of bacterial growth (sewer discharge to wastewater treatment facilities), groundwater pollution and soil salinization (evaporation ponds, deep-well injection, and land application), and aquatic environment pollution (surface water discharge) [7,14]. The lack of economically feasible and ecologically sustainable inland brine management/treatment options is a major barrier to the broad implementation of desalination technologies [2,15,16].

Brine treatment to achieve minimal liquid discharge (MLD) or zero liquid discharge (ZLD) is critical to recovering additional water for use and minimizing brine volume for disposal. ZLD aims to recover ~100% of the influent water as a product, whilst MLD is a near-zero liquid discharge that aims to recover freshwater at nearly 95% [17,18]. The primary focus of most treatment assessments has been centered on reducing the high energy and cost demand of desalination, evaporation, and crystallization stages in MLD/ZLD [18]. There is a growing emphasis on utilizing high-pressure reverse osmosis (HPRO) technologies (>120 bar) to treat hypersaline brines (TDS $\geq$ 70 g/L) for MLD applications, as they offer a more energy-efficient alternative to traditional thermal-based methods with energy-intensive phase-change-based desalination [19]. These membrane-based approaches lower the energy consumption and cost of hypersaline brine desalination by eliminating phase transitions. In addition to HPRO, desalination methods such as membrane distillation and forward osmosis have also been explored as other alternatives in MLD applications [20,21].

Pretreatment, as shown in Figure 1, is essential for both MLD and ZLD applications because it can ensure an effective operation, enable higher water recovery, and extend the lifetime of downstream treatment processes by minimizing fouling and scaling of treatment/desalination equipment [22,23].

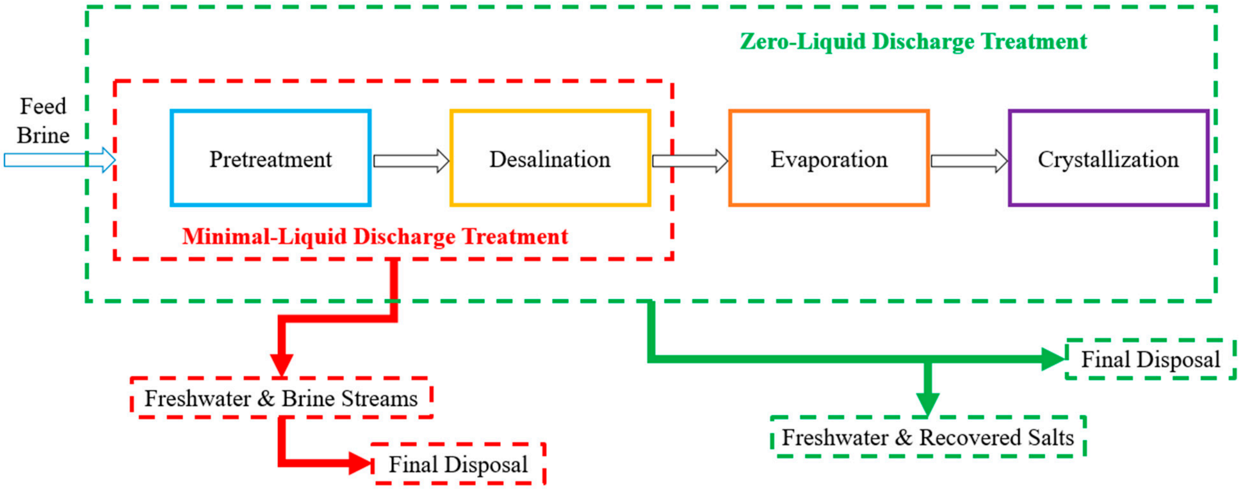

Figure 1. MLD and ZLD treatment stages.

Most evaluations of desalination and brine treatment assume the presence of primarily monovalent ions, e.g., sodium (Na^+) and chloride (Cl^-), in the brine. The presence and the impact of sparingly soluble minerals, e.g., calcium (Ca^{2+}), magnesium (Mg^{2+}), carbonates (HCO_3^- and CO_3^{2-}), sulfate (SO_4^{2-}), and silica (SiO_2), are often neglected [24]. An assumption for the exclusion of divalent ions in a desalination application is that they should have been completely removed in the pretreatment stage before desalination [17]. This, in turn, does not provide a complete outlook of the technoeconomic impacts when evaluating these applications and limits possible optimization options. The integration of pretreatment is, therefore, a crucial aspect in generating a complete picture of an MLD/ZLD treatment system. Providing a thorough economic, energetic, and environmental impact assessment can assist in evaluating the appropriate individual or combination of pretreatment technologies for scaling and fouling control.

This study is focused on the use and development of unit models with experimental data validation and evaluation of pretreatment technologies to demonstrate both the benefits and the downsides of the pretreatment units. Unlike previous studies that focus on individual treatment methods, this research provides a comparative analysis of standalone and coupled pretreatment strategies, identifying optimal configurations based on energy efficiency, operational cost, and performance in desalination brine treatment.

The main case study in this work is the desalination brine from the brackish water reverse osmosis (RO) process in the Kay Bailey Hutchison Desalination Plant (KBHDP) in El Paso, Texas, United States, which is the world's largest operational inland desalination plant. Process unit models were used to simulate the operation of different pretreatment processes to provide baseline approximations of the energy and operational costs and identify where improvements need to be made to minimize costs and/or energy consumption. The WaterTAP program, an open-source program developed by the National Alliance for Water Innovation, was utilized to provide model simulations of water treatment systems under steady-state conditions to estimate performance, energy, and costs [25]. In addition, the incorporation of other software, such as PHREEQC v3 (2021) [26] and Avista's AdvisorCi (Avista AdvisorCi Online) [27], was deemed useful to evaluate the need for pretreatment in a system based on the input and target water quality. For consistency in this evaluation, we assume that the water quality leaving each pretreatment process is comparable, enabling a direct comparison of unit performance in terms of cost, energy, and environmental impact. While variations in effluent water quality may exist in real-world applications, this assumption allows for a relative assessment of each process under similar operational conditions.

2. Pretreatment of Brine

Brine with a high concentration of organics and sparingly soluble salts can cause organic fouling and scaling in membrane desalination technologies, respectively. Multiple studies have reported scaling and fouling in pressure-driven membranes [28–33] and thermal-based [34–37] desalination plants can deteriorate system performance, leading to increased energy consumption and operational costs [29,33,38].

Organic fouling is usually associated with the total organic carbon (TOC) or natural organic matter (NOM) (e.g., humic substances, carbohydrates, amino acids, and carboxylic acid) present in the brine, which can cause fouling by interacting with the divalent ions present in solution [39] and the membrane surface in the desalination stage [40]. Apart from organic fouling, other forms of fouling, such as colloidal fouling and biofouling due to the adhesion and accumulation of microorganisms accompanied by biofilm development on the membrane, can account for up to 40% of the total fouling in pressure-based membrane desalination [41–43].

In the case of scaling, common inorganic scale-forming minerals consist of calcium carbonate ($CaCO_3$), calcium sulfate ($CaSO_4$), and SiO_2 due to their abundance in brines and low solubilities. $CaCO_3$ and $CaSO_4$ scaling depends on alkalinity, dissolved carbon dioxide (CO_2), temperature, ionic strength, and pH of the brine [44]. In particular, SiO_2 scaling remains a major problem for desalination due to the lack of understanding of the scaling mechanism [45]. Without removal in pretreatment, scaling will result in equipment and membrane damage, higher energy demand, increased operation and maintenance costs, and reduced water recovery and quality [23,45–49].

The complex nature of brines and their high TDS content limit the selection of pretreatment processes. Careful consideration of brine chemistry, removal requirements, cost and environmental limitations must be convoluted in designing appropriate pretreatment process combinations for effective MLD/ZLD applications [22,23]. For this study, chemical softening (CS), chemical coagulation (CC), and electrocoagulation (EC) are evaluated as pretreatment technologies due to their ability to remove a broad range of inorganic and organic constituents. Ion exchange (IX) is also considered because it is effective in selectively removing organic and inorganic compounds, heavy metals, nutrients, hardness, and other pollutants [22,23]. Table 1 reports the typical removal efficiencies for these pretreatment processes in relation to the feed TDS. Membrane filtration pretreatment technologies, including microfiltration, ultrafiltration, and nanofiltration, were excluded from this study due to their fouling propensity during brine treatment [22]. While nanofiltration (NF) can be effective for reducing brine volumes and is being explored in similar applications, its performance in this study is not directly evaluated due to its limitations in achieving a strong separation of monovalent and divalent ions, which impacts downstream recovery processes. Although silica scaling is often cited as a limitation [50,51], NF can still achieve ~50% recovery with antiscalants; however, the resulting permeate quality would differ significantly from other pretreatment options, making direct comparisons in this study impractical. In addition, biological treatment processes such as conventional activated sludge, microbial fuel cells, and microalgae are excluded due to operational challenges and toxicity of the brine to microorganisms [22]. Finally, advanced oxidation processes and adsorption through granular activated carbon, while commonly applied as a pretreatment alternative of brines with organics [22,23,52], were also excluded due to the low organic content of the KBHDP brine (as shown in Table 2).

Table 1. The removal efficiencies for the different pretreatment options reported in the literature for hardness and silica in brackish water and brine applications.

Pretreatment Unit [1]	Feedwater TDS, mg/L	Hardness	Silica	References [2]	Suitability of Treatment
Chemical Softening	39,100 5700 7800 6100	99.8% 60% 99.5% 99%	99% 71% 77% 81%	(Ayoub et al., 2014) [53] (Juby et al., 2008) [54] (Mohammadesmaeili et al., 2010) [55] (Subramani et al., 2012) [56]	Suitable for high salinity applications (>20 g/L of TDS) with high hardness content.
Chemical Coagulation	1050 32,000 3900	NR [3] NR NR	15% 94% 64%	(Ho et al., 2015) [57] (Sun et al., 2022) [58] (Chen et al., 2017) [59]	Suitable in medium to high salinity applications with low to medium silica content.
Electrocoagulation	3900 2500 1600–2058	NR NR 55%	89% 80% 95%	(Chen et al., 2017) [59] (Den and Wang, 2008) [60] (Liu et al., 2022b) [61]	New technology has yet to be tested thoroughly at full scale but has shown promise in medium or high salinity applications (>20 g/L of TDS) with high silica content.
Ion Exchange	NR NR 500	82% 55% 81%	NR NR NR	(Boonpanaid and Piyamongkala, 2023) [62] (Comstock and Boyer, 2014) [63] (Hailu et al., 2019) [64]	Suitable for lower salinity applications (<5 g/L of TDS) with medium to high hardness content.

Notes: [1] The reported removal percentages are dependent on the type of water and its respective water quality of the study, as well as operational goals, inputs, materials, and conditions established by the authors. [2] Salinity and removal efficiencies reported in order of citation. [3] NR = Not Reported.

Table 2. Water quality characteristics of the KBHDP brine.

Parameters	KBHDP Brine [c] Minimum	Mean	Maximum
pH	7.8	8	8.2
Temperature, °C	23	25	28
TDS, mg/L	10,300	10,725	11,200
Conductivity, µS/cm [a]	16,600	18,122	20,200
Total Hardness, mg/L [b]	2050	2300	2430
Total Alkalinity, mg/L [b]	400	430	445
Calcium, mg/L	281	610	935
Magnesium, mg/L	86	161	183
Sodium, mg/L	1730	2810	3260
Chloride, mg/L	4840	5090	5540
Silica, mg/L	27	130	173
Sulfate, mg/L	1050	1115	1200
Turbidity, NTU	0.06	0.30	1.94
TOC, mg/L	1.5	9	12

Notes: [a] Based on TDS measurements as sodium chloride (NaCl). [b] Units of mg/L as $CaCO_3$. [c] Data collected from [65,66].

CS pretreatment, which involves the addition of chemicals such as caustic soda (NaOH), hydrated lime ($Ca(OH)_2$), and/or soda ash (Na_2CO_3), is very useful in MLD/ZLD applications since it can effectively reduce scaling ions in brines such as Ca^{2+}, Mg^{2+}, and SiO_2 [22,53,55,67]. A high pH in the range of 9.5 to 11 can effectively remove SiO_2 in CS due to the co-precipitation or adsorption mechanism of $Mg(OH)_2$ and the Mg^{2+} and SiO_2 complexes being formed [68]. CC is a conventional treatment process for the removal of colloidal and dissolved substances using coagulants such as alum ($Al_2(SO_4)_3{\cdot}14H_2O$), ferric chloride ($FeCl_3$), and polymeric coagulants to destabilize colloidal particles and enhance floc formation [22,69]. CC has been tested as a pretreatment alternative in different types of brines and high TDS waters with successful removal of organic compounds upwards of 30% [70–75]. Coagulants have also demonstrated effective removal of SiO_2 due to its adsorption on the precipitates generated in the process, e.g., iron hydroxide ($Fe(OH)_3$) and aluminum hydroxide ($Al(OH)_3$), under basic conditions in the water, i.e., pH greater than 7 [58,59,76,77].

EC relies on in situ electrochemical generation of coagulants via dissolution of sacrificial anodes [78]. The sacrificial electrodes are typically metal (e.g., iron and aluminum) and dissociated by an electric current, producing hydroxy-metal coagulant species followed by floc formation that remove pollutants like suspended solids, colloids, and organic/inorganic compounds through complexation, enmeshment, or adsorption processes. EC has been explored as a viable pretreatment alternative for multiple saline streams before membrane or thermal desalination processes [59,79–83]. One of the advantages of EC applications in high salinity brines is that the high electrical conductivity of the stream eliminates the need for electrolyte addition, resulting in lower electrical resistances and less overall energy demand than treating other lower salinity water.

IX is a common advanced treatment approach that uses packed beds of resins or metal oxide/hydroxide granules (e.g., activated alumina) for the removal of inorganic ions via exchange of the unwanted ion for the mobile ion in the adsorbent or direct adsorption, respectively. Cations and anions can be removed by synthetic resins, while other constituents, such as iron and SiO_2, can adsorb directly onto hydrous metal oxides/hydroxides [84,85]. IX has proven to be a reliable barrier against the formation of sulfate, hydroxide, and carbonate scaling and a valuable approach for corrosion control of desalination equipment [86]. Because the removal mechanism for IX relies on the exchange of monovalent ions in the resin with divalent ions in the water matrix, the capacity of the resin can be rapidly depleted by high concentrations of influent TDS [87]. The maximum TDS and hardness that IX resins can be applicable range from 500 to 20,000 and 500 to 2000 mg/L, respectively [88–90].

3. Methods

3.1. Case Study Description

Bench experiments and pilot-scale testing of pretreatment technologies for RO brine treatment were conducted at the KBHDP to provide data for model validation. Table 2 presents the respective water quality characteristics for the KBHDP brine. The treatment flow rate for this study is designed as 3 MGD (11,356 m^3/d) of brine generated at the KBHDP, which is the actual flow rate of the brine at the facility.

The KBHDP desalinates brackish groundwater using RO to produce 27.5 million gallons per day (MGD, or 104,100 m^3/d) of drinking water at full capacity with an RO water recovery of 82.5%. The KBHDP is the largest operational inland BWRO desalination plant in the U.S., providing approximately 5% of the total annual water supply to El Paso, and is planned to be expanded to 33 MGD (124,918 m^3/d) [2]. Approximately sixteen production wells and blend water wells feed groundwater from the Hueco Bolson aquifer to the KBHDP, with TDS ranging from 2500 to 3600 mg/L. The KBHDP generates 3 MGD (11,356 m^3/d) of brine, which is disposed of through three gravity-driven injection wells. As previously discussed, deep-well injection, while being a low to medium-cost brine management alternative, can have environmental impacts such as increasing soil and groundwater salinization and contamination at the disposal site [7,14].

The Langelier Saturation Index (LSI) was used as an indicator of the scaling potential and was estimated to be 1.85 for the KBHDP brine using the proprietary software by Avista Technologies—AdvisorCi Online. PHREEQC was also used to identify possible minerals that can precipitate from the KBHDP brine and cause scaling in downstream processes. The key scaling minerals in the KBHDP brine with a high probability of precipitating due to supersaturation conditions (having a saturation index > 0) and their respective saturation indices obtained are presented in Table 3 if no pretreatment is considered. In addition, the scaling potential of the different minerals was evaluated, accounting for an additional 60% water recovery scenario and the removal of both hardness and SiO_2 on the brine with a process such as CS, assuming a similar removal efficiency as in [55], to show the changes on the saturation indexes of the different minerals. The goal of this evaluation was to verify how the scaling indexes change when considering downstream membrane-based processes that further concentrate the brine. The increased scaling potential of the brine can lead to additional complexity in its post-treatment since the higher concentration of scaling minerals may affect the subsequent desalination processes that aim to reduce brine volume and recover additional water. This can also affect deep-well injection disposal due to a greater risk of mineral precipitation that may clog the wells and lead to a significant increase in maintenance costs.

Table 3. Oversaturated mineral species present in the KBHDP brine and their change when considering an additional 60% water recovery on the brine.

Minerals—KBHDP	Saturation Index (Feed Brine)	Saturation Index (Additional 60% Recovery of the Feed)	Saturation Index (After Removing 90% of Hardness and 75% of Silica in the Feed)
Aragonite ($CaCO_3$)	1.61	2.48	0.82
Calcite ($CaCO_3$)	1.76	2.63	0.96
Chalcedony (SiO_2)	0.90	1.31	0.28

Table 3. *Cont.*

Minerals—KBHDP	Saturation Index (Feed Brine)	Saturation Index (Additional 60% Recovery of the Feed)	Saturation Index (After Removing 90% of Hardness and 75% of Silica in the Feed)
Chrysotile ($Mg_3Si_2O_5(OH)_4$)	3.52	8.27	−0.66
Dolomite ($CaMg(CO_3)_2$)	3.29	5.05	1.66
Sepiolite ($Mg_4Si_6O_{15}(OH)_2{\cdot}6H_2O$)	3.63	7.48	−0.19
Silica quartz (SiO_2)	1.33	1.74	−0.56
Strontianite ($SrCO_3$)	0.68	1.55	0.88
Talc ($Mg_3Si_4O_{10}(OH)_2$)	9.02	14.61	3.59

3.2. WaterTAP Program and Models

The case studies and unit models were simulated using the WaterTAP program [25], an open-source Python package designed to provide analysis of full water treatment trains through simulation, optimization and other advanced analysis. WaterTAP models are compatible with the Institute for Design of Advanced Energy Systems (IDAES) Platform, an advanced process systems engineering tool developed by the U.S. Department of Energy that provides the benefit of utilizing equation-oriented algebraic modeling, open-source and commercial solvers, libraries of process units and property packages, and a diverse set of analysis tools. WaterTAP can (i) build water-specific designs, (ii) provide treatment system cost optimization, (iii) improve existing systems, and (iv) enable the analysis of innovative designs through the incorporation of emerging technologies.

3.3. Pretreatment Unit Design Values

This assessment employed the unit models for CC, EC, CS, and IX that are available in the WaterTAP open-source library, of which both EC and CS were developed by the research team at New Mexico State University (NMSU) in collaboration with WaterTAP developers. In this study, we used \$0.03/kg for the final sludge disposal cost in addition to accounting for the costs of sludge processing units before disposal, such as thickening and dewatering. The detailed inputs and outputs of the different models are presented in the supporting information (SI). The CS, CC, and EC models are assumed performance models where the removal efficiency of target pollutants is based on reported efficiencies in the literature.

The dosing predictions from CS were based on approaches presented in water treatment handbooks [84,85], where dosing is based on incoming water quality (pH, hardness, alkalinity, and dissolved CO_2 concentrations). The general sludge generation in CS was estimated by adapting empirical equations from the Water Quality and Treatment: A Handbook on Drinking Water [85]. Effluent water quality for the CS model chemical dosing assumes that both Ca^{2+} and Mg^{2+} are lowered to their practical solubility limit levels of 30 mg/L as $CaCO_3$ and 20 mg/L as $CaCO_3$, respectively [84]. Inputs for the IX model were based on experimental data obtained from pilot-scale testing at the KBHDP (publication in development) with strong acid cation (SAC) resins for hardness removal, whilst EC model inputs were obtained based on common values reported in the literature for brine with similar composition. The inputs of the CC, EC, and IX models are presented in Table 4.

Table 4. WaterTAP model inputs.

Design Input	Value
Coagulant dose $Al_2(SO_4)_3$ [1]	650 mg/L (Dialynas et al., 2008) [70]
Coagulant dose $FeCl_3$ [1]	595 mg/L (Chen et al., 2017) [59]
Current density [2]	200 Amperes per m^2
Electrode gap [2]	0.02 m
Current efficiency [2]	100%
Fe^{2+} electrode dose [2]	200 mg/L
Al^{3+} electrode dose [2]	100 mg/L
Retention time—Flocculation basin [2]	15 min
Dimensionless Langmuir isotherm coefficient [3]	0.24
Resin capacity [3]	1.89 mol/kg
The service flow rate through resin bed [3]	12 bed volumes per hour
Resin diameter [3]	0.0006 m
Bed depth [3]	1.8 m
Bulk density [3]	0.8 kg/L
Porosity [3]	0.5
NaCl regenerant concentration [3]	0.08 kg/L

Note: [1] Chemical coagulation. [2] Electrocoagulation. [3] Ion exchange—NMSU experimental results.

The CS chemical costs adapted in this study were \$0.24/kg of 95% $Ca(OH)_2$, \$0.28/kg of 98% Na_2CO_3, and \$0.59/kg of 50% NaOH, respectively. In the case of CC, the costs of the $FeCl_3$ and $Al_2(SO_4)_3$ were adapted as \$0.88/kg $FeCl_3$ and \$0.69/kg $Al_2(SO_4)_3$ [59]. The electrode costs for the EC unit were adapted from the literature as \$2.23/kg Al and \$3.41/kg Fe [91]. For IX, this study includes the cost of the deionized (DI) water for preparing regenerant solutions, which increases the cost of the regenerant to \$0.60/kg of NaCl + DI water (CED and CO_2 emissions are not accounted for the DI water production). In addition, a safety factor of 10% on the incoming hardness and an increase in the annual replacement rate of the resins from 5% to 30% [92] were considered to account for the effect of the brine's ionic strength in the resins. Additional descriptions of costs considered in these units are further discussed in the SI.

The capital expenditure (CAPEX) and operational expenditure (OPEX) values in this study are used as a relative comparison of unit processes rather than absolute cost estimates, ensuring that all treatment options are evaluated under the same assumptions. While WaterTAP provides a structured framework for cost estimation, its capital cost models are not fully validated for real-world applications. To ensure consistency, all processes were assessed using the same methodology, allowing for meaningful relative comparisons of cost-effectiveness, even if individual cost values may deviate from actual project estimates. These findings should be interpreted as a relative economic assessment rather than direct cost projections for implementation, design, and construction.

3.4. Economic, Energetic, and Environmental Assessment

Providing an economic, energetic, and environmental assessment for pretreatment technologies can aid decision-making when considering the brine system design, optimization, and integration. Similar approaches have been presented in the literature, either with all three criteria evaluated together or individually [4,14,17,93], and in conventional desalination applications [94–97]. The points of evaluation considered and the exclusions in this study are presented in Figure 2. Emissions and energy demand from waste disposal, as well as chemical or waste transportation, were excluded from the analysis since these are dependent on their respective transportation distances. In addition, emissions and energy demand from the construction phase of the different units were excluded because the operational phase impact is larger than that of the construction phase and can be considered as impulse energy consumption and emissions [98,99]. The chemical and material manufacturing/production energy demand and CO_2 emission factors were based on an extensive search for the reported literature values, which are presented in the SI [100–106]. The goal of such material manufacturing/production energy demand and CO_2 emission factors is to quantify both the energy usage and emissions in the creation of key inputs in the pretreatment process.

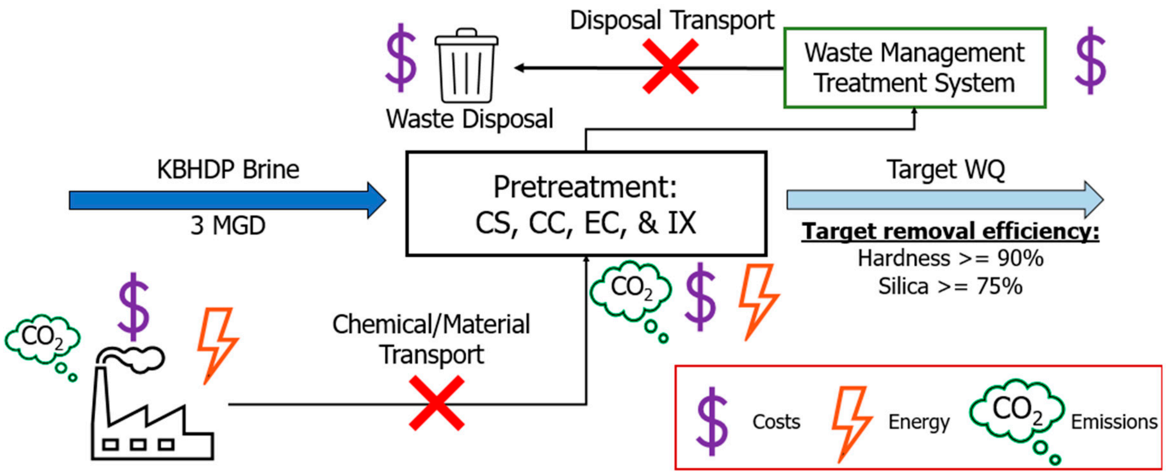

Figure 2. Evaluations considered in this study.

A comprehensive economic assessment can evaluate the economics of a treatment system and provide valuable information for its design and operations. The performance of these pretreatment technologies is evaluated based on four criteria, including (i) levelized cost of water (LCOW), (ii) specific energy consumption (SEC), (iii) cumulative energy demand (CED), and (iv) carbon emissions as carbon dioxide (CO_2). Formulas for these performance metrics are shown in Equations (1)–(4):

$$\text{LCOW} = \frac{\text{Annualized CAPEX}\left(\frac{\$}{\text{yr}}\right) + \text{OPEX}\left(\frac{\$}{\text{yr}}\right)}{\text{Treatment Unit Capacity}\left(\frac{\text{m}^3}{\text{yr}}\right)} \tag{1}$$

$$\text{SEC} = \frac{\text{Unit Energy Consumption}\left(\frac{\text{kWh}}{\text{yr}}\right)}{\text{Treatment Unit Capacity}\left(\frac{\text{m}^3}{\text{yr}}\right)} \tag{2}$$

$$\text{CED} = \frac{\text{Unit Energy Consumtion}\left(\frac{\text{kWh}}{\text{yr}}\right) + \text{Chemical/Material Manufacturing Energy Demand}\left(\frac{\text{kWh}}{\text{yr}}\right)}{\text{Treatment Unit Capacity}\left(\frac{\text{m}^3}{\text{yr}}\right)} \tag{3}$$

$$\text{CO}_2\text{ Emissions} = \frac{\text{Chemical/Material Manufacturing Emissions}\left(\frac{\text{kg CO}_2}{\text{yr}}\right)}{\text{Treatment Unit Capacity}\left(\frac{\text{m}^3}{\text{yr}}\right)} \tag{4}$$

This research uses the LCOW as the economic indicator with units of 2024 U.S. dollars ($) per treatment of one m^3 of brine ($\$/m^3$) accounting for the current market inflation. The LCOW was calculated to account for a time duration of 30 years and an interest rate of 5%. It includes all expenditures for project construction and operation, including fixed and variable components that influence the overall cost [107]. Costs considered account for both capital and operational expenses of the pretreatment technologies, as well as cost factors provided by WaterTAP presented in the SI.

An energy assessment can help identify opportunities for energy optimization and cost reductions when considering MLD/ZLD applications due to the high energy demand of most brine treatment technologies. The SEC (Equation (2)) is defined in this work as the energy required, in kilowatt-hours (kWh), for the treatment of one m^3 of brine (kWh/m^3). The CED metric (Equation (3)) is inclusive of both the pretreatment unit's energy demand and the energy demand for the manufacturing/production of the chemicals and materials used in these processes, where their input is normalized per volume of the treated brine (mass chemical/materials per volume treated). These energy inputs are not considered in the LCOW (Equation (1)) since the cost of the chemical/materials adapted in the LCOW accounts for the costs of the energy consumption in their production.

The environmental assessment in this study aims to quantify the CO_2 emissions produced in the manufacturing/production of the different chemicals, as well as the energy and materials needed for the operation of these units (Equation (4)). Focus on CO_2 emissions is emphasized due to current interests in the decarbonization of the water sector, with the European Union and the U.S. setting goals to become carbon neutral by 2050 [108–112]. Because water treatment, transportation, utilization, and storage account for up to 10% of global greenhouse gas emissions (GHGs), decarbonization of the water sector will play a major role in addressing climate change [110,113]. The unit for evaluation of CO_2 emissions is kilograms of $CO_{2\text{-eq}}$ for the treatment of one m^3 of brine (kg $CO_{2\text{-eq}}/m^3$).

4. Results and Discussion

WaterTAP was used to model the different pretreatment units of interest in this analysis to treat the KBHDP brine, focusing on removing the key scaling constituents (i.e., hardness and silica) in the brine to acceptable levels for the subsequent membrane desalination processes to achieve MLD or ZLD. The costs considered for the pretreatment models are available in the SI, and model details can be found in the online WaterTAP documentation [25]. The application of CS and IX processes is expected to remove more than 90% of hardness, while EC, CC, and CS target to remove more than 75% of the SiO_2. Each pretreatment unit and respective combinations were evaluated with a feedwater flow rate of 11,356 m^3/d (3 MGD).

4.1. Individual Pretreatment Units

The modeling results of the LCOW, CO_2 emissions and SEC for the different pretreatment units are shown in Figures 3 and 4 for the KBHDP brine. Table 5 summarizes the CAPEX and OPEX values of individual pretreatment technologies. The breakdowns of the individual components contributing to the CAPEX and OPEX of the pretreatment units are shown in Figures S1–S19 of the Supplementary Materials.

The calculated LCOW for both CS with $Ca(OH)_2$ and Na_2CO_3 (\$0.96/m^3) and CS with NaOH (\$1.38/m^3) is not consistent with the reported range in the literature of \$0.30–\$0.90/m^3 in brine treatment applications [114–117]. This discrepancy arises because the literature values primarily reflect operational costs, while our study includes capital costs and waste disposal expenses. The high costs in CS are largely driven by the high chemical costs of $Ca(OH)_2$, Na_2CO_3, and NaOH, discussed in Section 3.3, which are dependent on the doses required to remove incoming hardness. Since the KBHDP brine has a high non-carbonate hardness, 85–95% of the total operational cost for CS is for the purchase of Na_2CO_3 and NaOH.

Table 5. CAPEX and OPEX values for 11,356 m^3/d individual pretreatments in the KBHDP brine and scaled to 2024 U.S. dollars. (M = million).

Pretreatment Unit	CAPEX, $M	OPEX, $M/Year	Highest Contributor in the CAPEX	Highest Contributor in the OPEX
CS—Lime	$2.78 M	$3.79 M/yr	Sedimentation basin (30%)	Na_2CO_3 dosing (57%)
CS—Caustic	$3.70 M	$5.50 M/yr	NaOH feed system (33%)	NaOH dosing (82%)
CC—Alum	$3.40 M	$2.35 M/yr	-	Alum dosing (93%)
CC—Ferric	$3.54 M	$3.49 M/yr	-	$FeCl_3$ dosing (88%)
IX	$3.13 M	$5.90 M/yr	Regenerant and backwashing tank (81%)	NaCl regenerant (88%)
EC—Al	$3.41 M	$1.93 M/yr	Sludge management units (63%)	Electrode replacement (65%)
EC—Fe	$3.14 M	$4.34 M/yr	Sludge management units (63%)	Electrode replacement (87%)

Notes: CAPEX and OPEX account for the costs of sludge management units, gravity thickener and filter press. CAPEX values account for the application of the default WaterTAP cost factors. The highest contribution of CAPEX for CC units is not specified in the zero-order WaterTAP model.

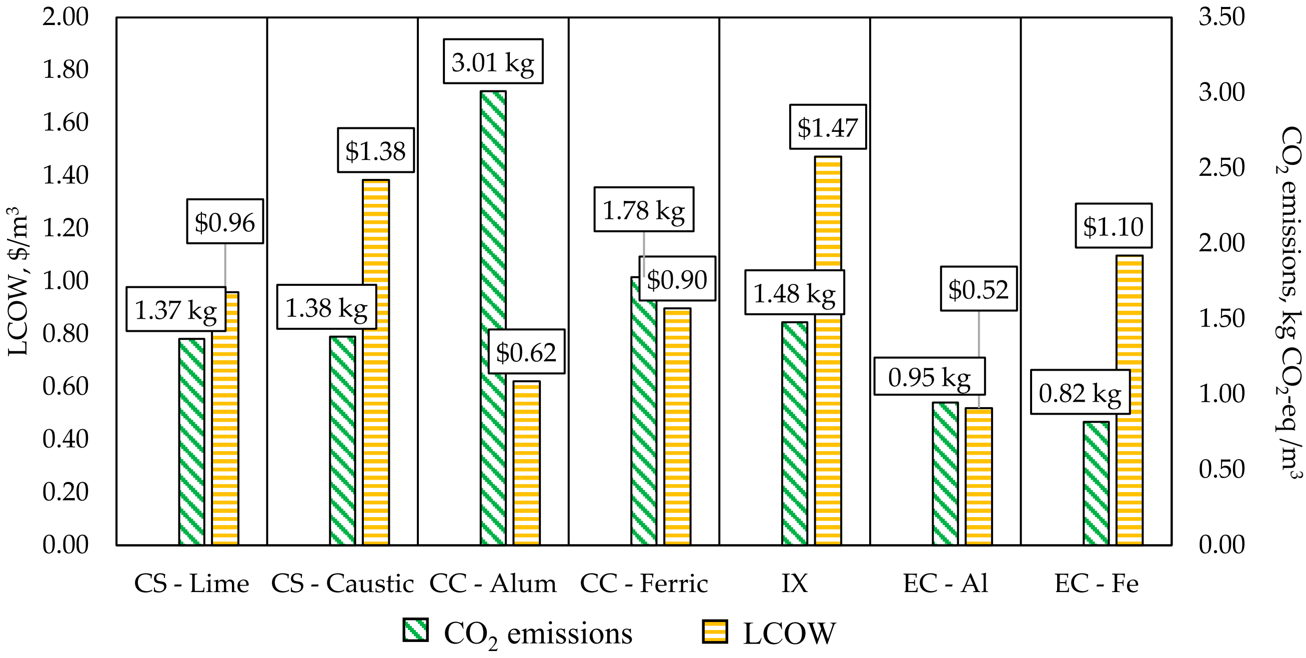

Figure 3. LCOW and CO_2 emissions for the individual pretreatment units in the KBHDP brine.

The LCOW of CC using both $Al_2(SO_4)_3$ and $FeCl_3$ falls in the reported literature range of \$0.05–1.2/m^3 [70,118,119], though like CS, prior studies often exclude capital and sludge management costs. $FeCl_3$-based CC has higher costs than $Al_2(SO_4)_3$-based CC due to its greater dosing requirement, with chemical costs comprising 88–93% of total OPEX, while sludge management accounts for only 2–5%. The highest associated CO_2 emissions are from CC with $FeCl_3$ (1.8 kg CO_2/m^3), and CC with $Al_2(SO_4)_3$ (3.0 kg $CO_{2\text{-eq}}/m^3$) as shown in Figure 3. This can be attributed to the high dosing requirement and the respective emission factors adapted in this assessment [100,105,120]. On the other hand, CS with $Ca(OH)_2$ and Na_2CO_3 (1.4 kg $CO_{2\text{-eq}}/m^3$) and with NaOH (1.4 kg $CO_{2\text{-eq}}/m^3$) are the lowest emissions of the chemical-based processes (Figure 3). Both CS and CC have similar treatment trains, including a rapid mixer and a flocculation basin. The mechanical design inputs for the rapid mixer and flocculation are the same in both systems, so the SEC of both CS and CC treatment units are similar. A more noticeable difference can be observed in the CED (Figure 4) between CS and CC applications when considering the energy demand for chemical production. Chemical and material production fractions of the total energy consumption can be significant, especially when the system operation depends primarily on the addition of chemicals and the replacement of key treatment materials that must be manufactured constantly. Accounting for this energy consumption aspect gives a broader view of the use of these units as pretreatment alternatives. An increase in the CED is observed when accounting for chemical production energy consumption in both the CS with $Ca(OH)_2$ and Na_2CO_3 (6.3 kWh/m^3) and CS with NaOH (4.7 kWh/m^3), as shown in Figure 4. Low energy consumption in the production of $Al_2(SO_4)_3$ and $FeCl_3$ can be observed in the CC pretreatment, and since these are the only chemicals added, the overall energy for producing only these chemicals is low compared to CS. Such differences in both coagulants may be primarily attributed to their different manufacturing processes.

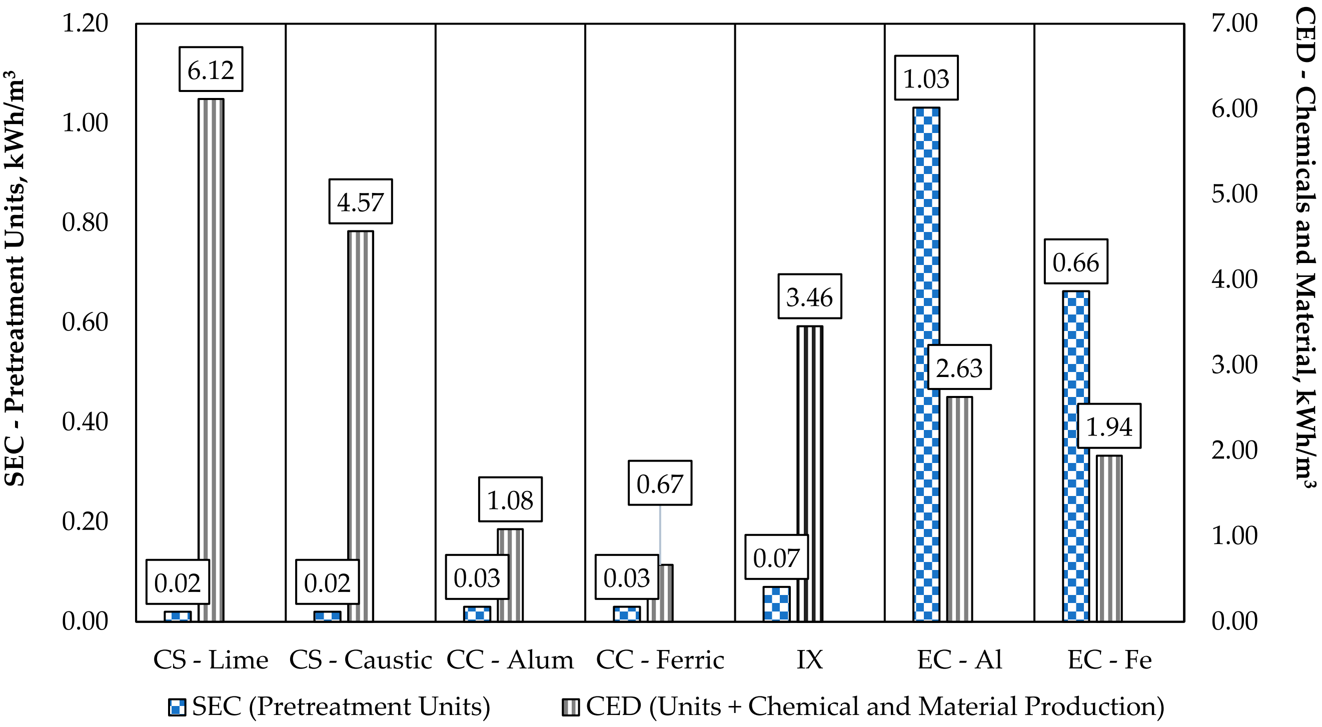

Figure 4. The specific energy consumption of pretreatment units and the cumulative energy demand of the pretreatment units with chemical/material energy in the KBHDP brine.

The IX system demonstrated 98% hardness removal efficiency in the WaterTAP model but showed high operational costs due to a short 2.5-h breakthrough time caused by high influent hardness. Regenerant consumption (8.5 million kg/year) accounts for 88% of OPEX, with backwash and regenerant solution tanks as the main CAPEX contributors. The LCOW for IX (\$1.47/m^3) is in the range documented in the literature from \$0.08 to \$1.8/m^3 [22,121]. The CO_2 emissions for IX are 2.1 kg CO_2/m^3, attributable to NaCl production and the polystyrene media replacement rate. The SEC of the IX unit for water pumping (0.07 kWh/m^3) falls in range with values reported in the literature [122], while the CED of the replacement and production of the media and regenerant represents up to 98% of the total. Longer breakthrough times via higher-capacity resins, feed dilution, or a lead-lag column configuration could reduce these costs.

The LCOW of EC using Al and Fe electrodes is estimated to be \$0.52/m^3 and 1.10/m^3, respectively. These costs fall in the range with reported values of \$0.40–\$12/m^3 in the literature for brine treatment applications [123–125]. Notably, reported values typically do not include capital costs, only operational ones, which are dependent on several factors (electrode material, current density and efficiency, electricity cost, constituent removal, and retention times). Same as CC, most of the reported costs in the literature only account for the operational costs and do not account for the capital costs involved in the system, such as reactors, initial electrode purchase, and power supply, which can typically account for up to 60% of the total capital cost in an EC system [126]. The difference in the costs of Al-EC and Fe-EC is mostly attributed to the difference in the electrode material costs, discussed in Section 3.3. The reactor material was assumed to be polyvinyl chloride (PVC) to avoid corrosion issues from the brine [127]. The CAPEX in the EC system was influenced by the sludge management units (61% for Al and 63% for Fe) as well as the power supply (19% for Al and 13% for Fe) and the flocculation basin (18% for Al and 19% for Fe). The main contributors to the OPEX consist of the replacement rate of the electrodes (65% for Al and 87% for Fe), energy consumption (17% for Al and 5% for Fe), and sludge management and disposal (18% for Al and 8% for Fe).

For CO_2 emissions, the replacement rate of the Al and Fe electrodes is based on the electrode dissolution dosages in the system (100 mg/L of Al and 200 mg/L of Fe), which were adapted from the literature [59,61]. The EC emission impact for the manufacturing of Al and Fe electrodes was estimated to be 0.95 kg $CO_{2\text{-eq}}/m^3$ and 0.82 kg $CO_{2\text{-eq}}/m^3$, respectively. The energy consumption of each is the driving factor in the difference of their emission rates as well as the adapted emission factor for the generation of Al and Fe sheets. The SEC for Al and Fe EC units are calculated at 1.03 kWh/m^3 and 0.66 kWh/m^3, respectively, and are the highest SEC values compared to the other pretreatment methods. The estimated energy consumption complies with the reported values treating brackish/brine water 0.1–2.90 kWh/m^3 [60,128]. The CED accounting to produce the Al (2.6 kWh/m^3) and Fe (1.9 kWh/m^3) materials is based on the replacement of the electrodes throughout their operation and is shown to have a minimal impact in comparison to the other pretreatment units, which require a higher quantity and a constant replacement of chemicals.

4.2. Coupled/Combined Pretreatment Processes

There have been limited studies exploring the coupling of different pretreatment units in terms of their impact on LCOW, CO_2 emissions, and SEC. This study evaluated various pretreatment combinations, with selections guided by the expected performance of each unit in removing both key constituents (hardness and silica) and the feasibility of integration within the system. The different combinations evaluated in this work were determined based on the performance of individual units while also considering cost-effectiveness and operational feasibility.

The integration of CS with $Ca(OH)_2$ and Na_2CO_3 was selected due to its lower overall costs in comparison with CS with NaOH in the previous section. Similarly, CC pretreatment with $FeCl_3$ was chosen as the primary coagulation method because it resulted in lower CO_2 emissions, CED, and SEC. Additionally, aluminum (Al) was the only electrode material considered for EC. Another critical factor in selecting coupled pretreatment processes was the effective minimization of waste disposal, particularly with the inclusion of IX.

The combinations of pretreatment options considered for each case study are shown in Figure 5. CC targets SiO_2 reduction, while IX is focused on hardness reduction. The EC + CS combination is designed to reduce both SiO_2 and hardness. Coupling CS and CC is a well-documented treatment approach [72,129,130], offering cost advantages by leveraging shared treatment infrastructure and equipment, as $Ca(OH)_2$, Na_2CO_3, and $FeCl_3$ dosing can be implemented at different points within the system. Treatment combinations such as EC + IX and CC + IX are also found in studies focusing on the treatment of industrial wastewater, leachate, and brackish water, demonstrating effective pollutant removal [131–136]. Figures 6 and 7 present the modeling results for different pretreatment combinations for KBHDP brine, while Table 6 presents the CAPEX and OPEX values of the evaluated pretreatment technologies.

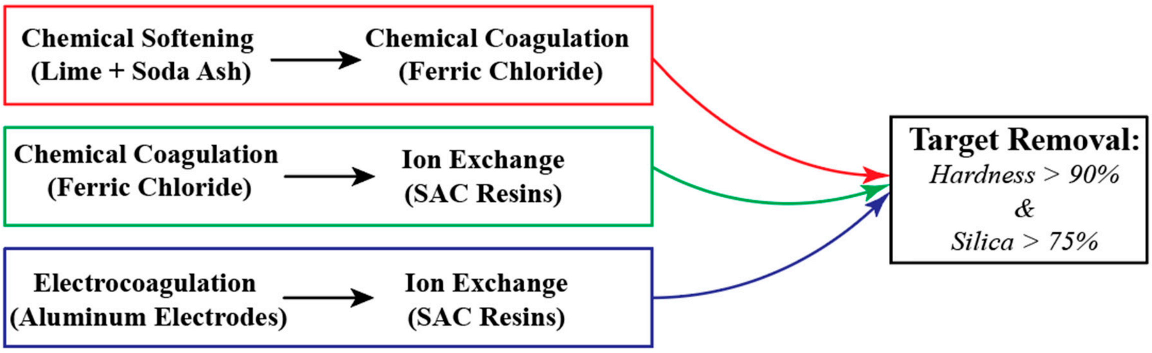

Figure 5. Pretreatment couplings targeting the removal of both hardness and silica.

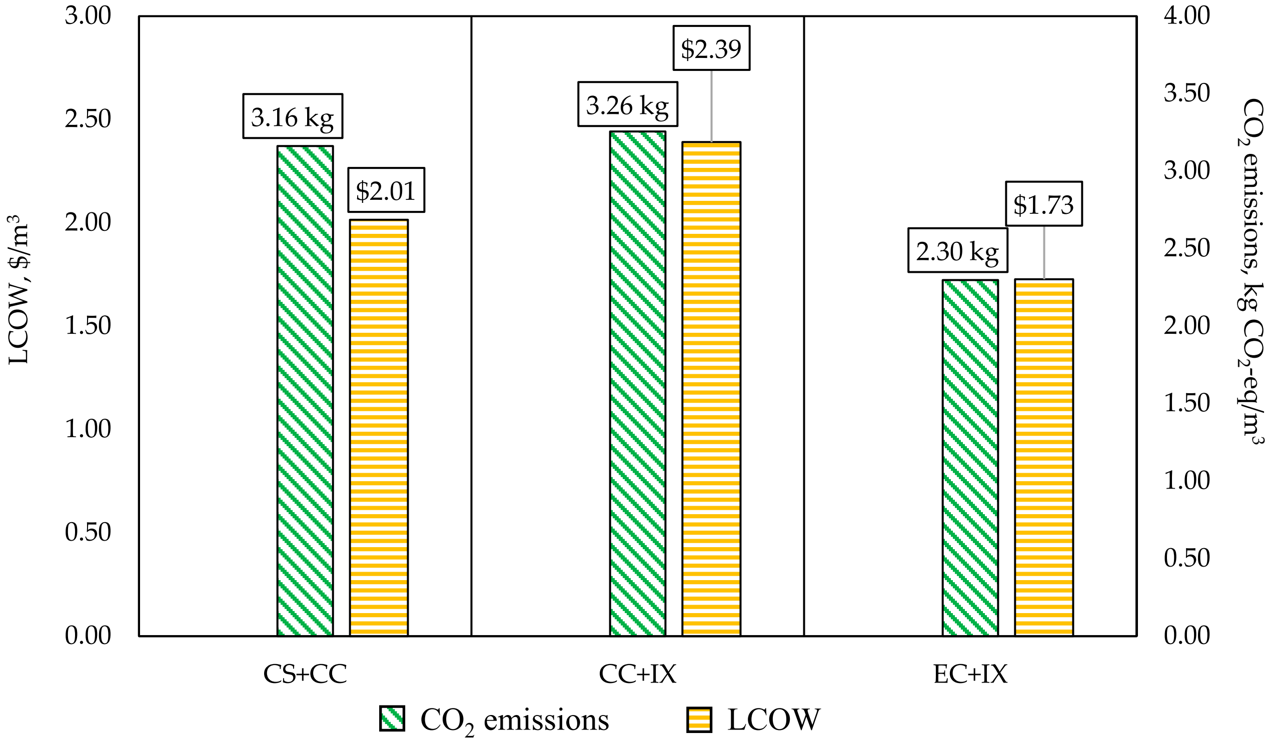

Figure 6. LCOW and CO_2 emissions for the different coupled pretreatment units for the KBHDP brine.

Table 6. CAPEX and OPEX values for 11,356 m^3/d pretreatment couplings in the KBHDP brine and scaled to 2024 U.S. dollars.

Pretreatment Coupling	CAPEX, $M	OPEX, $M/Year	Highest Contributor in the CAPEX	Highest Contributor in the OPEX
CS + CC	2.78	8.17	Sludge management units (32%)	$FeCl_3$ dosing (37%)
CC + IX	6.67	9.47	Coagulation system (73%)	NaCl regenerant (69%)
EC + IX	6.54	6.73	Sludge management units (50%)	NaCl regenerant (58%)

Notes: CAPEX and OPEX account for the costs of sludge management units (gravity thickener and filter press). CAPEX values account for the application of the default WaterTAP cost factors.

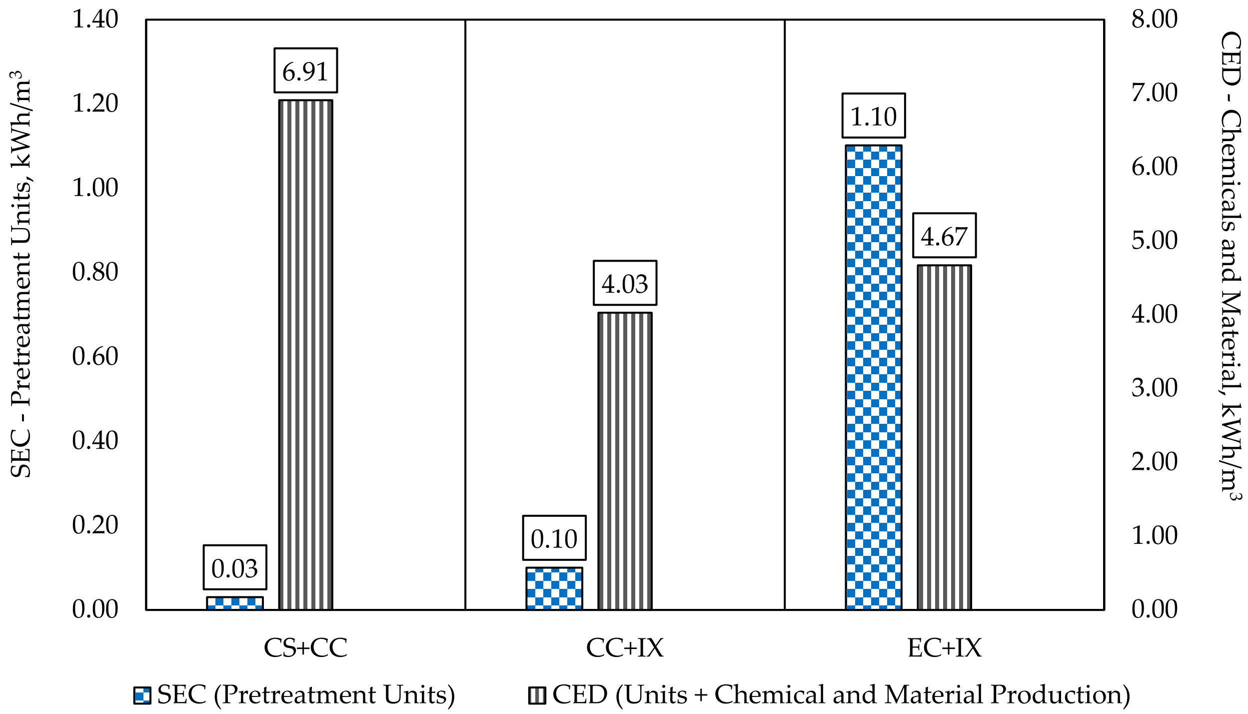

Figure 7. The specific energy consumption of pretreatment units and the cumulative energy demand of the coupled pretreatment units with chemical/material energy in the KBHDP brine.

The CC + IX coupling has the highest LCOW out of the pretreatment couplings ($2.39/m^3), with the major OPEXs attributed to the $FeCl_3$ chemical dosing (16%) and the IX resin regenerant (69%). The high requirement of NaCl regenerant for the IX pretreatment accounts for 44% of the total emissions and 73% of the CED in the production of the regenerant, while the production of $FeCl_3$ for the CC unit accounts for 56% of the total emissions and 13% of the CED. Coupling CS with CC results in the second-highest modeled LCOW of the combinations ($2.01/m^3), as shown in Figure 6. This combination accounts for the same treatment units but different chemicals for dosing. High non-carbonate hardness requires high dosages of $Ca(OH)_2$ and Na_2CO_3, while the dosing of the coagulant is assumed to be lowered by 50% to account for the removal of a smaller amount of the present SiO_2 [137]. Both the CO_2 emissions and SEC of the CS + CC pretreatment coupling was demonstrated to be the highest and the second highest out of the couplings, respectively. This is mostly attributed to the high chemical requirements in the coupling. Na_2CO_3 production accounts for 43% of the total emissions and 85% of the CED, while $FeCl_3$ production accounts for 56% of the total emissions and 12% of the CED.

The EC and IX coupling had the lowest LCOW of the combinations ($1.73/m^3). The use of EC before IX aims at reducing the hardness of the brine by at least 50%, which is beneficial for IX when treating the high salinity brine and lowers the quantity of regenerant needed for the column. The inclusion of the EC unit helped the IX operation by increasing the breakthrough time of the IX from 2.5 h to a more reasonable breakthrough time of 5 h due to the 50% reduction of the incoming hardness. With the adaptation of the EC reducing the hardness by 50%, the regenerant dosing requirement for the IX resins can be reduced by 41% in comparison to the individual pretreatment. The EC + IX coupling has the highest SEC of the pretreatment couplings due to the use of EC and the second highest CED due to the requirement of the NaCl regenerant, which represents 75% of the total energy demand, and the production of the iron electrodes, which represent the remaining 25%. In the case of CO_2 emissions, the EC + IX combination has the lowest CO_2 emissions out of the couplings.

The regenerant, iron electrode, and energy emissions account for 34%, 55%, and 11% of the total emissions, respectively.

5. Conclusions

This study utilized a modeling approach to evaluate the economic (Levelized Cost of Water, LCOW), energy (Specific Energy Consumption, SEC | Cumulative Energy Demand, CED), and environmental impacts (CO_2 emissions) of different pretreatment units for scaling minimization in KBHDP brine. Results indicate that high chemical usage significantly increases costs and environmental impacts, particularly in CS pretreatment, which has an LCOW of \$0.94–\$1.38/m^3 due to the large quantities of $Ca(OH)_2$, Na_2CO_3, and NaOH, and CC pretreatment (\$0.05–\$1.20/m^3) with $FeCl_3$ and $Al_2(SO_4)_3$, where chemical purchasing accounts for up to 93% of total operational costs. CC with $FeCl_3$ also had the highest CO_2 emissions (1.8–3.0 kg CO_2/m^3), primarily due to high coagulant demand.

Among the individual pretreatment units, the EC unit demonstrated lower LCOW (\$0.52 (Al) and \$1.10/m^3 (Fe)), lower CO_2 emissions (0.82 (Al) and 0.95 (Fe) kg CO_2/m^3), and moderate SEC (0.66 (Fe) and 1.03 (Al) kWh/m^3), making it a promising alternative. While IX showed a 98% removal efficiency for hardness, it incurred an LCOW of \$1.47/$m^{3,}$ which was primarily driven by regenerant costs (88% of total OPEX). The short breakthrough time due to high influent hardness is a key limitation, with potential mitigation strategies including higher-capacity resins, dilution, or a lead-lag column configuration.

For the KBHDP brine, CS can effectively mitigate both hardness and SiO_2 but incurs high sludge disposal costs. A more cost-effective alternative could be the EC + IX treatment combination, which can reduce hardness by 30–50% before IX, doubling the breakthrough time from 2.5 to 5 h and lowering regenerant demand by 41%. However, EC + IX has the highest SEC (due to EC energy use) and requires careful waste management.

The study's model-based approach provides approximate results and may not fully capture site-specific operational complexities such as brine quality variations. Additionally, limited data on energy consumption and emission factors for pretreatment units introduces uncertainties. Pilot-scale field testing is underway at KBHDP to validate model predictions and refine pretreatment strategies. Future work will focus on enhancing water recovery, reducing chemical costs, and converting brine into valuable byproducts (NaCl, NaOH, HCl, H_2SO_4) to achieve minimal waste discharge.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w17050708/s1.

Author Contributions: Methodology, A.L. and P.X.; Software, A.L. and K.S.; Investigation, A.L. and P.X.; Writing—original draft, A.L.; Writing—review & editing, A.L., C.M.-S., P.S.S., Z.S., K.S., H.W., K.K., S.K., V.F., P.K. and P.X.; Visualization, P.X.; Supervision, P.X.; Funding acquisition, P.X. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) under the Solar Energy Technologies Office (SETO) Award Number DE-AC36-08GO28308 to the National Renewable Energy Laboratory (NREL) with subcontracts to Columbia University and New Mexico State University (NMSU). The research at NMSU is also funded by the U.S. Bureau of Reclamation Pitch to Pilot Program, grant number R21AC10338, and the National Alliance for Water Innovation (NAWI), funded by the U.S. Department of Energy, Energy Efficiency and Renewable Energy Office, Advanced Manufacturing Office under Funding Opportunity Announcement DE-FOA-0001905. Any opinions, findings, conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the U.S. Department of Energy and Bureau of Reclamation. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information,

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Data Availability Statement: The original contributions presented in this study are included in the article/Supplementary Materials. Further inquiries can be directed to the corresponding author.

Acknowledgments: The authors are very grateful for technical support and discussions with the experts at Veolia Water Technologies and Solutions (Dr. Neil Moe, Dr. John Barber, and Kobe Thys). The authors thank El Paso Water for the financial and technical support of pilot testing at the Kay Bailey Hutchinson Desalination Plant (John Balliew, Arturo Ruiz, Hector Sepulveda, Andrew P. Aliyas, and all operators at the KBHDP).

Conflicts of Interest: The authors declare no conflict of interest.

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