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ARTICLE

Solvent-Driven Fractional Crystallization Applied to the Desalination of a Concentrated Wastewater by Reverse Osmosis

Edgar Vásquez * , ***Flavia Hurtado***

Department of Chemical Engineering, National University of Trujillo, Trujillo 13001, Perú

ABSTRACT

This paper reports the efficiency of the solvent-driven fractional crystallization (SDFC) process using ethanol, also known as antisolvent crystallization, in the treatment of a concentrated wastewater by reverse osmosis (RO). This experiment evaluated the effects of varying the volumetric mixing ratio of ethanol-to-RO concentrate, in conjunction with the incorporation of $Ca(OH)_2$, on the efficiency of magnesium and boron removal. The incorporation of $Ca(OH)_2$ resulted in an enhancement of the reduction of magnesium and boron concentrations at a mixing ratio of 85:15 (v/v) and a pH of 12. In these conditions, the removal efficiencies achieved for magnesium and boron were 98.64% and 90.82%, respectively. The findings indicate that $Ca(OH)_2$ has a significant impact on enhancing the removal efficiencies of these elements. The RO concentrated wastewater used in this experiment exhibited a salinity of 50,497.200 ppm prior to the SDFC test. The experimental results also showed a 48.10% reduction in salinity and 28.10% salt precipitation at the maximum mixing ratio and pH level examined. The tested process demonstrated significant reduction of scaling ions including calcium, magnesium, and sulfate. Similar behavior was observed for arsenic and manganese. Moderate removal efficiencies were observed for monovalent ions such as chloride, sodium, and potassium. However, the process was no effective for iron and lithium, which showed low removal efficiencies. Based on the results obtained, SDFC technology is seen as a promising technological option for application in the treatment of complex mining wastewaters.

Keywords: Fractional Crystallization; Antisolvent Crystallization; Scaling Ions; Monovalent Ions

*CORRESPONDING AUTHOR:
Edgar Vásquez, Department of Chemical Engineering, National University of Trujillo, Trujillo 13001, Perú; Email: edgarenrique231275@gmail.com

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1. Introduction

The expansion of desalination processes has increased the production of brine, which is one of the major environmental barriers to its current application. The brine that is a by-product of desalination activities has been shown to have significant adverse effects on marine life and the environment. These effects can be attributed primarily to elevated salinity levels, modifications in chemical composition, and the potential depletion of oxygen. These alterations have the potential to result in a decline in biodiversity and the degradation of habitats [1]. As indicated by the findings of numerous studies the potential environmental impacts of brine include eutrophication, pH fluctuations, and the accumulation of heavy metals in receiving bodies. The occurrence of these impacts has been demonstrated to result in severe degradation of receiving water bodies by disrupting aquatic ecosystems, harming aquatic life, and compromising water quality. Eutrophication, defined as the enrichment of a body of water with nutrients such nitrogen and phosphorus, can result in the proliferation of excessive algal blooms. This phenomenon can result in a depletion of oxygen, which can lead to fish kills and the production of toxins. The accumulation of heavy metals in sediments and biota has been demonstrated to generate risks to food webs and human health [2,3].

The inland desalination plants that use groundwater or support industrial activities such as mining, require the use of more cost-effective desalination technologies to treat the brine generated in their desalination processes. Therefore, the current trend of recovering valuable minerals from brine is an important aspect that should be exploited as a benefit to avoid disposal issues. Brines from desalination plants can be a potential source for the extraction of minerals due to the high concentration of certain salts of commercial interest to the chemical industry. The following minerals can be extracted: anhydrite ($CaSO_4$), calcite ($CaCO_3$), halite (NaCl), gypsum ($CaSO_4 \cdot 2H_2O$), hexahydroborite ($Ca[B(OH)_4]_2 \cdot 2H_2O$), sylvite (KCl), and hexahydrite ($MgSO_4 \cdot 6H_2O$). A variety of commercially viable compounds, including lithium, uranium, molybdenum, and nickel, have been identified in concentrated brines. These compounds hold immense potential for extraction in the mining industry, presenting a lucrative opportunity for economic development. A variety of applications exist that are contingent upon the specification of salts. These applications include, but are not limited to, the softening of water, the treatment of swimming pools, the chlor-alkali industry, the production of detergent, and the manufacturing of batteries, among others [1,4].

Various studies mention that saline streams with high salt concentrations and other contaminants, such as mine wastewater, pose significant technical challenges in their treatment, due to their varying chemical characteristics and concentrations, which depend on the water source, mineral extraction and production processes, recovery rate, purity of the produced freshwater, pre-treatment unit and chemical additives [1,4]. These streams typically contain high concentrations of dissolved salts, raw water compounds, and chemicals used in industrial processes [2,4].

Based on the above, Shah et al. point out that the proper management of saline water is mandatory for governments in all countries due to the high concentrations of contaminants in saline streams. However, they argue that current management methods are inadequate, potentially harmful to the environment, and costly [5]. Common brine disposal strategies such as surface water discharge, deep well injection, evaporation pond disposal, and land application, significantly contaminate the surrounding water and soil. Therefore, environmentally friendly and sustainable alternatives and even zero liquid discharge (ZLD) have been investigated in recent years [6].

According to studies conducted by Sappidi et al., several desalination technologies are currently in use. However, separating water from high-salinity brines is expensive, complicated, and energy-intensive. At present, most industrial desalination processes are classified into thermal or membrane-based separations. The most widely used mature desalination technologies to date include flash evaporation and reverse osmosis [7]. Boo et al. state that thermal separation processes such as multiple-effect evaporation and mechanical vapor compression (MVC), are currently the most common methods used by inland desalination plants to desalinate highly concentrated brines [8].

Tong et al. define the MVC process as a ZLD technology. ZLD is an ambitious wastewater management strategy that eliminates any liquid waste leaving the plant, allowing most of the water to be recovered for reuse [9]. Boo et al. mention that conventional ZLD systems usually have a thermal brine concentrator to dewater the saline feedwater by evaporation and a thermal crystallizer to evaporate more water and further concentrate the feed past saturation, precipitating mineral salts and other impurities[10]. The condensed water produced by the MVC process is collected for reuse, while the solids produced are either sent to a landfill or reused as valuable salt by-products[11]. However, due to its highly-ambitious water quality and sustainability standards[2], ZLD technologies such as MVC, result in high capital and operating costs. As Boo et al. state, these technologies involve evaporative phase change processes with very high energy intensities due to the large vaporization enthalpy of water (652–682 KWh/m^3). In addition, these processes also require high-quality thermal energy, e.g., temperatures > 100 °C, and a high-quality electrical energy for the mechanical compression units of the MVC system[10]. As a result, ZLD has been considered unfeasible and has only been applied in necessary cases[9].

Due to stricter environmental regulations and the need for more cost-effective desalination processes, sustainable brine management is now a key step toward harnessing the untapped resources in brine, according to Ogunbiyi et al. several water, energy, and mineral recovery technologies are currently being investigated for sustainable brine management, though little progress has been made in their large-scale application thus far[1].

As mentioned in our previous study[12] our search for new cost-effective desalination technologies as an alternative to the MVC process has led our study to further investigate the application of the solvent-driven fractional crystallization (SDFC) process for use in our treatment processes. Our main goal is to improve the removal efficiency of magnesium and boron by increasing alkalinity with $Ca(OH)_2$[12] and using ethanol as an antisolvent due to its ease of handling, recovery, logistics, and lower toxicity. Our study selected ethanol as an antisolvent for two main reasons. First, it reduces the thermal energy costs compared to traditional water evaporation processes. Second, we wanted to use an environmentally friendly antisolvent.

As reported by Z. Foo et al., SDFC is a process in which targeted solutes are selectively precipitated from multicomponent solutions by mixing a solution containing the desired solute with a miscible organic antisolvent. In this process, the liquid portion of the mixture remains a single phase from which the precipitated solids are isolated. Various empirical studies have shown that target solutes can be precipitated by the organic antisolvent on a 1:1 molar basis, allowing the efficient solute recovery with minimal antisolvent addition[13].

In practice, experimental laboratory tests have shown that the SDFC process can selectively extract ions, such as transition and lanthanide metals, nickel, cobalt, and other inorganic ions, from contaminated industrial wastewater streams, including those generated in mineral extraction processes. For example, studies conducted by Stetson et al., reported that applying a dimethyl ether-driven fractional crystallization process to treat rare earth element-bearing permanent magnet leachates resulted in the selective separation of lanthanide-rich or transition metal-rich products, with a recovery range of 62.50–95.90%[14].

Foo et al., describe several water-miscible antisolvents (such as ethanol, acetone, and polyethylene glycol) that have been studied for their ability to saturate aqueous brines and influence the solubility limits of the dissolved solutes. However, most of the studies have used laboratory-prepared brines. At present, there is limited practical technical data from experiments with industrial wastewater. Regarding the choice of antisolvent in SDFC experiments, previous studies have shown that an ideal antisolvent should have the following characteristics: 1) induce the solid-liquid equilibrium phase; 2) minimal antisolvent addition; 3) rapid antisolvent removal from the aqueous solution; and 4) high antisolvent recovery ratio[13].

Adopting the methodology established by Barbosa et al. as a foundation, the development of our study comprised the following steps: 1) alkalinization of the saline water; 2) preheating of the antisolvent and the saline water; 3) mixing and formation of the saline water-antisolvent emulsion; 4) removal and sedimentation of the brine phase; and 5) separation of the product water from the antisolvent[15].

This research examined the impact of adding $Ca(OH)_2$ and varying the ethanol-to-RO concentrate ratio on the removal efficiency of magnesium, boron, and major elements, such chlorides, sulfates, calcium, arsenic, manganese, iron, potassium, sodium, and lithium present in our wastewater. The objective was to validate and optimize the efficiency of the solvent-driven fractional crystallization process using ethanol in wastewater treatment processes[12].

2. Materials and Methods

2.1. Study Material

The study material consists of a reverse osmosis concentrate from mine wastewater that has undergone chemical precipitation, macrofiltration, and ultrafiltration processes. The characteristics of this concentrate are similar to those of the water tested in our previous study[12]. The initial salinity of the concentrate wastewater used in the experiment was 50497.200 ppm. It was primarily composed of the following elements, listed in order of concentration: 1) monovalent ions (e.g., chloride, sodium, and potassium); 2) scaling ions (e.g., sulfate, calcium, and magnesium); 3) metalloids (e.g., boron and arsenic); and 4) metal ions (e.g., lithium, manganese, and iron). See **Table 1** for additional details.

To validate and improve upon the results of our initial study[12], we collected the reverse osmosis concentrate sample used in this experiment as a composite sample after operating the water treatment plant continuously for ten days (**Figure 1**)[12].

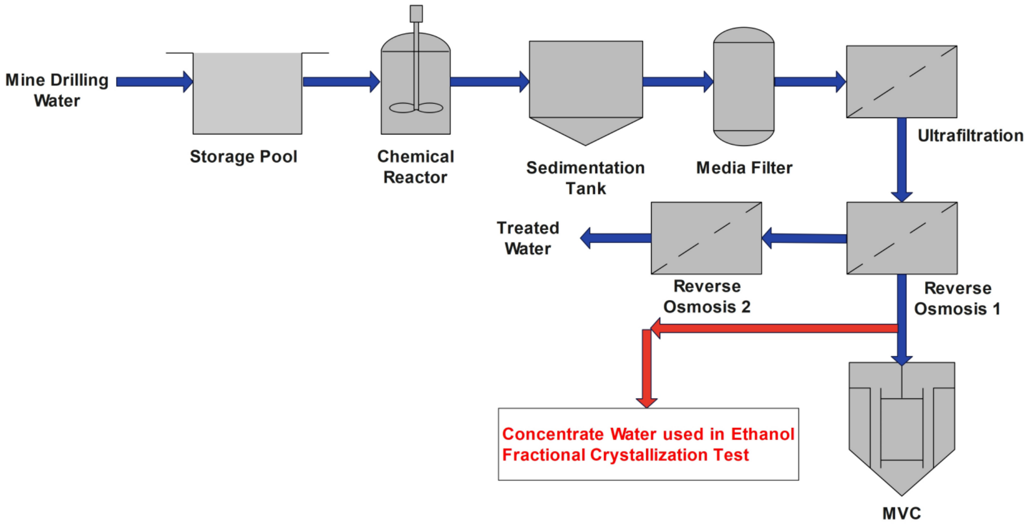

Figure 1. Water treatment plant flow diagram. (Adapted from Figure 1 in the article "Ethanol extraction desalination test using pre-treated mine wastewater concentrated by reverse osmosis," Desalination and Water Treatment, January 2024).

The characteristics of the untreated reverse osmosis concentrate are shown in **Table 1**.

Table 1. Characteristics of untreated reverse osmosis concentrate.

Parameter	Units	Quantity
pH	-	7.500
Specific conductivity	us/cm	64,740.000
Total dissolved solids (TDS)	mg/L	50,497.200
Total hardness (as mg/L CaCO$_3$)	mg/L	1,427.000
Chlorides	mg/L	22,454.700
Sulfates	mg/L	4,357.000
Calcium	mg/L	444.010
Magnesium	mg/L	77.170
Arsenic	mg/L	0.122
Manganese	mg/L	0.086
Iron	mg/L	0.050
Potassium	mg/L	860.380
Sodium	mg/L	15,652.500
Lithium	mg/L	73.342
Boron	mg/L	570.504

2.2. Experimental Equipment

The experimental process stages and materials used in this experiment were similar to those in our initial study, except for the inclusion of brine alkalinization and pre-heating, as described in the experimental process stages in the item 2.3 Methods. The aim of this experimental test was to improve the performance of the solvent-driven fractional crystallization process using ethanol based on our initial research. The wastewater used in this experiment underwent several industrial-level treatment processes, including chemical precipitation, sedimentation, macrofiltration, ultrafiltration, and reverse osmosis. **Figure 1** displays the flow diagram of the process[12].

The following materials were used in the experimental phase: 1 Finezza FZ-202D3N heater, 1 VELP SCIETIFICA JLT 4 jar test equipment, 1 Isolab separating funnel of 1.0 L capacity, 1 Isolab Kitasato flask of 1.0 L capacity, 1 ROCKER 610 vacuum pump, 1.0 um filter papers from Pall

Corporation, 1 Henkel Bq 003 analytical precision balance, 1 Eurolab thermostat oven, 1 three-mouth Biohall bottle of 1.0 L capacity, 1 Thermo Scientific Electrothermal 04641-45 heating blanket with stirrer, 1 laboratory fractional distillation equipment with Vigreux type column, 1 frosted nozzle measuring cylinder of 1.0 L capacity, 1 IWAKI EH-E31 cooling water pump, 1 HANNA Hi 98501 digital thermometer, 1 Hach HQ 30D digital multi-parameter meter, 1 Eurolab graduated cylinder of 250 ml capacity, 2 Pyrex beakers of 50 ml capacity, 2 Eurolab 70 mm diameter watch moons, and 1 Eurotech alcohol degree meter[12].

The following chemical reagents were used in the experiment: a 10% (w/w) calcium hydroxide solution as an alkalizing agent and 94 °GL ethanol as an antisolvent for the crystallization process. The experimental process scheme is illustrated in **Figure 2**.

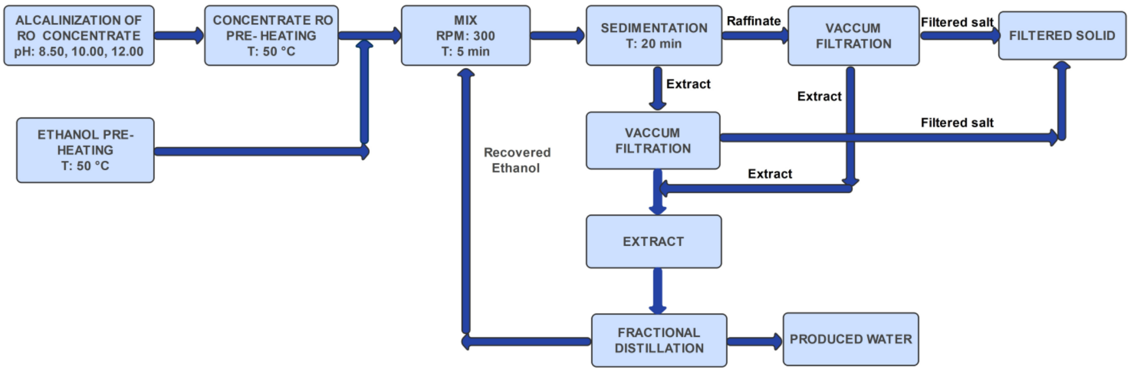

Figure 2. Diagram illustrating the solvent-driven fractional crystallization laboratory experiment using ethanol.

2.3. Method

Based on our initial studies, we carried out the solvent-driven fractional crystallization test using ethanol through the following stages: 1) brine alkalinization; 2) brine and ethanol pre-heating; 3) liquid extraction: ethanol-reverse osmosis concentrate mixture; 4) raffinate separation (precipitated salt) from biphasic mixture of ethanol-brine; 5) precipitated salt filtration; 6) salt drying; and 7) separation of ethanol from product water through fractional distillation[12].

The experimental tests were conducted under the following operating conditions: 1) alkalinization of RO concentrate at pH:8.50, 10.00, and 12.00; 2) ethanol : RO concentrate mixture ratios of 85:15 (680 ml ethanol:120 ml RO concentrate), 70:30 (560 ml ethanol:240 ml RO concentrate), and 50:50 (400 ml ethanol:400 ml RO concentrate); 3) extraction temperature of 50 °C; 4) stirring velocity of 300 rpm; 5) stirring time of 5 min; and 6) sedimentation time of 20 min[12].

As in our initial research, which aimed to obtain experimental data on the process, the solvent-driven fractional crystallization process was carried out using a jar test equipment. A separation funnel was used for the sedimentation process. The percentage of precipitated salt was determined by drying it. The filtrate solution from the extract and the raffinate underwent fractional distillation (using a Vigreux column) to recover the ethanol antisolvent for reuse and to separate the product water[12].

2.4. Control and Analysis

2.4.1. Parameters Measured During the Experiment

This investigation analyzed the same parameters as our initial study[12], which examined the primary constituents present in our wastewater. Using the "Standard Methods for the Examination of Water and Wastewater", we analyzed the following chemical and physical parameters: pH (Standard methods: Electrometric Method. Part–4500–H^+ B), sulfates (Standard methods: Turbidimetric Method. Part–4500–SO_4^{2-}), total hardness (Standard methods: EDTA Titrimetric Method. Part–2340 C–Hardness), conductivity (Standard methods: Laboratory Method. Part–2510 B–Conductivity), total dissolved solids (Standard methods: Total Dissolved Solids Dried at 180 °C Method. Part 2540 C), total solids (Standard methods: Total Solids Dried at 103–105 °C Method. Part 2540 B), chlorides (Standard methods: Chloride Argentometric Method. Part–4500–Cl^-

B). We analyzed the elements arsenic, boron, calcium, iron, potassium, lithium, magnesium, manganese, and sodium using "EPA, 2020: Approved CWA Chemical Test Methods"[12,16,17].

The physico-chemical parameters analyzed in our test were validated through the use of calibrated alternative instruments, repeated sample measurements, analysis of blind samples, use of blank samples, and use of reference standards. Additionally, samples were sent to an external laboratory for proficiency testing to compare results.

3. Results and Discussion

SDFC technology, also referred as antisolvent crystallization, is a separation process in which two or more solutes are recovered from a multicomponent solution. This process occurs through the addition of substance known as antisolvent with the aim of reducing the solubility of the solute in the original solvent and thus achieve supersaturation[14]. Supersaturation, the driving force of this process, is created by mixing a solution containing the desired solutes with a miscible antisolvent[18]. In our experiment, we assume that the antisolvent (ethanol) interacts strongly with the solvent water in the saline solution, primarily through hydrogen bonding caused by the intrinsic polarity of the solvents used, which increases their strength and causes the system to crystallize[14,19].

While the molecular interactions between water, salt ions, and antisolvents remain unclear[20], the application of the SDFC process using ethanol has yielded promising results in removing elements of interest, as demonstrated in **Tables 2–4**. These results confirm the hypothesis that hydrogen bond strength dominates the ion-dipole interaction, leading to a higher supersaturation and influencing the nucleation rate and growth velocity[19]. **Figure 3** shows the proposed mechanism for developing the SDFC process in a saturated sodium chloride solution. It illustrates the formation of hydrogen bonds and ion-dipole interactions between ethanol and sodium ion, as well as between ethanol and chloride ion.

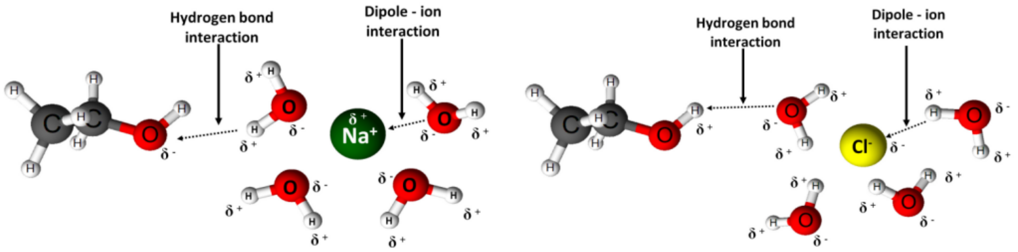

Figure 3. Mechanisms of hydrogen bond formation and ion-dipole interactions for ethanol with sodium ion (**left**) and chloride ion (**right**).

Table 2. Characteristics of the product water at an ethanol-RO concentrate mixing ratio of 85:15 (v/v) and concentrate pH values of 8.530, 10.110, and 12.100.

Volumetric Mixing Ratio Ethanol – RO Concentrate (85:15)							
Parameter	**Units**	**pH:8.530**	**%**	**pH:10.110**	**%**	**pH:12.100**	**%**
Specific conductivity	us/cm	36510.000	-	34890.000	-	33600.000	-
Total dissolved solids (TDS)	mg/L	28477.800	43.61	26865.300	46.80	26208.000	48.10
Total hardness (mg/L $CaCO_3$)	mg/L	62.000	95.66	31.000	97.83	23.000	98.39
Chlorides	mg/L	19383.280	13.68	19378.392	13.70	19355.440	13.80
Sulfates	mg/L	116.000	97.34	114.000	97.38	83.000	98.10
Calcium	mg/L	8.970	97.98	9.160	97.94	7.750	98.25
Magnesium	mg/L	9.530	87.65	1.155	98.50	1.050	98.64
Arsenic	mg/L	< 0.008	93.44	< 0.008	93.44	0.009	92.62
Manganese	mg/L	0.004	95.35	0.006	93.02	0.005	94.19
Iron	mg/L	0.045	10.00	0.046	8.00	0.044	12.00
Potassium	mg/L	731.323	15.00	732.021	14.92	733.146	14.79
Sodium	mg/L	12224.263	21.90	12165.810	22.28	12182.639	22.17
Lithium	mg/L	70.888	3.35	70.858	3.39	70.508	3.86
Boron	mg/L	518.481	9.12	170.891	70.05	52.363	90.82

Note: %: percentage of removal efficiency.

Table 3. Characteristics of the product water at an ethanol-RO concentrate mixing ratio of 70:30 (v/v) and concentrate pH values of 8.550, 10.080, and 12.130.

Volumetric Mixing Ratio Ethanol – RO Concentrate (70:30)							
Parameter	**Units**	**pH:8.550**	%	**pH:10.080**	%	**pH:12.130**	%
Specific conductivity	us/cm	36260.000	-	35300.000	-	34130.000	-
Total dissolved solids (TDS)	mg/L	28282.800	43.99	27181.000	46.17	26621.400	47.28
Total hardness (mg/L $CaCO_3$)	mg/L	222.000	84.44	107.000	92.50	56.000	96.08
Chlorides	mg/L	19252.020	14.26	19323.603	13.94	19188.920	14.54
Sulfates	mg/L	796.000	81.73	663.000	84.78	528.000	87.88
Calcium	mg/L	28.710	93.53	25.300	94.30	22.00	95.05
Magnesium	mg/L	36.890	52.20	1.920	97.51	1.100	98.57
Arsenic	mg/L	< 0.008	93.44	< 0.008	93.44	0.008	93.44
Manganese	mg/L	0.006	93.02	0.007	91.86	0.006	93.02
Iron	mg/L	0.043	14.00	0.046	8.00	0.044	12.00
Potassium	mg/L	732.078	14.91	731.104	15.03	732.521	14.86
Sodium	mg/L	11944.251	23.69	11774.063	24.78	11724.180	25.10
Lithium	mg/L	70.696	3.61	70.467	3.92	69.986	4.58
Boron	mg/L	515.746	9.60	169.974	70.21	113.880	80.04

Note: %: percentage of removal efficiency.

Table 4. Characteristics of the product water at an ethanol-RO concentrate mixing ratio of 50:50 (v/v) and concentrate pH values of 8.520, 10.000, and 12.080.

Volumetric Mixing Ratio Ethanol – RO Concentrate (50:50)							
Parameter	**Units**	**pH:8.520**	%	**pH:10.000**	%	**pH:12.080**	%
Specific conductivity	us/cm	35830.000	-	34120.000	-	34165.000	-
Total dissolved solids (TDS)	mg/L	28305.700	43.95	27296.000	45.95	26990.350	46.55
Total hardness (mg/L $CaCO_3$)	mg/L	382.000	73.23	212.000	85.14	210.000	85.28
Chlorides	mg/L	19090.971	14.98	19135.325	14.78	19121.513	14.84
Sulfates	mg/L	2307.000	47.05	1814.000	58.37	1073.000	75.37
Calcium	mg/L	59.250	86.66	80.940	81.77	89.290	79.89
Magnesium	mg/L	57.020	26.11	2.630	96.59	1.085	98.59
Arsenic	mg/L	< 0.008	93.44	< 0.008	93.44	0.008	93.44
Manganese	mg/L	0.006	93.02	0.004	95.35	0.005	94.19
Iron	mg/L	0.044	12.00	0.045	10.00	0.045	10.00
Potassium	mg/L	734.570	14.62	731.470	14.98	730.720	15.07
Sodium	mg/L	11832.498	24.41	11789.362	24.68	11815.492	24.51
Lithium	mg/L	70.891	3.34	69.859	4.75	70.758	3.52
Boron	mg/L	438.102	23.21	246.316	56.82	187.888	67.07

Note: %: percentage of removal efficiency.

The test results (**Tables 2–4**) reveal that, despite the higher magnitude of the ion-dipole interaction energy (40–600 KJ/mol), the relatively weaker hydrogen bonds (10–40 KJ/mol) are strong enough to define the structure and properties of water. This leads to the formation of hydrogen bonds within their molecules or with other similar hydrophilic molecules such as ethanol[19]. Furthermore, the results demonstrate that the quantity of antisolvent used significantly impacts the level of supersaturation achieved, as well as the strength and stability of the resulting hydrogen bonds. Higher ionic removal efficiencies are achieved with higher ethanol: RO concentrate mixing ratios. The following sequence is established: 85:15 (680 ml ethanol:120 ml RO concentrate) > 70:30 (560 ml ethanol:240 ml RO concentrate) > 50:50 (400 ml ethanol:400 ml RO concentrate).

Figure 4 shows that the highest salt removal efficiencies were achieved with the highest ethanol to RO concentrate mixing ratios. Regarding the TDS parameter, which represents the total ionic charge in water (i.e., minerals, metals, and dissolved salts), the ionic removal efficiency was found to increase with higher mixing ratios and pH. The experiment achieved TDS removal efficiencies of 48.10%, 47.28%, and 46.55% for mixing ratios of 85:15, 70:30, and 50:50, respectively, relative to the TDS concentration of the wastewater used in the experiment (50497.200 ppm). The pH levels tested in this experiment ranged from 12.080 to 12.130. Additionally, the TDS removal efficiencies achieved with the various mixing ratios and pH levels tested maintained a direct relationship with the percentage of salt that precipitated, as shown in **Figure 4**. Similarly, the percentage of salt precipitated increased with the mixing ratio and pH. In this case, 28.10%, 25.90%, and 23.60% of salt was precipitated for the same mixing ratios and pHs used in the previous experiment. Preliminary results indicate that the ionic separation efficiency is related to the quantity of antisolvent and precipitant agent ($Ca(OH)_2$) used in the crystallization process. **Figure 5** shows images of the precipitated salts for the different mixing ratios and pH values.

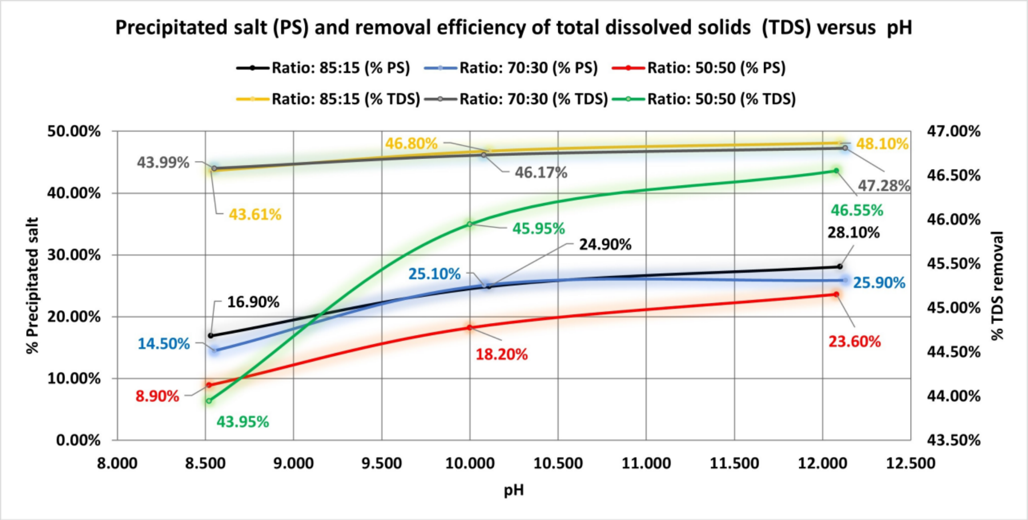

Figure 4. Graph depicting the relationship between% salt precipitated and% TDS removal versus pH at a mixing ratios of 85:15, 70:30, and 50:50.

Figure 5. Images depicting the precipitated solids at: 1) a mixing ratio of 85:15 and pH levels of 8.530 (**a**), 10.110 (**b**), and 12.100 (**c**); 2) a mixing ratio of 70:30 and pH levels of 8.550 (**d**), 10.080 (**e**), and 12.130 (**f**); 3) a mixing ratio of 50:50 and pH levels of 8.520 (**g**), 10.000 (**h**), and 12.080 (**i**).

Figure 5 shows that a more compact and voluminous filter cake forms at higher pH levels and mixing ratios than at lower levels. Conversely, a more brittle and thinner filter cake formed at lower pHs and mixing ratios. The results presented thus far demonstrate that the highest salinity removal efficiency was achieved at a mixing ratio of 85:15

and a pH of 12.100. This experiment achieved a total dissolved solids (TDS) removal efficiency of 48.10%, which is higher than tests with lower mixing ratios (70:30 and 50:50) that achieved TDS removal efficiencies of 47.28% and 46.55%, respectively, within a similar pH range. These results confirm the importance of the quantity of antisolvent and $Ca(OH)_2$ on the performance of the SDFC process using ethanol. Additionally, the results from **Tables 2–4** show that salt removal is primarily related to the high reduction of the scaling ions, such as calcium, magnesium, and sulfates, as well as metalloids, such as arsenic and boron, and the metal ion manganese. There is a moderate reduction of non-metals, such as chlorides, and of metal ions, such as sodium and potassium. Lithium and iron are reduced the least.

The solvent-driven fractional crystallization process using ethanol exhibited high selectivity for reducing the main scaling ions. The highest removal efficiencies were achieved at the highest mixing ratios and pH levels, as shown in **Figure 6**. The best removal efficiencies were obtained at a mixing ratio of 85:15 and a pH of 12.100. The results showed removal efficiencies of 98.39%, 98.25%, and 98.64% for total hardness, calcium, and magnesium, respectively. These results were obtained using an experimental wastewater concentration of 1427.000 ppm for total hardness, 444.010 ppm for calcium, and 77.170 ppm for magnesium. The higher removal efficiencies obtained for total hardness are directly related to the removal efficiencies obtained for calcium and magnesium, the main constituents of total hardness. These results confirm the effectiveness of the solvent-driven fractional crystallization process for removing these elements. In addition to the precipitation of calcium and magnesium, which is believed to occur due to the formation of hydrogen bonds and molecular interactions, some reduction in total carbonate hardness may occur due to the warm softening process. This process occurs within the temperature range of 49 °C–60 °C and can be explained by the following chemical reactions [Equations (1) and (2)]:

$$\mathrm{Ca}\left(\mathrm{HCO}_3\right)_2 \; + \; \mathrm{Ca(OH)}_2 \; \leftrightarrow \; 2\mathrm{CaCO}_3 \; + \; 2\mathrm{H}_2\mathrm{O} \tag{1}$$

$$\mathrm{Mg}\left(\mathrm{HCO}_3\right)_2 + 2\mathrm{Ca(OH)}_2 \leftrightarrow \mathrm{Mg(OH)}_2 + 2\mathrm{CaCO}_3 + 2\mathrm{H}_2\mathrm{O} \tag{2}$$

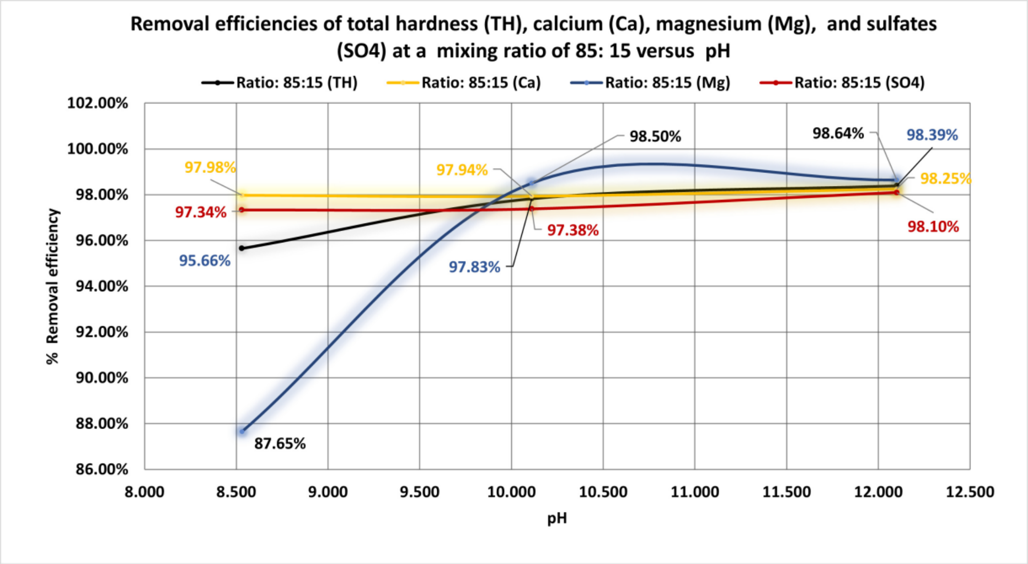

Figure 6. Graph depicting the relationship between the removal efficiency of total hardness, calcium, magnesium, and sulfates at a mixing ratio of 85:15 versus pH.

In the case of magnesium, its reduction is a function of the excess of hydroxyl alkalinity (OH^-) maintained as a result of the addition of calcium hydroxide ($Ca(OH)_2$).

For a sulfate concentration of 4357.000 ppm in wastewater, which is another important compound in scale formation in the presence of calcium, a removal efficiency of 98.10%

was achieved. However, the probability of removing of non-carbonate hardness is low, because it requires the addition of chemicals, i.e., a combination of lime and sodium carbonate, as well as coagulant and flocculant chemicals. These chemicals were not used in this experiment. Therefore, its reduction in this case could be mainly associated with a supersaturation effect of the solution[21].

Similar to the scaling ions, the SDFC process using ethanol successfully removed metalloids, such as arsenic and boron, as shown in **Figure 7**. An average removal efficiency of 93.35% was achieved at an inlet arsenic concentration of 0.122 ppm. No significant variation in removal efficiency was observed for different mixing ratios and pH levels tested, probably due to the low arsenic inlet concentration (0.122 ppm). Our previous study, which used ethanol as an extracting antisolvent in the same type of water[12], showed a higher arsenic removal efficiency (97.32%) for a higher arsenic inlet concentration (0.299 ppm). These results confirm the high affinity of ethanol for the selective crystallization of arsenic. Studies conducted by Guo et al.[22], using decanoic acid as an extracting antisolvent also confirmed the efficiency of the SDFC process in reducing arsenic, achieving removal efficiencies greater than 91.00% and 97.00% for As-III and As-V respectively.

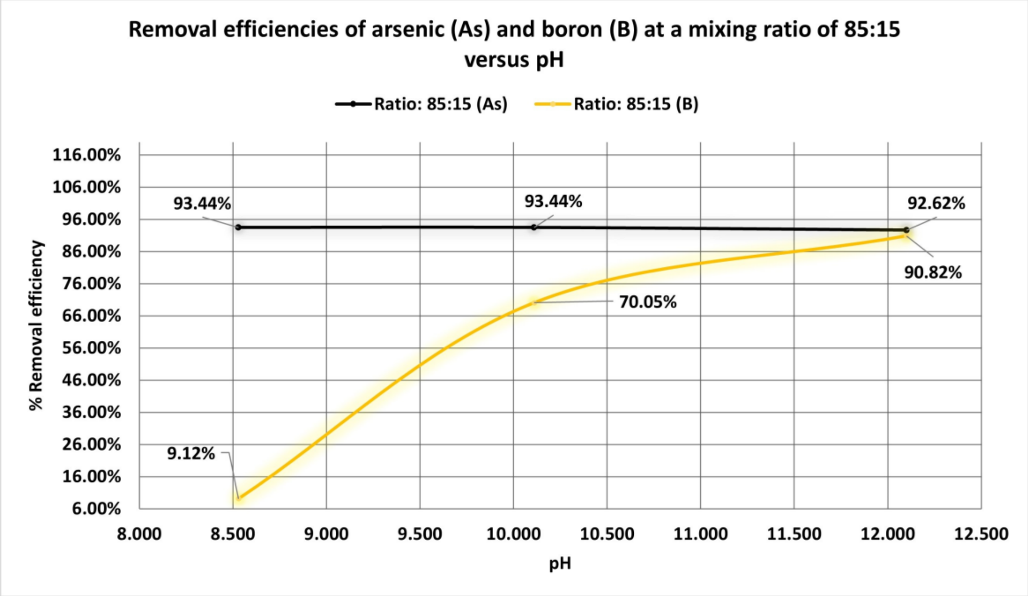

Figure 7. Graph depicting the relationship between the removal efficiency of arsenic and boron at a mixing ratio of 85:15 versus pH.

For a boron concentration of 570.504 ppm, the results showed an increase in the removal efficiency with an increased mixing ratio and pH. The highest boron removal efficiency (90.82%) was achieved at a mixing ratio of 85:15 and a pH of 12.100, which is higher than the results obtained in our previous ethanol crystallization study without using $Ca(OH)_2$ (9.91%–12.14%)[12]. This improvement in boron removal efficiency can be explained by these two main reasons: a) chemical precipitation by calcium hydroxide, and b) a probable reaction between boron and ethanol.

In the first case, the presence of calcium and borate ions in the solution could lead to the formation of borate salts. This process is favored by an increase in temperature, which consequently increases the diffusion rate of borate ions across the boundary layer and into the internal pores of the $Ca(OH)_2$ particle. Studies conducted by Yilmaz et al.[23], determined, via X-ray diffraction (XRD) analysis, that the solid phase formed as a result of adsorption/precipitation experiments between the borate anion and $Ca(OH)_2$ showed diffraction peaks indicative of $CaB_3O_3(OH)_5{\cdot}4H_2O$ (inyoite) formation. Based on these findings, it was concluded that the Ca^{2+} and borate ions would react as follows [Equation (3)]:

$$\mathrm{Ca^{2+}_{(aq)}} + 3\mathrm{H_3BO_{3(aq)}} + 2\mathrm{OH^-} + \mathrm{H_2O} \rightarrow \mathrm{CaB_3O_3(OH)_{5(s)}} + 4\mathrm{H_2O} \tag{3}$$

In the second case, a possible reaction between the borate ion and ethanol would take place as follows [Equation (4)]:

$$B(OH)_4^- + CH_3CH_2OH \rightarrow C_2H_8O_4B^- + H_2O \tag{4}$$

Studies conducted by Bai et al. [24] on the influence of pH on boric acid/borax reactions with simple hydroxyl compounds, using Raman spectroscopy investigation and DFT (Density Functional Theory) calculation, showed that the calculated Gibbs free energy results for $B(OH)_4^-$ reactions with the tested alcoholic compounds were smaller than zero. This indicates that alcohols spontaneously react with boron. The Gibbs free energy value found for the reaction of ethanol with $B(OH)_4^-$ was -18.7129 KJ/mol. According to this theoretical result, ethanol would react with $B(OH)_4^-$. However, the Raman spectroscopy images showed that the reactivity of the hydroxyl compounds with boric acid seems to depend on the type of the hydroxyl compound, with reactivity following the order of monohydric alcohol < dihydric alcohol < trihydric alcohol < polyol [24]. This indicates that complexation between boric acid and monohydric alcohols is insignificant. Conversely, Ayers et al. [25], reported that boric acid can be extracted by mono-alcohols or di-hydroxy alcohols from low to high ionic strength solutions through an esterification reaction [25,26]. Zhang et al. [27], proposed the following esterification extraction reaction mechanism as shown in the Equation (5):

$$H_3BO_3 + nROH \leftrightarrow H_3BO_3 \cdot nROH \tag{5}$$

These studies revealed that the esterification reaction has a slow kinetic, suggesting that processes such as hydrogen bonding and molecular interactions, in addition to esterification, should not be excluded.

Currently, there is no established process for the liquid extraction of boron from high-salinity brines and further research is needed to better understand the processes governing boron removal.

The results showed no significant variation in chloride removal at the different mixing ratios and pH levels tested. On average, the chloride removal efficiency at a mixing ratio of 85:15 was 13.73% at an inlet chloride concentration of 22454.700 ppm (**Figure 8**, **Table 1**). Similar behavior was observed for metal ions such as sodium, potassium, and lithium. These ions achieved average removal efficiencies of 22.12%, 14.90%, and 3.53%, respectively, at inlet concentrations of 15652.500 ppm for sodium, 860.380 ppm for potassium, and 73.342 ppm for lithium (**Figure 8**, **Table 1**). According to the results, the SFDC process using ethanol showed moderate removal efficiency for monovalent ions, such as sodium, chloride, and potassium. However, the results were not satisfactory for lithium removal due to the low percentage removed. The mechanism governing the SFDC process remains unclear; however, it is believed that the association pathway for their reduction is a consequence of hydrogen bonding effects and molecular interactions. Further research is needed to better understand the mechanisms governing the removal of these elements.

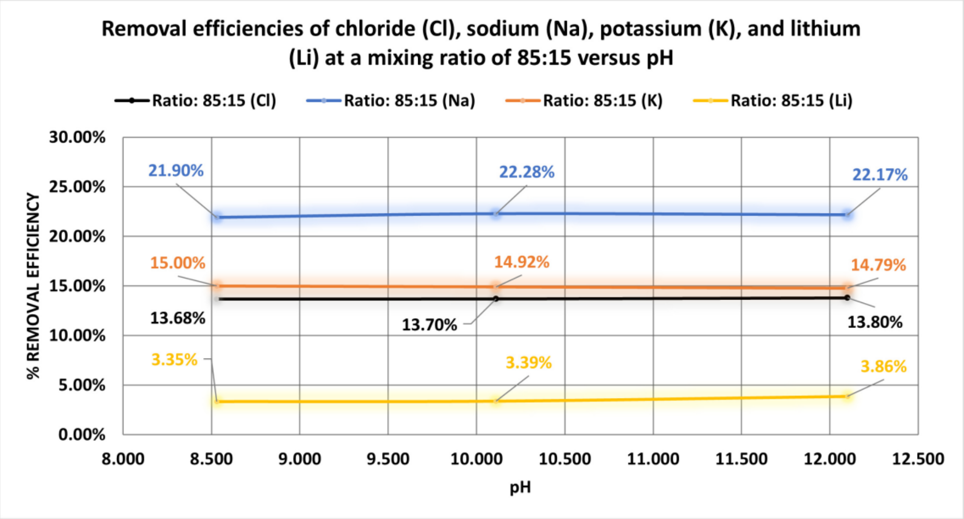

Figure 8. Graph depicting the relationship between the removal efficiency of chlorides, sodium, potassium, and lithium at a mixing ratio of 85:15 versus pH.

As with the monovalent elements, no significant variation was observed in the mixing ratios and pH levels tested for iron. The results showed an average removal efficiency of 10.00% (**Figure 9**, **Table 1**) at an inlet iron concentration of 0.050 ppm. For a manganese concentration in wastewater of 0.086 ppm, the average removal efficiency was 94.19% (**Figure 9**, **Table 1**). Although the SFDC process using ethanol did not show favorable results for iron removal, it demonstrated high selectivity for manganese reduction. Despite the low inlet concentration of manganese (0.086 ppm), the removal efficiency was high and comparable to the results obtained in our previous study (94.48%–97.24%). The higher removal efficiency in the previous study could be attributed to the higher inlet concentration of manganese (0.189 ppm)[12]. As with arsenic, these results confirm the high affinity of ethanol for reducing manganese concentrations, whose abatement is also of great interest for our process.

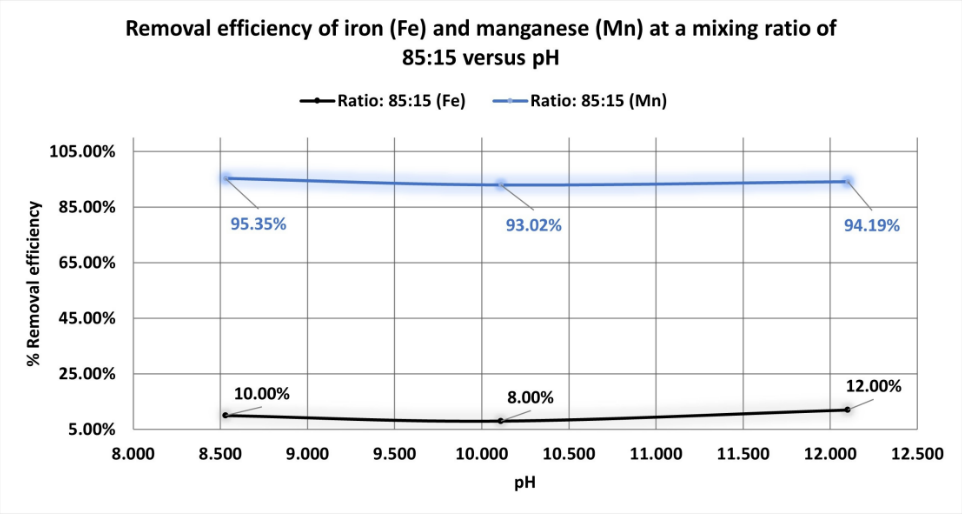

Figure 9. Graph depicting the relationship between the removal efficiency of iron and manganese at a mixing ratio of 85:15 versus pH.

The results obtained so far under similar test conditions (mixing ratio, pH, reaction temperature, stirring velocity, stirring time, and sedimentation time) are comparable to those obtained in our previous study (**Table 5**). Similar trends in the removal of ionic compounds were observed, except for magnesium. The higher removal efficiency of magnesium in the later test could be related to the increase in hydroxide alkalinity (OH^-). Therefore, the practical results obtained thus far validate the solvent-driven fractional crystallization process using ethanol for application in our treatment processes.

Table 5. Ionic removal efficiency results of desalination tests with ethanol without using $Ca(OH)_2$ (1st Desalination Test) and using $Ca(OH)_2$ (2nd Desalination Test).

Parameter	1st Desalination Test (pH: 8.080 - 8.120, T: 55 °C) (Mixing ratio: 85:15) (Sedimentation Time: 20 min) (%)	2nd Desalination Test (pH: 8.530, T: 50 °C) (Mixing ratio: 85:15) (Sedimentation Time: 20 min) (%)
Total dissolved solids (TDS)	43.94–48.03	43.61
Chlorides	11.26–14.76	13.68
Sulfates	90.82–96.09	97.34
Calcium	98.69–98.97	97.98
Magnesium	27.14 - 35.30	87.65
Arsenic	97.32	93.44
Manganese	94.48–97.24	95.35
Iron	0.00–10.00	10.00
Potassium	14.57–16.42	15.00
Sodium	24.95–26.17	21.90
Lithium	2.46–13.87	3.35
Boron	9.91–12.14	9.12

Source: Adapted from the article “Ethanol extraction desalination test using pre-treated mine wastewater concentrated by reverse osmosis,” Desalination and Water Treatment, January 2024.

Based on the results of this experiment, SDFC technology using ethanol and a pre-alkalinization stage with $Ca(OH)_2$ is a highly efficient desalination process for extracting important elements such as magnesium and boron, as well as other elements, including calcium, sulfate, arsenic, manganese, chloride, sodium, and potassium, from complex saline streams. However, a better understanding of the thermodynamic and kinetic transport behavior associated with the SDFC process is still needed. This includes the principles governing the transport of solvent, water, and salt molecules; the interaction between components at different salinities and temperatures; the role of the antisolvent position; the effects of different stereochemical arrangements; and the thermal effects on solvation behavior, among others [20]. Currently, few studies have evaluated the effectiveness of using SDFC technology to treat mining wastewater, particularly with regard to removing magnesium and boron. Therefore, more research is needed to further develop and apply this technology.

4. Conclusion

It is concluded that the solvent-driven fractional crystallization process using ethanol is an important technological alternative for treating complex, high-salinity brines, such as those found in mining wastewater. However, while SDFC is a powerful purification technique, it is limited in its application to low-conductivity wastewater due to factors such as a low concentration of target solutes, which can hinder effective crystallization, as well as challenges in solvent recovery and efficiency due to the large volumes of solvent required. This process yielded satisfactory results when tests were conducted at the highest mixing ratio (85:15) and pH (12.100). The results showed that the quantity of antisolvent and $Ca(OH)_2$ used in the experiment significantly affects the efficiency of removing magnesium and boron. Under these conditions, reductions of 98.64% and 90.82%, respectively, were achieved for magnesium and boron. The experiment achieved salinity and precipitated salt removal efficiencies of 48.10% and 28.10%, respectively. Salinity reduction was primarily related to the reduction of major scaling ions such as calcium, magnesium, and sulfate, as well as metalloids, such as arsenic and boron, and the metal manganese. To a lesser extent, salinity reduction was related to elements, such as chloride, sodium, potassium, iron, and lithium. The solvent-driven fractional crystallization process using ethanol was highly efficient at removing scaling ions, achieving 98.25% and 98.10% removal efficiencies for calcium and sulfate, respectively. A removal efficiency of 92.62% was achieved for metalloids such as arsenic. Analysis of the experimental results obtained in our trial indicates that pre-alkalinizing the brine with $Ca(OH)_2$ and using a high ethanol to RO concentrate ratio favored the reduction of the boron concentration level. However, further research is still required to validate and understand the predominant mechanism governing the reduction of this element. For monovalent elements such as chloride, sodium, and potassium, the results showed moderate removal efficiencies, achieving values of 13.80%, 22.17%, and 14.79% respectively. As with arsenic, ethanol showed high selectivity for reducing manganese, achieving a value of 94.19%. However, the results for lithium and iron were not satisfactory, with removal efficiencies of 3.86% and 12.00% respectively-the lowest in the tested process.

The results obtained in our investigation were comparable to those of our previous study in terms of ionic removal levels of the studied elements, except for magnesium and boron. Their higher removal efficiency was mainly due to the addition of $Ca(OH)_2$. These results validate the effectiveness and applicability of the process for treating complex wastewater.

Further research is still needed to understand the molecular interaction mechanisms of water–antisolvent–salt systems for crystallization to be feasible. This includes understanding the thermodynamic behavior of the system and the phenomena governing the process, such as the co-precipitation of other elements. It is important to mention that the practical results have been positive. Consequently, SDFC technology using ethanol has the potential to serve as a promising alternative to existing thermal processes. Ethanol has been shown to be less toxic than other organic antisolvents than have been tested. Furthermore, it requires less thermal energy because of the difference in the volatility of the components to be separated. The SDFC process is a good option for saving thermal energy. The distillation of ethanol for reuse requires less thermal energy in comparison to the process of water evaporation. Further pilot-level studies are necessary to evaluate the complete performance of the SDFC process. Such a performance evaluation should encompass product water and antisolvent recovery, electrical and thermal energy consumption, and salt filterability. This comprehensive evaluation will determine the potential scalability of the process. However, further research is necessary to identify specific antisolvents that exhibit high separation and recovery capabilities.

Author Contributions

Conceptualization, E.V. and F.H.; methodology, E.V.; software, E.V.; validation, E.V.; formal analysis, E.V.; investigation, E.V.; data curation, E.V.; writing—original draft preparation, E.V.; writing—review and editing, E.V. and F.H.; supervision, E.V.; project administration, E.V. All authors have read and agreed to the published version of the manuscript.

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Informed Consent Statement

Not applicable.

Data Availability Statement

All data generated during this study are included in this published article.

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Conflicts of Interest

The authors declare no conflicts of interest.

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