

Article

Catalytic Partial Desalination of Saline Water

David D. J. Antia 

DCA Consultants Ltd., The Bungalow, Castleton Farm, Falkirk FK2 8SD, UK; dcacl@btconnect.com

Abstract: More than 1 billion ha of land is adversely affected by salinization, including about 54 million ha of irrigated cropland. This study trials a batch flow, bubble column, static bed, catalytic, pressure swing adsorption–desorption, zero valent iron, and diffusion reactor train, which is designed to partially desalinate water, for use as either livestock feed water or partially desalinated irrigation water. ZVI desalination produces a partially desalinated water product, without producing a waste brine product. The trial demonstrates sequential batch processing of 50 (0.86 m³) batches of saline water (43 m³ total), using a single ZVI charge, without loss of activity. The trialed feed water contained between 1 and 9 g NaCl L^{−1}. The average desalination was 41.84% (standard deviation was 15.61%). The optimum batch processing time is determined as being between 12 and 24 h. For each batch, the first-order forward rate constants, for both Cl[−] and Na⁺ ion removal, decline with time. The study considers the irrigation application of the product water on crop yield for 70 crop varieties; the application of the technology to desalinate a saline aquifer; applications of the technology to improve the environmental efficiency of conventional desalination plants.

Keywords: catalytic desalination; catalytic pressure swing adsorption desorption; crop yield; desalination; irrigation water; zero valent iron



Citation: Antia, D.D.J. Catalytic Partial Desalination of Saline Water. *Water* **2022**, *14*, 2893. <https://doi.org/10.3390/w14182893>

Academic Editor: José Luis Sánchez-Lizaso

Received: 13 August 2022

Accepted: 13 September 2022

Published: 16 September 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Irrigated cropland currently accounts for around 40% of global food production [1,2]. Global food demand is expected to rise by between 60% and 100% by 2050 [1,2]. This rise in food demand results from the expected increase in global population, from 7.7 billion in 2017 [3] to 9.1 billion people in 2050 [1,2] and 11.2 billion by 2100 [3].

The majority of the future increase in food production required to meet this demand will be confined to areas that are salinized or are currently irrigated with saline water or become newly irrigated with saline water. The crop yield decreases as a function of increasing soil salinity.

More than 1 billion ha of land is negatively affected by salinization, including about 20% to 33% of the global irrigated cropland (54 million ha) [3,4]. The term salinized is used to refer to soil or water, with an electrical conductivity of >4 dSm^{−1} (mScm^{−1}) [3]. The potential future global cropland land resource in areas where the soil is salinized has been estimated at >200 million ha [3].

In areas affected by soil salinization, the irrigation water may also be saline. As a very rough guide, the soil salinity is typically 10–30% greater than the irrigation water salinity [5]. However, the actual relationship is soil and location specific, varying with the salinity of the irrigation water [6,7].

Blending saline water with freshwater (or desalinated water) has sometimes been considered to increase the supply of irrigation water [8]. This approach can be effective in increasing overall crop yields, but may result in long-term soil salinization [8]. Some studies have demonstrated higher crop yields when crops are irrigated with desalinated water compared to irrigation with freshwater [9].

Conventional desalination plants use physical processes, such as evaporation or membrane separation (e.g., reverse osmosis), to produce a low-salinity product water and

a high-salinity brine waste. While irrigation with a low-salinity product water will increase crop yields, disposal of the high-salinity brine may create environmental problems and may adversely affect local aquifers. An alternative solution is to use a chemical desalination approach. These approaches produce a partially desalinated product water and no high-salinity brine waste. Two groups of chemical desalination can potentially be used to produce a partially desalinated product water, suitable for irrigation water. They are CO₂ desalination and zero valent iron (ZVI, Fe⁰) desalination [10].

CO₂ desalination was first conceptualized in the mid-1990s (US Patent US6180012B1) as a method of desalinating seawater [10]. It has since evolved into a process that could be used to remove Na⁺ and Cl[−] ions, associated with the waste brine from conventional desalination plants (Canadian patent CA2744264A1) [10]. More recently, it has been used in pilot plants, which are designed to strip CO₂ from air [10]. This technology requires a CO₂ source, which can be air, and a source of ammonia (NH₃) (e.g., US Patents US6180012B1; US7531142B2; US10322371B2; world patent WO2007094691A1; Canadian Patents CA2669964; CA2744264A1; Australian Patent AU2012321057A1; European patents EP1335881B1; EP1958683A2; EP1961479A2; EP2134811A2). The products are: NaHCO_{3(s)}, Na₂CO_{3(s)}, and NH₄Cl_(s) + partially desalinated water [10].

The simpler, alternative chemical process, ZVI (Fe⁰) desalination, was first reported in the academic literature in 2010 [10] (it has been described in 1 thesis, 1 Conference paper, 6 book chapters, and 11 academic papers).

The ZVI desalination process has been defined in patents (US Patents US8636906B2; US9624113B2; US9828258B2; US2018/0009678A; US10919784B2; French patent FR2983191A1; Spanish Patent ES2,598,032; UK Patent GB2520775A). The various types of ZVI desalination are described and defined in reference [10]. They use one of four different groups of reactor processes; these processes are: (i) n-ZVI + saline water in a continuous flow reactor, where the n-ZVI + NaCl is recovered by magnetic separation (Spanish Patent ES2,598,032); (ii) Emulsified n-ZVI + saline water + surfactant, where the Cl[−] ions are removed by an undefined process (US Patents US9624113B2; US9828258B2); (iii) n-ZVI in a fluidized bed reactor, where the NaCl is concentrated in the ZVI particles (US Patent US10919784B2); (iv) diffusion bed reactors using n-Fe⁰, m-Fe⁰, or Fe⁰ to remove Na⁺ and Cl[−] ions (UK Patent GB2520775A). This study uses a diffusion bed reactor.

Initially, it was discovered that if n-Fe⁰ or m-Fe⁰ was placed in saline water, the water salinity gradually declined [11]. Typical removals equated to <0.2 g NaCl g^{−1} Fe⁰. Removal was by inclusion in green rust structures and by concentration of NaCl (FeCl₃, NaHCO₃, and NaOH) in pores, contained within the hydroxy-oxide crust. This crust develops around a corroding iron particle [11]. Feⁿ⁺ ions hydrolyze to form different ion polymers (e.g., Japanese patent JP6017768B2; Chinese patent CN111606464A). These polymers include mono-nuclear hydroxyl complexes (termed Fe(a)); a polynuclear hydroxyl complex (e.g., Fe(OH)₂⁴⁺; Fe(O₂H₆)³⁺; Fe₃(OH)₄⁵⁺; Fe₅(OH)₉⁶⁺), termed Fe(b) (e.g., Chinese patent CN113880208A; CN210261456U; CN210261453U; CN210261454U; CN113197151A); and an inert macro-molecular coagulation (termed Fe(c)). Fe(b) has a high flocculation activity and the flocculates can grow aggregation and accretion [11]. This polymer (Fe(b)) is an effective pollutant scavenger and may be largely responsible for pollutants removed in Fe polymer flocculants.

Two innovations changed this flocculant removal perception for ZVI desalination. They were:

- The discovery that, if n-Fe⁰ was added to a conduit containing turbulent, flowing saline (seawater) water, in a concentration of about 20 g L^{−1} and the entrained ZVI-water mixture passed through a magnetic separator (to recover the n-Fe⁰ + attached NaCl + LiCl + KCl), after a contact time of <10 min, then the process produced a partially desalinated water (Spanish Patent ES2,598,032). This patent indicated that removal could involve physical adsorption rather than just chemical adsorption.
- The discovery that if an oxygenated gas was bubbled through saline water in the presence of Fe⁰, the product water was partially desalinated [10]. This process discovered

that the bulk of the NaCl removal involved a physical adsorption–desorption process, where the products were retained in the water and not in the ZVI bed.

These innovations resulted in the discovery that removals could equate to $>1 \text{ g NaCl g}^{-1} \text{ Fe}^0$ [10]. This high level of removal implied that, while the removal included removal by reaction to form a green rust and removal by adsorption and concentration into adjacent pores by desorption, it may be possible to develop a desalination solution that was catalytic [11]. It also implied that a single batch of ZVI could be used to process multiple batches or volumes of water.

If it is possible to develop a commercially viable catalytic desalination solution, then the range of potential applications could be increased from the remediation of saline water, associated with hydrocarbon production and mining, to the partial desalination of saline water for irrigation and the processing of reject brine from conventional desalination plants, to allow either reuse in the desalination plant or disposal into the riparian, marine, or groundwater environment.

The end product from catalytic ZVI desalination is unknown. It is known that the product water associated with ZVI desalination shows desalination, using ion chromatography, electrical conductivity (EC) measurements, ion selective electrode (ISE) measurements of Cl^- and Na^+ concentrations, and by water evaporation [10].

An earlier study using a ZVI desalination reactor train operated as a batch flow, bubble column, static bed diffusion reactor [10], without water recirculation, established an average of 24.5% desalination over 70 sequential, 0.24 m^3 water batches, and indicated that the overall desalination may be increased if:

- The reactor type was switched to a batch flow, bubble column, static bed, or recirculating diffusion reactor;
- The reaction period was increased;
- The pressure wave (and fluid circulation pattern) associated with the bubble column was shaped;
- The ZVI was changed from steel wool to a smaller quantity of $n\text{-Fe}^0$, or $n\text{-Fe}_x\text{O}_y\text{H}_z$ ($n\text{-Fe(a,b,c)}$).

This study tests this hypothesis by adopting these recommendations. This study uses a 0.86 m^3 reactor train and demonstrates its efficiency using a single catalyst charge to process 50 sequential batches of water.

2. Materials and Methods

This study describes the desalination results associated with scoping pre-commercialization trials associated with a commercial-scale reactor train. All construction materials and chemicals used in the study were purchased from commercial suppliers.

2.1. Reactor

The reactor train process flow used in this study is summarized in Figure 1. It comprises a feed water tank, a product water tank, a bubble column reactor, a recycle water tank, an air compressor, and an air storage tank. These units are connected by conduits.

The reactor type is a batch flow, bubble column, static bed, recirculating diffusion reactor [10]. The reactor train has three active components: (a) a bubble column reactor; (b) a ZVI cartridge; and (c) a recycle water tank.

The reactor train is filled from a saline water feed tank. Product water is discharged to a product water tank. The reactor train filling procedure used was: (i) the valve between the recycle tank and the product water tank was closed (Figure 1); (ii) the valve between the feed water tank and the recycle tank was opened (Figure 1); and the recycle tank was filled by gravity feed. When the recycle tank was full, this valve was closed. All filling and discharge conduits were constructed from 22 mm O.D. PEX barrier pipe. Water flow was controlled using brass 22 mm lever ball valve fittings. PEX = high density polyethylene.

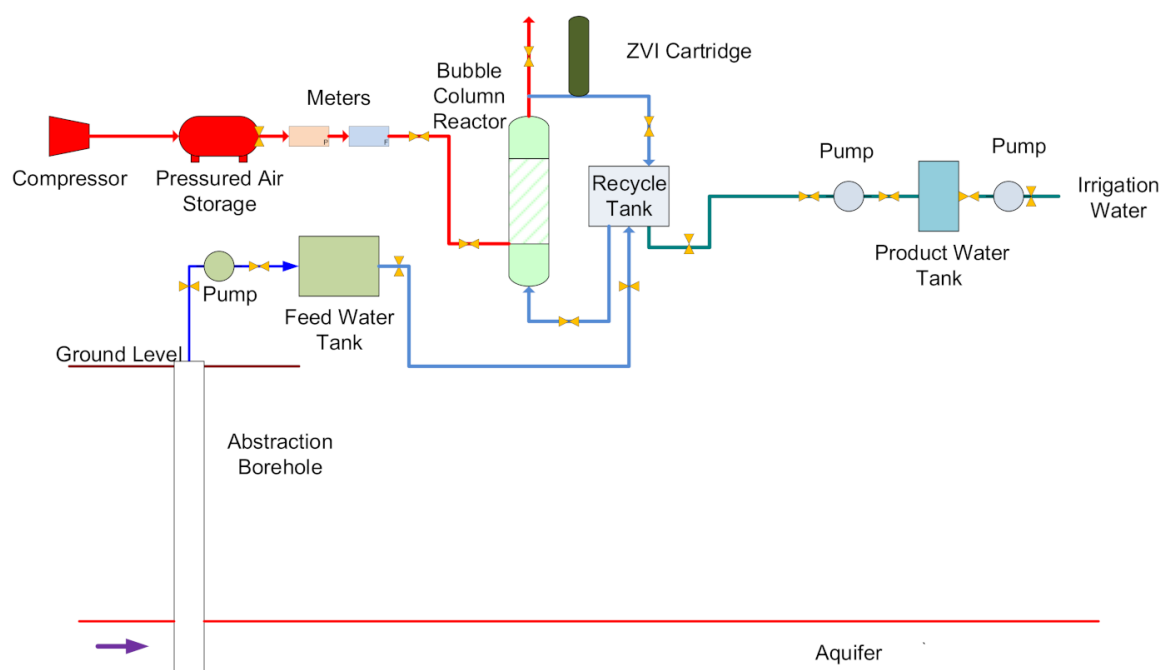


Figure 1. Process flow diagram for the reactor train used in this study.

The recycle tank was a 900 L flat D shaped polyethylene tank (1.5 m long $\times$ 0.81 m high $\times$ 0.81 m wide) with a 40.6 cm diameter top access sealed hatch (Figure 1). Fusion welded sockets were used to provide pipe access to the tank.

A 22 mm O.D. PEX barrier pipe (Conduit 1) connected the recycle tank to the base of the bubble column reactor (Figure 1). The bubble column reactor was constructed from 12 m of 22 mm O.D. Cu⁰ conduit. It received air from a pressured air storage tank through a 6 mm O.D. Cu⁰ conduit with a gas distributor, located at an elevation 10 cm above the base of the bubble column (Figure 1). A 22 mm O.D. brass branch fitting was placed at the top of the bubble column. A 22 mm O.D. copper return conduit (Conduit 2) was used to take recycled water from the bubble column reactor to a second 22 mm O.D. brass branch fitting. This fitting gave the water access to a ZVI cartridge (Figure 1). The throughflow discharged recycled water through a 22 mm O.D. PEX barrier pipe to the recycle tank (Figure 1).

The gas exiting the bubble column passed through 1.5 m of 22 mm O.D. Cu⁰ tubing before the discharge pipe diameter was restricted via 15 mm O.D. and 10 mm O.D. tubing to a 6 mm O.D. Cu⁰ vent stack (Figure 1).

An air compressor was used to pressurize and fill a pressured (0.8 MPa) gas tank (20 L) with air (Figure 1). The air compressor was used to supply 60 L air h⁻¹ to the bubble column reactor.

2.1.1. Reactor Structuring

The reactor structure used in this study is compliant with the construction and design requirements of a multi-functional ZVI diffusion reactor described in UK Patent GB2520775A. This patent required the reactor to contain a concurrent flow of water and air in the bubble column and the flowing fluids to interact with the ZVI cartridge by diffusion.

This fluid flow generated a pressure wave in Conduit 2 and in the ZVI cartridge is compliant with the processing requirements of an “oscillating flow reactor” defined in UK Patent GB 2470764B. This patent structures the reaction environment into an upstream storage area (USA)—upstream plenum, elastic permeable barrier (EPB) and a downstream storage area (DSA)—downstream plenum (Figure 2). The EPB controls the rate of gas flow between the USA and DSA. In this study the EPB is a bubble column reactor (Figure 1), which is designed to create a product gas flow rate, which oscillates between 0 m³ s⁻¹

and $\text{m}^3 \text{s}^{-1}$. An example of flow periodicity through a bubble column is illustrated in Figure 3. The wave amplitude, wavelength, wave periodicity, and wave morphology can be modified by both changing operating conditions and reactor design.

The rising air (gas) bubbles displace an equal volume of water from the bubble column reactor into Conduit 2 (Figures 1 and 2). The water flow rate in Conduit 2 resulting from this fluid displacement creates a confined, travelling pressure wave within Conduit 2. This confined pressure wave travels from the bubble column reactor to the recycle tank (Figure 2). The pressure wave interacts with the fluids in the ZVI cartridge to create an oscillating pressure and fluid flow environment within the cartridge. The travelling pressure water crest will result in both fluid flow into the cartridge and pressure increases within the cartridge. The travelling pressure wave trough will result in both fluid flow out of the cartridge and pressure decreases within the cartridge.

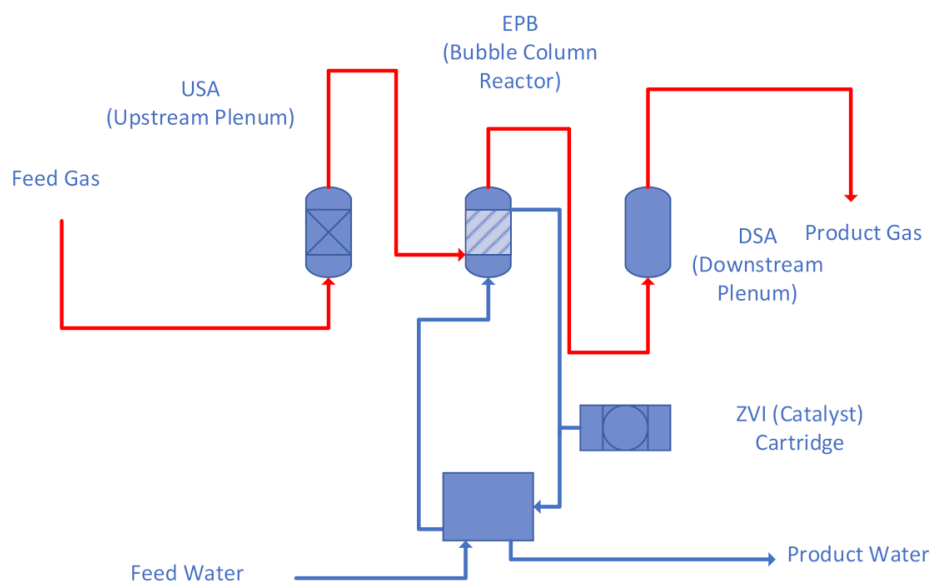


Figure 2. Gas management, oscillating flow structure adopted in the reactor. The bubble column used in this study acts as an EPB. The EPB discharges product water to a recycle tank and receives feed water from the recycle tank (Figure 1).

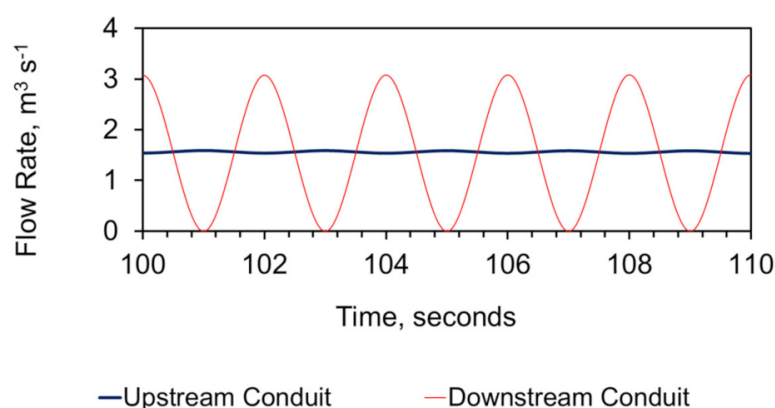


Figure 3. Example wave structuring created by an EPB, where the USA receives a constant gas flow rate through the upstream conduit and the gas is discharged in pulses from the USA to the DSA via the EPB. This results in a pulsed gas outflow through the downstream conduit from the DSA.

2.1.2. Fluid Flow within the Bubble Column Reactor

The bubble column reactor (EPB) (Figure 2) is structured to provide a concurrent flow of gas and water. A single rising gas bubble pushes the overlying water within the

bubble column into Conduit 2. The rising gas bubble draws water into the bubble column reactor, through Conduit 1, to replace both the displaced water and the gas bubble, when it discharges into the gas body located above the water column.

This flow structuring (Figure 2) creates a situation where the general flux equation for gas transport in the bubble column can be described by the equation:

$$J_g = k_g \cdot P_{bc}, \quad (1)$$

where J_g = flux; k_g = a permeability constant; P_{bc} = the pressure differential between the gas pressure in the plenum (USA) feeding the gas distributor and the gas pressure in the gas discharge plenum (DSA) located between the gas vent location and the air–water contact in the bubble column. The maximum value of P_{bc} is: P_{bc} = Pressure in the compressed tank (300,000 Pa)—Atmospheric pressure (100,000 Pa). Gas is bubbled into the water column (EPB). The gas flow rate, J_g , must oscillate (Figure 3) between a period of no gas flow (time interval between bubbles) and a period of gas flow (associated with a rising gas bubble).

J_g can only be >0 when $[k_g \cdot P_{bc}] > 0$. The gas distributor plenum (USA) has a volume, V_A , and receives a constant pressured gas supply. When the plenum (USA) is fully discharged, its gas volume = V_A and its gas pressure is $[P_{dc1}]$. When the plenum (USA) is full, its gas volume = V_B and its gas pressure is $[P_{dc2}]$. This volume represents the pressured gas volume, which is required to displace the water column in the bubble column (EPB) and allow gas flow. The pressure in the gas distributor plenum will continually oscillate between $[P_{dc1}]$ and $[P_{dc2}]$.

Rises in pressure, $[P_{gp1}]$, in the gas distributor plenum (USA) will be associated with decreases in pressure within the gas discharge plenum (DSA) and vice versa. The rise in pressure is associated with the receipt of the gas bubble and the associated water slug. Pressure relaxation, $[P_{gp2}]$, in the gas discharge plenum (DSA) is associated with water discharge from the EPB into Conduit 2 and gas discharge from the DSA through the vent stack. These pressures can be termed $[P_{gp1}]$ and $[P_{gp2}]$, respectively. It follows that the pressure, P_{bc} , will cyclically oscillate between:

$$P_{bc(\text{minimum})} = P_{dc1} - P_{gp1}, \quad (2)$$

$$P_{bc(\text{maximum})} = P_{dc2} - P_{gp2}, \quad (3)$$

Gasification of the bubble column will reduce its viscosity and increase its permeability, k_g , to gas flow. The pressured gas bubble will expand in size as it rises within the water column.

This pulsed gas flow creates a pulsed discharge of product water into Conduit 2 from the bubble column and a pulsed inflow of feed water into the bubble column through Conduit 1 (Figure 2).

2.1.3. Pressure Oscillations in the ZVI Cartridge

The pulsed flow of water through Conduit 2 to the Recycle Tank creates a fluid pressure oscillation in the ZVI cartridge. Fluid flows into the cartridge as the pressure rises and out of the cartridge, as the pressure, associated with the pressure wave, reduces.

Cyclic pressure increases are associated with adsorption onto the ZVI catalyst, while the associated cyclic pressure decreases are associated with product desorption from the ZVI catalyst [10].

2.2. ZVI or Catalyst Cartridge

An earlier study used a batch flow, bubble column, static bed, diffusion reactor, without fluid recirculation [10]. It trialed a metal polymer catalyst constructed from steel wool with a basic formulation $\text{Fe}^0:\text{n}-\text{Fe}(\text{a,b,c})@\text{urea}$. This study trials the use of a $\text{SiO}_2@\text{n}-\text{Fe}(\text{a,b,c})@\text{urea}$ polymer.

The $\text{SiO}_2@\text{n}-\text{Fe(a,b,c)}@\text{urea}$ polymer was constructed by placing 400 g Iron Sulphate + 10 L FeOOH -coated quartz sand grains (0.1 to 3 mm) + 200 g Urea + water with $<0.2 \text{ g/L Cl}^-$ and $<0.2 \text{ g/L Na}^+$, in a 10 L vessel with an air–water contact. The vessel was left for 4 weeks at a temperature of between 4 and 15°C . Then, 0.88 L of the damp solute mixture was placed in an acrylonitrile butadiene styrene (ABS) cartridge (0.7 m long $\times$ 0.04 mm O.D.). The cartridge was attached to Conduit 2, via a 22 mm O.D. connector. The cartridge contained between 7 and 10 g Fe. The active desalination catalyst (Figure 4) is a $\text{n}-\text{FeO}_x\text{H}_y$ polymer, which coats the quartz grains. It is termed here a $\text{SiO}_2@\text{n}-\text{Fe(a,b,c)}@\text{urea}$ polymer and comprises a mixture of $\text{SiO}_2@\text{n}-\text{Fe(a,b,c)}@\text{urea}$ polymer and $\text{SiO}_2@\text{n}-\text{Fe(a,b,c)}$ polymer.

Characterization of the polymeric catalyst in terms of detailed chemical analyses and detailed morphology are outside of the scope of this study.

In this study, the following polymer terminology is used. M = metal. M(a) = mono–nuclear hydroxyl complexes, e.g., Fe^{3+} , $\text{Fe}(\text{OH})^{2+}$, $\text{Fe}(\text{OH})_2^+$, $\text{Fe}(\text{OH})_3$, $\text{Fe}(\text{OH})_4^-$ ($\text{Fe}_2(\text{OH})_2^{4+}$ and $\text{Fe}_3(\text{OH})_4^{5+}$), some small polymers, and instantaneous reaction products. M(b) = polynuclear hydroxyl complexes, with medium and high molecular mass, e.g., $\text{Fe}(\text{OH})_2^{4+}$; $\text{Fe}(\text{O}_2\text{H}_6)^{3+}$; $\text{Fe}_3(\text{OH})_4^{5+}$; $\text{Fe}_5(\text{OH})_9^{6+}$, etc. M(c) = larger polymer or colloidal species, which include inert macro–molecular coagulation, of the form $\text{M}(\text{OH})_x$ and MOOH . In practice most metal polymers are a mixture of M(a) + M(b) + M(c).

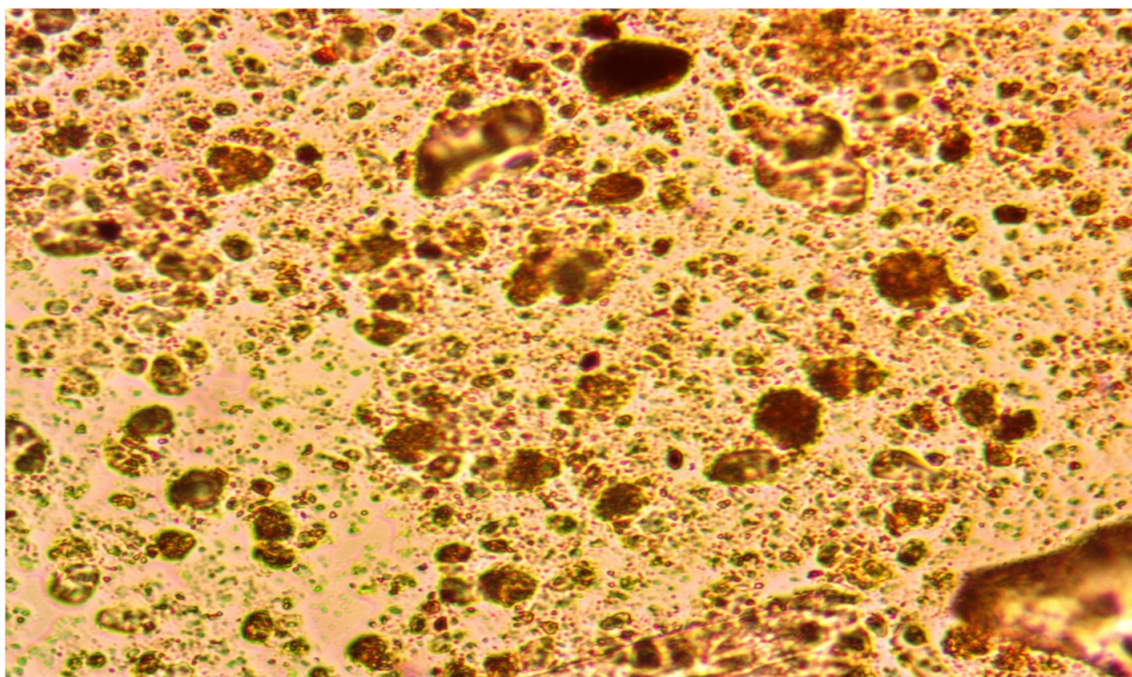


Figure 4. Catalyst, transmitted light, field of view = 0.5 mm. Particles are quartz grains coated in $\text{n}-\text{FeO}_x\text{H}_y$ polymers.

2.3. Water

The sequential reactor trials processed synthetic saline water, which was manufactured by dissolving halite in natural spring water. The water was sourced from a natural freshwater spring, at National Grid Reference: NO 02817 14399; $56^\circ 18' 43'' \text{N}$, $003^\circ 34' 21'' \text{W}$. The water was abstracted from fractured andesitic rocks and was placed in a 5 m^3 storage tank (Figure 1). A typical groundwater ion composition is: Anions: $\text{Cl} = 11.67 \text{ mg}\cdot\text{L}^{-1}$; $\text{N}(\text{NO}_3) = 11.28 \text{ mg}\cdot\text{L}^{-1}$; $\text{S}(\text{SO}_4) = 4.16 \text{ mg}\cdot\text{L}^{-1}$; $\text{P}(\text{PO}_4) \leq 0.10 \text{ mg}\cdot\text{L}^{-1}$; $\text{F} = 0.024 \text{ mg/L}$; $\text{N}(\text{NO}_2) = 0.04 \text{ mg}\cdot\text{L}^{-1}$; $\text{HCO}_3^-/\text{CO}_3^{2-} \leq 10 \text{ mg}\cdot\text{L}^{-1}$; Cations: $\text{K} = 1.69 \text{ mg}\cdot\text{L}^{-1}$; $\text{Ca} = 32.91 \text{ mg}\cdot\text{L}^{-1}$; $\text{Na} = 6.32 \text{ mg}\cdot\text{L}^{-1}$; $\text{Al} \leq 150.0 \text{ }\mu\text{g}\cdot\text{L}^{-1}$; $\text{Fe} \leq 30.0 \text{ }\mu\text{g}\cdot\text{L}^{-1}$; $\text{Mn} = 1.70 \text{ }\mu\text{g}\cdot\text{L}^{-1}$; $\text{P} \leq 0.005 \text{ mg}\cdot\text{L}^{-1}$; $\text{S} = 4.31 \text{ mg}\cdot\text{L}^{-1}$; $\text{B} = 29.40 \text{ }\mu\text{g}\cdot\text{L}^{-1}$; $\text{Ba} = 135.60 \text{ }\mu\text{g}\cdot\text{L}^{-1}$; $\text{Cd} \leq 0.2 \text{ }\mu\text{g}\cdot\text{L}^{-1}$; $\text{Co} \leq 0.2 \text{ }\mu\text{g}\cdot\text{L}^{-1}$; $\text{Cr} \leq 0.2 \text{ }\mu\text{g}\cdot\text{L}^{-1}$; $\text{Cu} = 77.7 \text{ }\mu\text{g}\cdot\text{L}^{-1}$; $\text{Ni} \leq 3 \text{ }\mu\text{g}\cdot\text{L}^{-1}$; $\text{Pb} \leq 10 \text{ }\mu\text{g}\cdot\text{L}^{-1}$; $\text{Si} = 5.21 \text{ mg}\cdot\text{L}^{-1}$; $\text{Sr} = 144.9 \text{ }\mu\text{g}\cdot\text{L}^{-1}$; $\text{Zn} = 37.4 \text{ }\mu\text{g}\cdot\text{L}^{-1}$; $\text{As} \leq 5 \text{ }\mu\text{g}\cdot\text{L}^{-1}$; $\text{Mo} \leq 20 \text{ }\mu\text{g}\cdot\text{L}^{-1}$; $\text{Se} \leq 20 \text{ }\mu\text{g}\cdot\text{L}^{-1}$; $\text{Sn} \leq 20 \text{ }\mu\text{g}\cdot\text{L}^{-1}$;

$S_b \leq 10 \mu\text{g} \cdot \text{L}^{-1}$. The halite (NaCl) was purchased from Wickes Ltd., Perth, UK, and in addition to NaCl contains 30 ppm sodium ferrocyanide and a mixture of Ca^{2+} , Mg^{2+} , K^+ , and Fe^{3+} cations, plus SO_4^{2-} and CO_3^{2-} anions and clay minerals. These constitute about 6% of the solid halite mixture.

2.4. Measurements

The following parameters were measured for each feed water and product water sample: pH, Eh, EC, Cl^- ion concentration, Na^+ ion concentration, and temperature. These measurements are placed in Appendix A, Tables A1–A3, and Figures A1–A6.

The instruments used were:

- ORP (oxidation reduction potential) meter (HM Digital) calibrated at ORP = 200 mV; measured ORP (oxidation reduction potential) values are converted to Eh, mV as: $\text{Eh, mV} = -65.667\text{pH} + 744.67 + \text{ORP (mV)}$, using a quinhydrone calibration at pH = 4 and pH = 7.
- pH meter (HM Digital) calibrated at pH = 4.01; 7.0; 10.0.
- EC (electrical conductivity) meter (HM Digital meter calibrated at $\text{EC} = 1.431 \text{ mScm}^{-1}$).
- Cl^- ISE (Ion Selective Electrode); Bante Cl^- ISE, EDT Flow Plus Combination Cl^- ISE; Cole Parmer Cl^- ISE attached to a Bante 931 Ion meter. Calibration was undertaken using 0.001, 0.01, 0.1, and 1.0 M NaCl calibration solutions.
- Na^+ ISE (Ion Selective Electrode); Bante Na ISE, Sciquip Na ISE, Cole Parmer Na ISE attached to a Bante 931 Ion meter. Calibration was undertaken using 0.001, 0.01, 0.1, and 1.0 M NaCl calibration solutions.
- Temperature measurements were made using a temperature probe, attached to a Bante 931 Ion meter.

2.5. Control Reactor

2.5.1. Control Experiment 1

A control reactor was placed in operation, containing a gas distributor, with no air feed and a single ZVI cartridge. The product water salinity was sampled after 48 h. The feed water and product water salinities remained unchanged at $0.88 \text{ g Cl}^- \text{ L}^{-1} + 0.43 \text{ g Na}^+ \text{ L}^{-1}$.

2.5.2. Control Experiment 2

A control reactor was placed in operation, containing a gas distributor and an air feed of 60 L h^{-1} and no ZVI cartridge. The product water salinity was sampled after 48 h. The feed water and product water salinities remained unchanged at $0.88 \text{ g Cl}^- \text{ L}^{-1} + 0.43 \text{ g Na}^+ \text{ L}^{-1}$.

2.5.3. Control Experiment 3

A control reactor was placed in operation, containing a gas distributor and an air feed of 65 L h^{-1} and a ZVI cartridge. The product water salinity was sampled after 8.95 h. The feed water salinities reduced from $0.88 \text{ g Cl}^- \text{ L}^{-1} + 0.43 \text{ g Na}^+ \text{ L}^{-1}$ to provide a product water salinity containing $0.57 \text{ g Cl}^- \text{ L}^{-1} + 0.21 \text{ g Na}^+ \text{ L}^{-1}$. This control experiment indicated that no desalination could be expected with this reactor construction, unless the reactor contained both a flow of air and a ZVI cartridge.

3. Results

The quantitative data results generated by this study are provided in Appendix A, Tables A1–A6, and Figures A1–A7.

3.1. Relationship between Electrical Conductivity and Salinity

There are strong statistical relationships between measured salinity (g L^{-1}) and electrical conductivity (EC), for both the feed water and the product water (Appendix A, Figure A1). The feed water is artificial saline water constructed using halite. This construction results in the 1 mScm^{-1} approximating to $0.95 \text{ g NaCl L}^{-1}$ (Appendix A, Figure A1).

When saline water is constructed by dissolving pure NaCl in pure water, the EC relationship will approximate: $1 \text{ mScm}^{-1} = 0.54 \text{ g NaCl L}^{-1}$ (e.g., US Patent US10919784B2).

The product water salinity, measured as EC or g NaCl L^{-1} , is lower than the feed water salinity (Appendix A, Figure A1).

3.2. Removal of Salinity

The trials demonstrated a significant removal of salinity (chloride + sodium ions), with a median removal of about 43%, with 75% of trials removing >30% (Table 1; Appendix A, Figure A2). There is a weak statistical trend of increasing ion removal with increasing feed water salinity (Appendix A, Figure A2).

Table 1. Desalination statistics: data: Appendix A, Table A2. Values are the proportion removed.

	NaCl	Na ⁺ Ions	Cl ⁻ Ions
Mean	41.84%	41.33%	41.74%
Standard Deviation	15.61%	16.35%	17.99%
Minimum	5.54%	0.00%	4.62%
1st Quartile	30.01%	31.38%	26.16%
Median	43.39%	41.14%	42.21%
3rd Quartile	51.09%	53.67%	55.25%
Maximum	73.59%	69.77%	75.51%

3.3. Change in Reactor Efficiency with Increasing Number of Trials

Each sequential water batch has a different degree of desalination (Appendix A, Figure A3), with no apparent loss of desalination efficiency after 50 batches (Appendix A, Table A2). This outcome variability (Appendix A, Figure A3) will require the water from sequential or parallel batches to be aggregated to form a finished product water.

3.4. Change in Redox Parameters

The desalination process is associated with an increase in pH and a decrease in Eh (Appendix A, Table A1; Appendix A, Figures A4 and A5). It is independent of temperature over a temperature range 273 K to 293 K (Appendix A, Figure A5).

3.5. Salinity Removal as a Function of Reaction Time

A graphical plot of the observed rate constant (k_{obsf}) versus time (t) spent in the reaction environment, where $t = n$ establishes a general decline in (k_{obsf}) with increasing t , which could be described using a first-order reaction, regression equation (Appendix A, Table A3), where:

$$k_{obsf} = (-\ln(C_{t=n}/C_{t=0}))/t, \quad (4)$$

$C_{t=0}$ = ion concentration at $t = 0$, g L^{-1} ; $C_{t=n}$ = ion concentration at $t = n$, g L^{-1} ; ($t = n$) = time spent in the reaction environment in seconds.

A best fit regression analysis was made, using the MS Excel 2019 trendline functions of k_{obsf} vs $[a]$, where $[a] = 3600 \times (t = n)$ ($[a]$ is expressed in hours) for each of the Cl^- ions and Na^+ ions for each sequential water batch. This analysis is summarized in Appendix A, Table A3.

These regression equations indicate that:

- The amount of ion removal increases with increased reaction time (Appendix A, Figure A6).
- The amount of ion removal associated with a specific reaction time is variable (Appendix A, Figure A6).

The regression equations (Appendix A, Table A3) allow the outcome variability (or outcome probability distribution) to be assessed as a function of reaction time (Appendix A, Figure A7). This analysis indicates that:

- The median desalination increases for the initial 10–12 h; thereafter, the amount of desalination is stable (Appendix A, Figure A7).
- There is a wide range of desalination outcomes for a specific reaction time (Appendix A, Figure A7). Therefore, aggregation of sequential and parallel trains will be required to produce a stable product composition.

3.6. Expected Desalination Outcome Associated with a Multi-Train Reactor

The analysis in Appendix A, Figure A7, indicates that a multi-train reactor could be operated with a 20 h reaction time, processing $0.86 \text{ m}^3 \text{ d}^{-1} \text{ train}^{-1}$. This is expected (Appendix A, Figure A7) to provide each batch with a median desalination outcome of 40.39%; a mean desalination outcome of 39.89%; and standard deviation of 15.14%.

An agricultural holding of 10 ha may require $50,000 \text{ m}^3 \text{ a}^{-1}$ of irrigation water. If the irrigation was split over a 90-day period, this would require an average of $555 \text{ m}^3 \text{ d}^{-1}$. This could be achieved (with excess capacity) using a 650–1000 train reactor. A 650 train reactor would be expected to have a mean desalination outcome of 39.89% and standard deviation of 3.86%. The expected desalination outcome for the daily aggregated product water is provided in Figure 5. This indicates that there is a 90% probability that the amount of desalination will exceed 35%. An example set of plant layout requirements for a plant processing $555 \text{ m}^3 \text{ d}^{-1}$ is provided in Figure 6. The actual layout will be site specific.

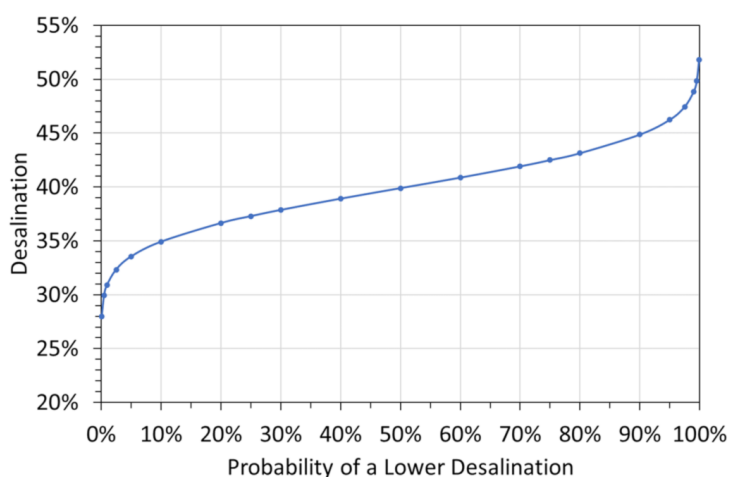


Figure 5. Expected desalination distribution associated with a 650 train reactor, processing $555 \text{ m}^3 \text{ d}^{-1}$ ($200,750 \text{ m}^3 \text{ a}^{-1}$). 1000 iteration Monte Carlo Analysis; assumptions: 20 h batch operating time; Fe charge = 6.5 kg; Fe replacement period: 50 days; air required: $13 \text{ m}^3 \text{ m}^{-1}$; water reactor emptying/filling period = <4 h; air compression requirements: $12 \times 1.140 \text{ m}^3 \text{ m}^{-1}$ air compressors (indicative requirements/screw compressor: power 7.5 kW (400 V, 50 Hz, 3 phase); delivery pressure = 0.8 MPa; weight = 170 kg; size (m) = $0.85 \times 0.72 \times 0.98$; these requirements are based on an Airpress compressor APS Basic; other makes and models can be used); estimated plant compression power requirement: 90 kW h^{-1} ; 3.35 kW m^{-3} ; estimated water storage: 600–2000 m^3 feed water; 600–2000 m^3 product water; 600 m^3 recirculating water.

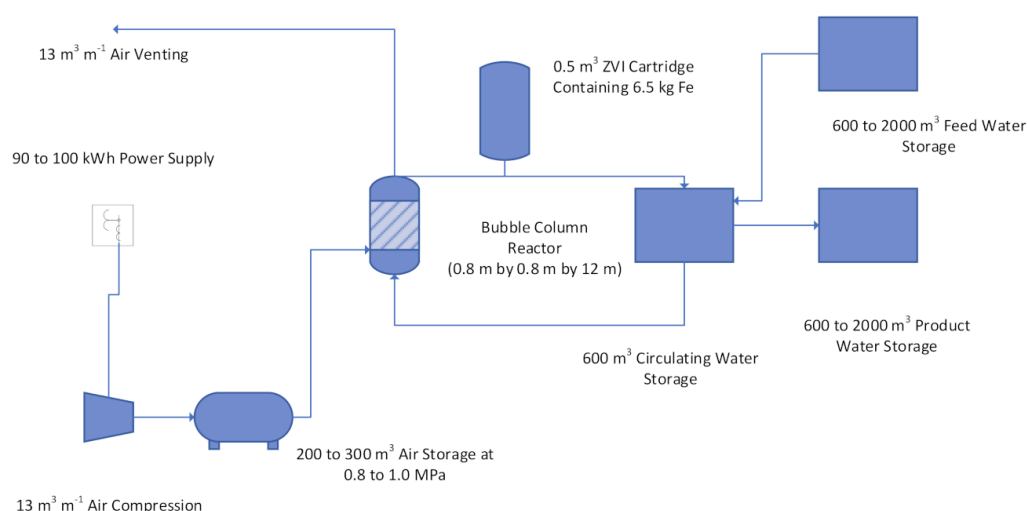


Figure 6. Expected plant layout associated with a 650 train reactor, processing $550 \text{ m}^3 \text{ d}^{-1}$ ($200,750 \text{ m}^3 \text{ a}^{-1}$).

4. Discussion

This study demonstrated that 1 t Fe (held as Fe polymers) would be expected to process 4.3 million m^3 saline water (i.e., 43 m^3 processed in 50 batches using 7–10 g Fe). This compares with the proven 3.86 million m^3 water processed t^{-1} Fe by a $22,500 \text{ m}^3 \text{ d}^{-1}$ ZVI water treatment plant, removing dissolved organic material [11].

Furthermore, this study established that a reactor containing 7–10 g Fe can remove 51.6 kg Cl^- and 22.2 kg Na^+ ions (Appendix A, Table A2). This removal process does not deteriorate with an increased number of sequential batches (Appendix A, Figure A3). This observation is interpreted as indicating that the desalination process leaves the FeO_xH_y species unchanged and that the FeO_xH_y species act as a catalyst.

The exact nature of the catalytic products of desalination has not been elucidated in this study. They are not present in the ZVI cartridge and are assumed to be present in the product water. An interpretation of the nature of the desalination products, associated with this type of desalination process, is provided elsewhere [10].

Further, 2.2 L samples of the product water (and feed water) were placed in storage (at ambient temperatures, in a range from 0 to 20°C) and their salinities remeasured after 2 years. The feed water samples were used to provide an additional measurement control. These analyses indicated that the majority of the water samples continued to desalinate following removal from the reactor (Figure 7a). However, a small proportion of the stored samples (<15%) showed some level of re-salination (Figure 7b). This implies that at least some of the removed salinity is retained in the product water in another form.

4.1. Nature of the Desalination Process

In this study, the desalination process required the presence of a pulsed oxygen recharge of the water, which created a pulsed water circulation and a pressure wave, which interacted with the ZVI cartridge. The control experiments indicated that each of these elements must be present before desalination is observed.

The control experiment observations indicate that the desalination process can be operated using a catalytic, pressure–swing–adsorption–desorption process [10]. Catalytic pressure–swing–adsorption–desorption (CPSAD) processes are not widely used in reactors. However, the basic principles of their operation are documented elsewhere (e.g., UK Patent GB2470764B), specifically:

- Using Cu^0 , a CPSAD process is demonstrated to increase reaction yields by up to 400% for a specific space velocity [12];

- The reactor used in this study falls within the group of reactors that combine adsorption, reaction, and separation, within the pressure swing process [13,14].

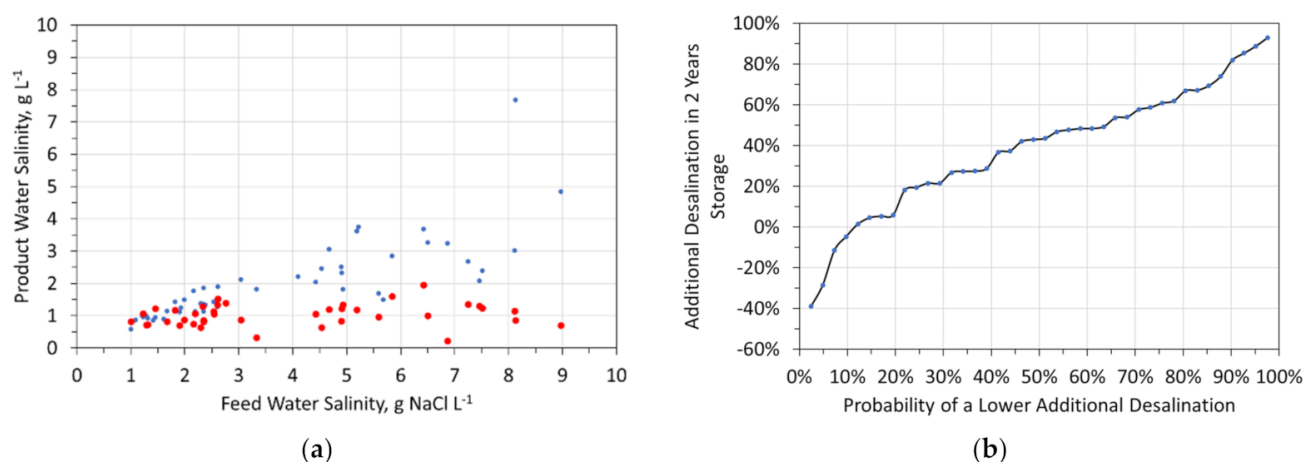


Figure 7. Analysis of stored product water. (a) Feed water salinity vs. product water salinity. Blue circles = product water salinity on removal from the reactor; larger red circles = product water salinity following two-year storage; (b) additional desalination resulting from 2-year storage.

The observation that desalination may continue following removal of the product water from the reactor (into a sealed quiescent environment) indicates that the catalytic nano-agents are contained in the product water or that there is a micro-biological element to the removal process.

4.2. Indicative Plant Sizes and Process Costs

A single standalone 860 L reactor train had the following manufactured cost structure, excluding labor and site costs:

- D-tank (900 L capacity) = USD 400
- Compressor = USD 200
- Pipework, fittings, and conduits = USD 150
- ZVI for the ZVI cartridge = USD 20

Total capital cost = USD 770. Operating energy (electricity) consumption = 0.3 kW h⁻¹ (6 kWh for 20 h operation). Current UK grid supplied electricity prices are around USD 0.5 kWh. Switching to an off-grid, solar-battery power complex, and amortizing the cost to around 20 years can potentially reduce the energy cost (excluding pumps) to around USD 0.1 kWh to USD 0.3 kWh (assuming no maintenance is required). This potentially reduces the energy cost for a 20 h batch processing time to around USD 0.6 to USD 1.8 batch⁻¹ (USD 0.7 to USD 1.4 m⁻³) from around USD 3 batch⁻¹ (USD 3.5 m⁻³).

This cost structure (without considering economies of scale (e.g., Figures 5 and 6)) will limit the process applications to markets or operations, which can withstand a cost structure of USD 0.6 to USD 5 m³ for partially desalinated water.

Impact of Economies of Scale

Economies of scale can arise in the area of tank costs. For example, switching from an individual tank for each bubble column train to a single shared tank could reduce the tank cost expressed in USD m⁻³, from around USD 440 m³ to a lower value. For example, a 1000 m³ galvanized corrugated steel tank (diameter = 17.51 m; height = 4.59 m), with an EPDM or butyl rubber lining, costs around USD 30,000 + assembly costs. The tank is constructed on any flat, firm ground or on a concrete base. The 1 mm thick butyl liners have a life expectancy of >30 years.

Similar cost savings resulting from economies of scale are associated with the conduits, pumps, valves, and compressors.

A plant processing $1000 \text{ m}^3 \text{ d}^{-1}$ would need a power supply capable of delivering around $125\text{--}180 \text{ kW h}^{-1}$. The capital cost of a renewable energy plant capable of producing an average of $125\text{--}180 \text{ kW h}^{-1}$ (including energy storage) varies as a function of the technology used, location, and supplier. A reasonable budget estimate range for an off-grid unit with a 20-year life expectancy is probably around USD 2 to USD 6 million + annual service + site costs + engineering costs + local regulatory costs + environmental costs/taxes + maintenance costs + feed water and product water tanks, pumps, and distribution costs. This unit would expect to power the delivery of around $1.1 \text{ m}^3 \text{ m}^{-1}$ of compressed air. For a plant processing around 7.3 million m^3 over 20 years, this would provide an expected energy cost of between USD 0.2 and USD 0.7 m^3 .

Energy and operating manpower costs are considered to represent the largest element of the cost associated using this process to produce partially desalinated water. On the basis of current costings (excluding location-specific costings), a budget product water cost estimate within a range USD 0.7 to USD 2.0 m^{-3} may be realistic for a plant processing $500\text{--}1500 \text{ m}^3 \text{ d}^{-1}$.

5. Practical Implications

The process has a number of potential applications. They include:

- Partial desalination of saline irrigation water;
- Partial desalination of saline livestock feed water;
- Partial desalination of reject brine from a conventional desalination plant;
- Partial desalination of feed water for a conventional desalination plant;
- Partial desalination of a saline aquifer;
- The injection of partially desalinated water into an aquifer to reverse or check seawater incursion into a freshwater aquifer.

5.1. Partial Desalination of Irrigation Water

Saline irrigation water has a negative impact on crop yield and crop value, when compared with irrigation using freshwater [5]. However, irrigation with saline water may provide a higher crop yield than no irrigation. The number of crop varieties that can be grown decreases with increasing irrigation water salinity.

Saline irrigation results in a gradual salinization of the soil. This is associated with a decrease in the soil's vertical permeability and confines the principal throughflow to the topsoil or the upper part of the subsoil. As a rough guide, the pore water salinity of the soil will be 20 to 30% higher than the salinity of the irrigation water.

Crop yield is a function of many parameters, of which irrigation water salinity is an important factor. Other factors, such as climate, soil type, and agricultural practice, can have a major impact on yield. As a rough indicative guide, the expected crop yield, Y_e , can be defined [5,15] as:

$$Y_e = Y_s (1 - (a(1 + c)S - b)), \quad (5)$$

Y_s = expected crop yield when irrigated with freshwater (t ha^{-1} or another yield unit). S = Irrigation water salinity. $[a]$, $[b]$, and $[c]$ are constants; the values of these constants used in this study are derived from the graphs in [15]; $(1 + c)S$ = soil water salinity. Appendix A, Table A4, provides an indication of indicative crop yield versus irrigation water salinity for a variety of crops.

This study indicates (Table 1, Figure 5) that an average of 40% desalination may be possible. This changes the indicative crop yield equation to:

$$Y_d = Y_s (1 - (a(1 + c)(1 - e)S - b)), \quad (6)$$

where $[e]$ is the expected desalination. Y_d = the expected crop yield using partially desalinated water. Desalination increases the expected yield of a crop. This is demonstrated in Appendix A, Table A5.

Irrigation with partially desalinated water will not be an economic solution for all crops, which are currently irrigated with saline water. The expected increase in crop yield due to irrigation with desalinated water can be assessed as:

$$\text{Increase in crop yield due to desalination} = Y_d - Y_e \quad (7)$$

Appendix A, Table A5 provides an indication of the expected increase in crop yield associated with desalination for a variety of crop types, expressed as a proportion of the crop yield, when the crop is irrigated with freshwater. For most vegetable and fruit crops (and staple crops, such as rice, potato, and tomato) currently irrigated with water with a salinity of 1 to 3 g L⁻¹, partial desalination of irrigation water may provide a yield increase, which is equivalent to 30–60% of the freshwater irrigation yield (Appendix A, Table A5). A yield increase, which is equivalent to 20–50% of the freshwater irrigation yield, may arise for some grass crops, which are currently irrigated with water with a salinity of 1 to 5 g L⁻¹ (Appendix A, Table A5).

5.2. Partial Desalination of Saline Livestock Feed Water

About 25% of the global land area is used to rear livestock [10]. Different animals have different degrees of tolerance to different water salinities [15]. Their tolerance to water salinity can be split into three categories [15]: (i) safe, where they are tolerant to the salinity and gain weight; (ii) suitable, where they can tolerate the salinity, but will only gain weight at a slow rate; (iii) poor, where the high salinity will result in weight loss. The salinity ranges associated with these categories vary with animal type and variety. The boundaries associated with each of these categories are subjective and will vary with geographical region, livestock type, soil conditions, available feed type, and environmental conditions.

What this study demonstrates is that in the event of drought or another environmental event, which results in salinization of livestock feed water, it will be possible to reduce the salinity of the associated livestock feedwater pools by up to 40% over a short timeframe (e.g., <24 h). Partial desalination of livestock water may increase the number of livestock that can be farmed on some land (number ha⁻¹).

Cattle may cost USD 300–700 head⁻¹ (pedigree > USD 2000 head⁻¹). In many drought-affected areas, a small reduction in feed water salinity (e.g., 10–20%) may be sufficient to allow for livestock survival. This study established (Appendix A, Table A3; Appendix A, Figure A7) that this can potentially be achieved after about 1 to 3 h processing (Figure 8). Cattle may require 50–200 L d⁻¹ head⁻¹ of feed water. The single train reactor trialed in this study would be able to process 5000 L d⁻¹ (with an average processing time of 3 h) to 8600 L d⁻¹ (with an average processing time of 2 h). Further, 3 h processing would give a 50% probability of achieving a 12–26% desalination (Figure 8) and 2 h processing would give a 50% probability of achieving a 9–22% desalination (Figure 8). This analysis indicates that the process may provide a low-cost method of providing a rapid salinity reduction for livestock feed water.

5.3. Partial Desalination of Reject Brine from a Conventional Desalination Plant

The observed average 40% desalination may allow reject brine from a conventional desalination plant to be partially desalinated and returned to the conventional desalination reactor. The reject brine volume is typically 80% of the feed volume to the conventional desalination reactor. Processing this reject brine in a ZVI desalination reactor may allow all or part of this reject brine to be recycled to the conventional desalination reactor or may allow it to be discharged into the environment, without increasing the salinity of the surrounding groundwater, riparian water, or seawater (Figure 9).

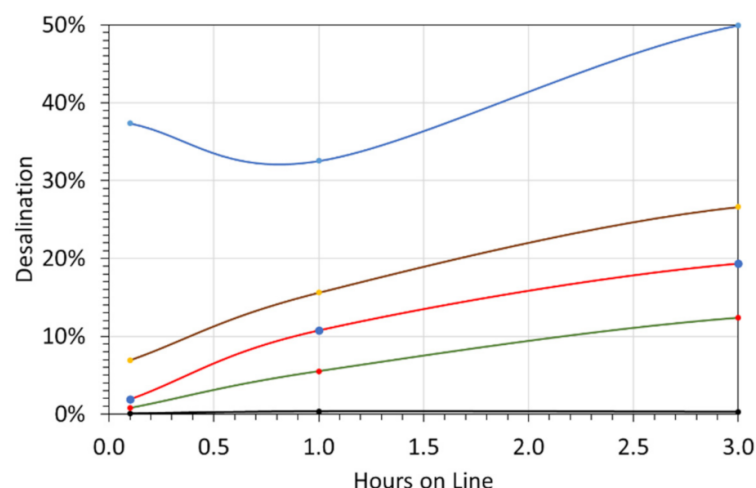


Figure 8. Outcome distribution associated with a single reactor train. Blue line = maximum desalination; brown line = 25% probability of a higher desalination; red line = 50% probability of a higher desalination; green line = 75% probability of a higher desalination; black line = minimum desalination. Source: Appendix A, Figure A7.

A conventional reverse osmosis plant producing $140 \text{ m}^3 \text{ d}^{-1}$ of potable water may have a feed water consumption of $690 \text{ m}^3 \text{ d}^{-1}$ of brackish or saline water and produce $550 \text{ m}^3 \text{ d}^{-1}$ of reject brine (Figure 9). The ZVI desalination process has the potential to reduce the salinity of the reject brine to below that of the feed water (Figure 10). This could potentially result in the average water salinity entering the reverse osmosis plant being about 50% of the salinity of fresh feed water entering the system (Figure 10).

The integrated plant configuration shown in Figure 9 was not trialed at this time. Therefore, it is not known whether the modelled results (for the process configuration in Figure 9), shown in Figure 10, will occur. Additional treatment of the recycled water (Figure 9) leaving the product water storage tank may be required. Additional trials will be required to prove the conceptual process flow shown in Figure 9.

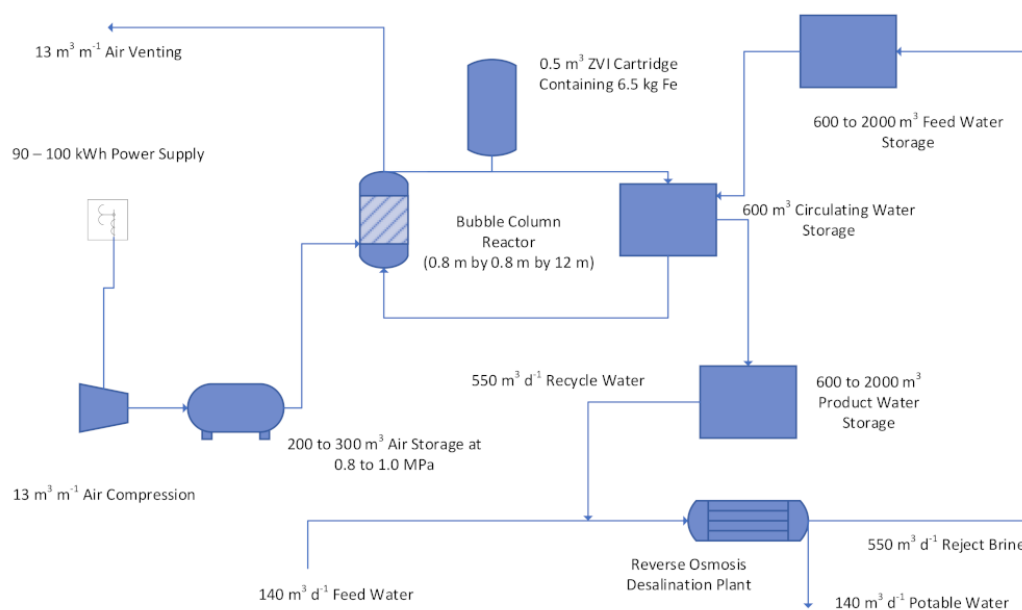


Figure 9. Expected plant layout associated with a 650 train reactor, processing $550 \text{ m}^3 \text{ d}^{-1}$ ($200,750 \text{ m}^3 \text{ a}^{-1}$) and designed to handle the reject brine associated with a reverse osmosis desalination plant.

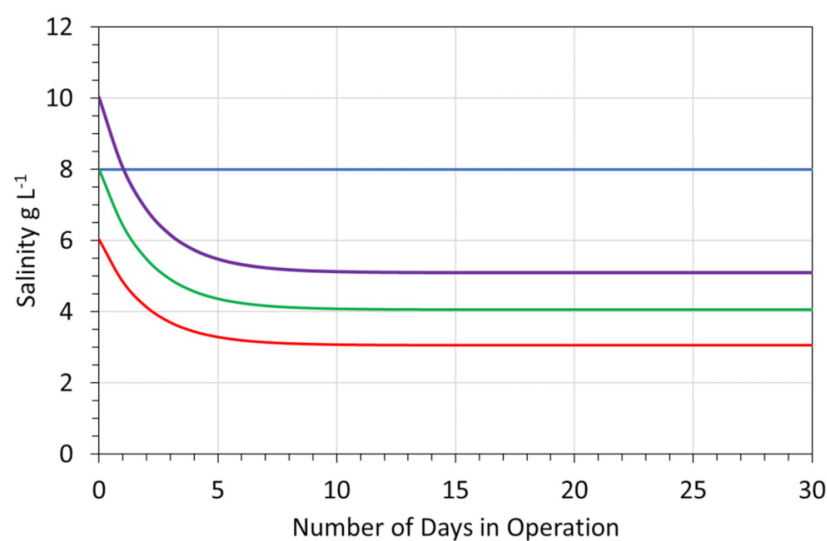


Figure 10. Expected water salinities associated with the plant layout in Figure 9. Blue line = fresh feed water salinity; red line = product water from the ZVI desalination plant; green line = average water salinity entering the reverse osmosis plant; purple line = average reject brine salinity exiting from the reverse osmosis plant.

5.4. Partial Desalination of Feed Water to a Conventional Desalination Plant

The operating (and capital) costs of a conventional desalination plant decrease as the salinity of the feed water decreases. Processing the water in a ZVI desalination reactor prior to entry into a conventional desalination plant has the potential to reduce the capital and operating costs associated with a conventional desalination plant. This is achieved by reducing the salinity of the feed water entering the conventional desalination plant by 40% (Table 1; Appendix A, Figure A7).

5.5. Partial Desalination of a Saline Aquifer

Desalination of an aquifer can be undertaken by enclosing an area of the aquifer by a rim marked by or defined by the presence of a series of infiltration wells or boreholes (Figure 11). This is termed the desalination zone. Water is abstracted from the center of this field and is processed in a ZVI desalination reactor before being returned to the aquifer via the infiltration wells (Figure 11). An associated process flow diagram is provided in Figure 12.

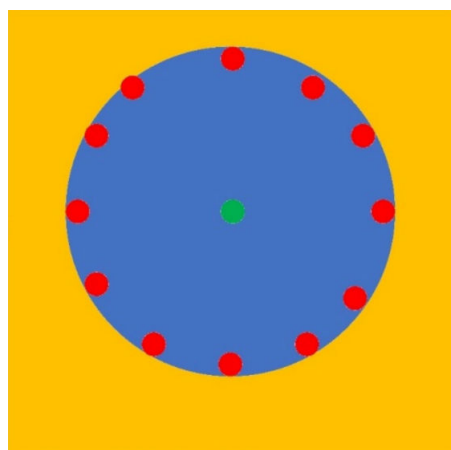


Figure 11. Schematic drawing of an aquifer in the process of being desalinated. Orange = aquifer; blue circle = part of aquifer which is being desalinated (desalination zone). Red = infiltration boreholes/wells; green = abstraction borehole/well.

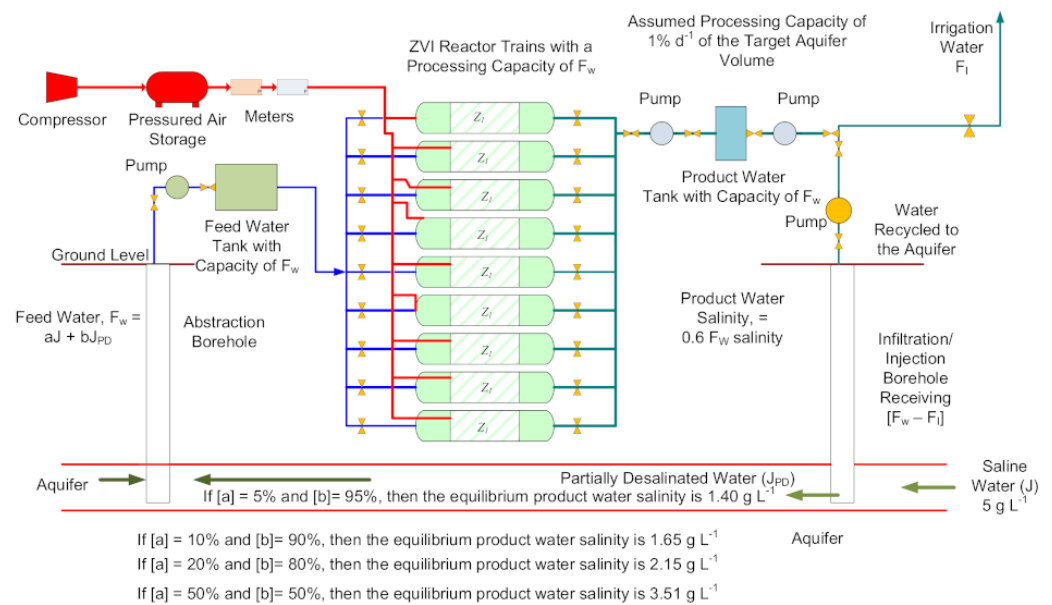


Figure 12. Schematic process flow diagram for aquifer desalination. The assumptions provided by the example numerical analysis are: (i) volume of water processed each day is 1% of the water volume enclosed by the infiltration wells (Figure 11); (ii) the aquifers normal salinity is 5 g L^{-1} .

The number of infiltration wells and their spacing will, for a specific aquifer abstraction rate, control the amount of inflow into the desalination zone (Figure 11) from the wider aquifer. This, in turn, will control the amount of aquifer desalination that will be achievable (Figure 13). This analysis indicates that it may be possible to target converting saline aquifers into repositories of partially desalinated water, which could be used for groundwater abstraction for irrigation.

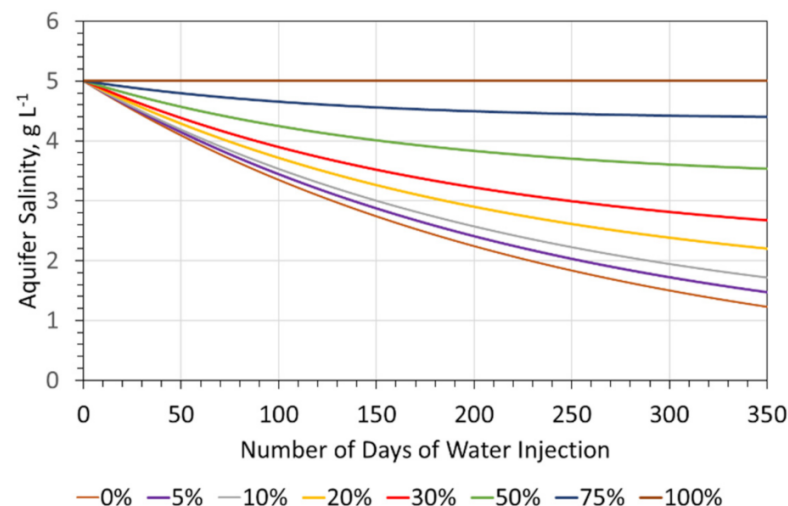


Figure 13. Change in aquifer salinity within the desalination zone, as a function of time, and the proportion of water within the desalination zone, which is fresh saline feed water, derived from the wider aquifer. The initial aquifer salinity = 5 g L^{-1} . The volume of water processed each day is 1% of the water volume enclosed by the infiltration wells (Figure 11).

For example, if the aquifer salinity is 5%, the normal influx from the aquifer to the desalination zone is 5% and the stable average salinity in the partially desalinated aquifer (desalination zone) after 1 year is 1.4%, then abstraction from the desalination zone, where part of the water is used for irrigation and part of the water is reinjected (Figure 12), will result in a gradual increase in the irrigation water salinity (I_s), such that $1.4\% < (I_s) < 5\%$.

Following cessation of water abstraction for irrigation, the aquifer salinity will continue to decline.

5.6. Reversal of Seawater Incursion

Seawater incursion into an aquifer can be reversed by injecting less-saline water into the aquifer (Figure 14). The general process flow (Figures 11 and 12) will result in a zone of reduced salinity developing between the seawater incursion front and the infiltration/injection wells within the aquifer (Figure 14).

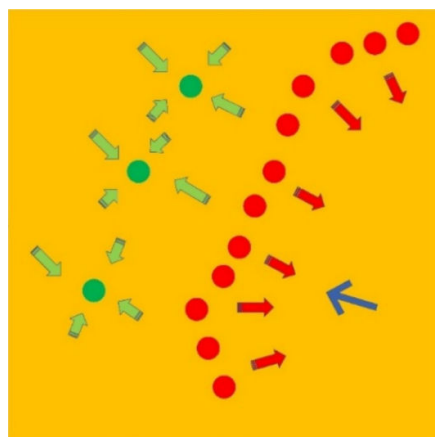


Figure 14. Example of an aquifer where a reversal of seawater incursion is attempted. Green circles = abstraction wells; red circles = infiltration/injection wells; green arrows = abstracted water flows in the aquifer; red arrows = infiltrated/injected water flows of partially desalinated water; blue arrow = direction of seawater incursion.

6. Novelty

6.1. Water Volume Processed

ZVI desalination normally requires a ZVI concentration of around $20\text{--}100\text{ g L}^{-1}$ [10,15,16] and is commonly used to treat a single batch of water [15]. A typical treatment ratio is between 10 and 50 L of water for each 1 kg of Fe used [15,16]. Reference [10] demonstrated that it was possible (for desalination), using a bubble column reactor, to increase this ratio to $42\text{ m}^3\text{ kg}^{-1}\text{ Fe}$.

This study demonstrated a significant advance in the amount of saline water that can be processed by a unit weight of Fe, from $42\text{ m}^3\text{ kg}^{-1}\text{ Fe}$ [10] to $4300\text{ m}^3\text{ kg}^{-1}\text{ Fe}$. This represents an increase in Fe utilization by 2 orders of magnitude.

This was achieved by making the following assumptions:

- The desalination process involves catalytic sites on Fe^0 or $\text{Fe}_x\text{O}_y\text{H}_z$ species [10];
- The catalytic process involves a physical reactant adsorption and a physical product desorption [10];
- Only a small amount of energy is required to force adsorption of a reactant and desorption of a product and this process can be achieved through the use of a pressure wave [10];
- Adsorption is favored by the pressure rise created by the crest of the pressure wave [10];
- Desorption is favored by the pressure trough created by the trough of the pressure wave [10];
- Different species may compete for the same adsorption sites [10];
- Different species may desorb from the sites at different rates. This results in a reduction in the number of available adsorption sites with time. This results in a decline in the desalination rate with increasing reaction time [10];
- The principal interaction between the water body and the catalyst is by diffusion [10]. This assumption allows the catalyst to be placed in a removable cartridge, which is attached to the water body;

- The pressure waves can be constructed by gases bubbling through the water body, displacing water. Reference [10] adopted an approach where 60 L h^{-1} was bubbled through a conduit with a 0.45 m I.D. This created an unstructured and complex wave pattern with significant interference waves. In this study, the same air flow rate was confined to a conduit with a 0.02 m I.D. This created a more consistent and compact wave pattern, which was transmitted along the conduit.
- Changing the reactor construction type from a batch flow, bubble column, static bed, diffusion reactor [10] to a batch flow, bubble column, static bed, recirculating, diffusion reactor will improve pressure wave transmission efficiency.

This category of reaction process is a catalytic pressure swing adsorption desorption process [13,14] or a sorption-enhanced process [12].

This study used air to create pressure waves and it is possible that O_2 plays a role in the desalination process [10]. An alternative source of a pressure wave is an ultrasound source. ZVI degradation experiments for *p*-nitrophenol (PNP) established that degradation rates are enhanced by the presence of ultrasound [17] and for a constant ultrasound frequency of 19.87 kHz, the reactor shape controls the degradation rate [17]. The degradation rate is higher in a conical reactor than in a cylindrical reactor [17]. The proportion of PNP removed for any specific reaction period was directly proportional to the amount of power applied (between 100 W and 500 W), where the regressed removal (vs. power) followed a power function [17].

This observation [17] implies that it may be possible to accelerate the desalination rates documented in Appendix A by increasing the air flow rate, by changing the reactor shape, changing the location of the ZVI, by adding another wave source, or a combination.

6.2. Nature of the Desalination Process

The exact nature of the desalination process is unknown. An earlier study [10] established:

- The process reduces the measurable concentration of Na^+ ions, Cl^- ions, and EC in the water;
- Evaporation of the product water confirms removal of NaCl;

This study confirmed that the measured first-order rate constant declines with increasing reaction time (Appendix A, Table A3). This is an established phenomenon associated with diffusion reactions [18]. The controls on this decline were not investigated in this study. The decline does control the variability in batch salinity outcome (Appendix A) and the overall outcome probability distribution as a function of time (Appendix A, Figure A7). Any decrease in the rate constant decline will boost the average desalination achieved for a specific reaction time. This is, therefore, an important future potential area of research.

6.3. Technology Readiness

The trial results were for a commercial-scale reactor train (Appendix A). They established that the reactor train could achieve a 40% desalination of water. This is the first ZVI desalination reactor train to achieve the desalination of 43 m^3 of saline water. Its reactor increased the batch volume processed from $0.24 \text{ m}^3 \text{ batch}^{-1}$ [10] to $0.86 \text{ m}^3 \text{ batch}^{-1}$, while reducing the air requirement from $250 \text{ L m}^{-3} \text{ h}^{-1}$ [10] to $69 \text{ L m}^{-3} \text{ h}^{-1}$ and the Fe catalyst charge from 1.67 kg m^{-3} [10] to 0.012 kg m^{-3} . After 3 h operation, the 0.24 m^3 reactor train achieved [10]: mean desalination = 24.5%; standard deviation = 22.8%; minimum = 0%; 1st quartile = 9.2%; median = 14.3%; 3rd quartile = 33.9%; maximum = 91%. As a direct comparison, after 3 h, the 0.86 m^3 reactor train achieved: mean desalination = 19.40%; standard deviation = 9.41%; minimum = 0.28%; 1st quartile = 12.36%; median = 19.33%; 3rd quartile = 26.61%; maximum = 49.93%.

6.3.1. Reducing the Outcome Variability

The process design changes used in this study relative to the 0.24 m^3 reactor increased the expected downside desalination from 9.2% to 12.36% at the 1st quartile. The median

desalination expectation was increased from 14.3% to 19.33%. The flip side of these outcome changes was a reduction in the upside desalination potential. These changes changed the standard deviation/mean outcome ratio from 0.93 for at 0.24 m³ reactor to 0.48 for a 0.86 m³ reactor. This compares with the initial reactor structuring trials, which used a 0.01 m³ reactor and achieved a standard deviation/mean outcome ratio (M_o) of 2.0 (i.e., a very wide output range). The data regresses to provide a relationship of the form ($R^2 = 98.1\%$):

$$M_o = 0.513359(\text{reactor volume, m}^3)^{-0.305178}, \quad (8)$$

The expectation from these results is that increasing the reactor train size into a range 2 to 10 m³ will further reduce the standard deviation/mean outcome ratio and further narrow the batch outcome range around the mean value. This hypothesis has still to be confirmed by sequential trials processing 10 m³ batch^{−1}. The expectation from Equation (7) is that M_o for a 10 m³ reactor will be 0.254 and that this will reduce with a 100 m³ reactor to 0.1259. For a normal distribution, the 1st quartile value is: the mean value -0.674 (standard deviation).

6.3.2. Switching from Batch Flow Operation to Continuous Flow Operation

The process trials have all operated using a batch flow. Automation would be made simpler if the overall water flow management was switched from a batch flow to a continuous flow. An example structuring for a continuous flow reactor is provided in Figure 13. This structuring allows the volume of water (m³ d^{−1}), which can be processed by the reactor, to be increased by about 20%. The effectiveness of this structuring (Figure 13) has still to be confirmed by long-term testing.

Initial small-scale testing (using a different ZVI catalyst) of this process flow (Figure 15) was undertaken using 1 L and 2.5 L reactors with a continuous flow feed rate. These small-scale trials indicated that the process flow shown in Figure 15 can work on a small scale, over trial periods of up to 14 days. Commercial-scale reactor train trials of the process flow illustrated in Figure 15 were not undertaken at this time, with a continuous water feed.

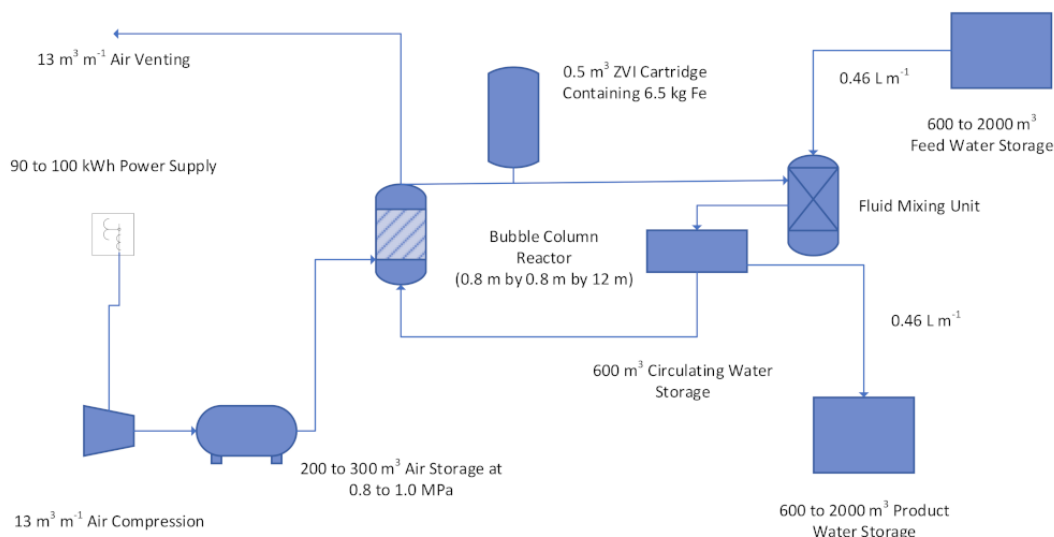


Figure 15. Expected structure of a reactor unit processing, continuously, 660 m³ d^{−1}.

6.4. Shaping the Pressure Wave

The modelling and design of pressure waves can be simple or complex. From a design perspective in a catalytic–pressure–swing–adsorption–desorption environment, the principal objectives are to maximize the wave frequency while maximizing the wave amplitude.

The permeability of the water to the gas is k_g . The bubbling of the gas through the water column creates a primary pressure wave. All continuous flow reactors (fixed bed and fluidized bed) have a constant driving force between an upstream plenum (USA) and

a downstream plenum (DSA). This is achieved by maintaining a constant pressure in the upstream plenum (USA) and the downstream plenum (DSA). In the reactor trains used in this study, the pressures in the upstream plenum (USA) cycle between lower and higher pressures and the pressures in the downstream plenum (DSA) cycle between higher and lower pressures. This creates a variable driving force across the water column. At any instant in time, the pressure in the upstream plenum (USA) is greater than or equal to the pressure in the downstream plenum (DSA). The relationship between the pressure in the upstream plenum (USA) and the pressure in the downstream plenum (DSA) is in a continual state of flux. This continual pressure variation creates pressure waves within the bubble column reactor and the discharge conduits associated with it (Figures 1 and 2).

This reactor structuring has a number of characteristics. These include:

- Kinetic energy received in the upstream plenum (USA) is temporarily converted to potential energy. The amount of kinetic energy converted to potential energy cyclically varies with time.
- Potential energy stored in the upstream plenum (USA) is cyclically converted to kinetic energy.
- The flow rate through the water column cyclically varies with time. The maximum flow rate through the water column in a flow cycle is greater than the average flow rate into the upstream plenum (USA). The minimum flow rate through the water column in a flow cycle can be zero (Figure 3).

This structuring is highly flexible and can accommodate a feed to the upstream plenum (USA), which is delivered at a constant rate, a variable rate, an irregular rate, intermittently, or episodically. This structuring can also accommodate a demand for product from the reactor, which is continuous, intermittent, or variable.

The bubble column reactor (Figure 1) is structured to contain a water column: an upstream plenum (USA), a downstream plenum (DSA), a downstream conduit, which removes product from the downstream plenum (DSA), and an upstream conduit, which delivers a feed to the upstream plenum (USA) (Figure 2).

The difference in potential energy between the upstream plenum (USA) and the downstream plenum (DSA) (less any pressure (potential energy) losses) is the driving force for the fluid flow. The driving force (ΔP) is approximated as:

$$\Delta P = P_U - P_D - P_L, \quad (9)$$

where P_L = pressure losses (Pa) associated with the flow across the water column; P_U = the pressure (Pa) in the upstream plenum (USA); P_D = the pressure (Pa) in the downstream plenum (DSA). The pressure P_U is exerted by a standing (static) body of fluid (which can be pressurized), a flowing fluid (which can be pressurized), or a combination thereof.

The pressure (Pa) exerted by a static fluid on a basal surface (e.g., a fluid–fluid contact or a membrane or a surface) is calculated as: $d_f gh$, where d_f = fluid density (kg m^{-3}); g = acceleration due to gravity (m s^{-2}); h = a column (m) of a given fluid of mass density d_f , which would be necessary to produce this pressure.

Conventional reactors require that ΔP , P_U , P_D , and P_L through the catalyst bed remain constant and do not change with time. In this reactor (Figure 1), ΔP , P_U , and P_D cyclically change from higher to lower values with time. P_L may change with time or may remain constant.

The fluid flow rate through the water column is described by the equation:

$$Q = k \Delta P, \text{ or } Q = k (\Delta P - \Delta \chi), \quad (10)$$

where Q = flow rate ($\text{m}^3 \text{m}^{-2} \text{s}^{-1}$); k = permeability ($\text{m}^3 \text{m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$); ΔP = driving force (Pa); $\Delta \chi$ = correction for fugacity, or another form of correction. Permeabilities may change with flow type (e.g., viscous flow, diffusion flow, turbulent flow, laminar flow) and fluid type. Flow type (and permeability) can change with ΔP . Flow can be turbulent or laminar. ΔP across the water column must vary with time.

The water column is used to create a continual disequilibrium within the reactor, where ΔP , P_U , P_D , and P_L are in a continual state of flux. This results in the fluid flow rate, Q , through the water column cyclically varying with time, even if the flow rate into the reactor through the upstream conduit is constant (Figure 3). The flow rate through the downstream conduit can remain constant or may vary with time (Figure 3).

An ΔP wave can be constructed and designed or may have a random construction or a combination thereof. The ΔP wave can assume any shape, amplitude, and frequency, including, but not limited to, symmetrical, asymmetrical, sinusoidal, triangular, harmonic, Fourier, square, spiral, scroll, trigger, pulse, a wave train, another type of wave, or a combination. The wave can be a shock wave resulting from an abrupt change in force level, an impulsive force, pulsed force, or a combination thereof. The wave form can be damped, undamped, underdamped, overdamped, or a combination thereof. The wave amplitude can decline with time, increase with time, remains constant with time, or a combination thereof. The wave can be a kinematic wave, a phase wave, or a combination thereof. The wave can be a pulse wave.

Higher periodicity waves can be supplemented with shorter periodicity waves. Wave structures can be composite. A pressure management system can optionally be used to control or define one or more aspects of the waves. Waves can be supplemented by artificially induced waves associated with ultrasonic equipment, wave generating equipment, heating, or cooling of fluids located in one or more of the upstream plenum, upstream conduit, downstream plenum, downstream conduit, and water column. Wave periodicity can take any form and can have any duration.

In the reactor design used in this study (Figures 1 and 2), the ΔP wave cyclically alters P_U and P_D . In the earlier reactor design [10], the ΔP wave cyclically altered P_U but left P_D unchanged as a function of time.

The wave can be generated by alterations to k in the water column or by the use of apparatus, which has the effect of cyclically altering P_U and P_D or a combination thereof. The alterations to k can be induced by changes in ΔP ; or by chemical changes in the water column; or by changes in the adsorption or desorption of specific fluids; or by osmotic changes within the water column.

P_M is the minimum driving force or pressure required to initiate viscous liquid flow. For gases, the minimum driving force (P_M) can be defined by the Knudsen Number (K_N) or another parameter associated with a specific type of diffusion. When the driving force is less than P_M , the principal flow mechanism is bulk diffusion or Knudsen Diffusion. $\Delta P < P_M$ during part of a flow cycle and $\Delta P > P_M$ during part of a flow cycle.

Pressure Applied by the Water Column

In this reactor (Figure 1), the pressure applied by the water column on the exit of the upstream plenum (USA) was 0.117 MPa (above atmospheric pressure). A gas flow could only be initiated if the buoyant pressure in upstream plenum (USA) exceeded 0.117 MPa (above atmospheric pressure). This initiation pressure reduces as the volume of gas entrained within the water column increases. By way of comparison, the pressure exerted by the water column in the 0.24 m³ reactor train described in reference [10] was 0.0147 MPa.

Experimental work established that the rate of lateral attenuation of the pressure wave created by the rising bubble column decreases as the effective bubble size increases [19]. For a given bubble size, the amplitude of the pressure wave decreases exponentially with increasing lateral distance. For example, the amplitude of the pressure wave (A_x) at a lateral distance x from the bubble can be expressed as [20]:

$$A_x = A_0 e^{(-\eta(x-x_0))}, \quad (11)$$

A_0 = initial wave amplitude; x_0 = initial bubble position; η = the attenuation coefficient of the pressure wave. In a conduit, the attenuation coefficient decays as a function of x , as [20]:

$$\eta = \ln(A_0/A_x)/(x - x_0), \quad (12)$$

The pressure wave propagation velocity is a function of the air fraction in the bubble column and increases as the void fraction exceeds 0.5 [20]. η increases as the void fraction increases [20]. While the modelling of bubble flow and associated pressure waves in a bubble column reactor is complex, some general design conclusions can be drawn:

- Increasing the bubble column length will increase the air fraction in the water during bubble flow and will increase both the pressure wave amplitude and propagation speed;
- Decreasing the bubble column diameter while maintaining the same air flow rate will increase the air fraction in the water during bubble flow and will increase both the pressure wave amplitude and propagation speed;
- Forcing the rising air bubbles to displace water into a lateral conduit (Figure 1) creates a propagating pressure wave in that conduit with a lower air fraction and a low value of η . This has the effect of slowing the rate of decline in A_x , with increasing distance and maximizing the pressure wave amplitude, as it interacts with the ZVI cartridge (Equation (11)).

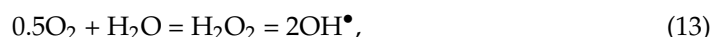
The design innovations created in this reactor (Figures 1 and 2), when compared with the 0.24 m³ reactor [10], resulted in increased pressure wave amplitudes, increased wave propagation speeds within the bubble column, and a decreased value of η in the wave intersecting the ZVI cartridge. This, in turn, resulted in a reduced variation in pressure wave amplitude reaching the ZVI and may account for the observed reduced desalination variation (expressed as standard deviation/average value).

7. How Might the Desalination Process Work?

The exact mechanism used by the reactor train to remove Na⁺ and Cl[−] ions from the water remains unknown. This section considers some of the possibilities, which may account for the ion removal.

7.1. Impact of Air

Desalination involves the removal of Na⁺ and Cl[−] ions from water. If air is bubbled through water, then the following reactions can be expected:



The sodium ions would be expected to react as follows:



These reactions do not remove the Na⁺ or Cl[−] ions. They will increase pH and change Eh, but will not change EC or ion concentrations measured by a Na⁺ ISE or Cl[−] ISE. The observed reductions in the measured EC, Na⁺ ISE, and Cl[−] ISE readings (Tables A1 and A2) imply that the NaCl product either forms no part of the dissolved matter in the water or if it is still present in the water, it is present in a product form, which has a lower electrical conductivity.

The relative EC ratio of NaCl:Potential soluble products varies with ion concentration [21], but can be approximated as: NaCl:NaClO₄ = 1:0.93; NaCl:NaOH = 1:1.98; NaCl:HCl = 1:3.41 [21]. Therefore, the most probable soluble products (NaOH, HCl) are likely to significantly increase rather than decrease EC. The observed position is a decrease in EC.

7.2. Ion Interference

Cl^- and Na^+ ion selective electrodes respond to changes in Cl^- and Na^+ ion concentration. They use an approach based on the Nikolsky–Eisenman equation [22]. This equation [23] is:

$$E_1 = E' + s(\text{Log}[a_i + K_{ij}^{\text{pot}} (a'_j)^{z_i/z_j} + D]), \quad (16)$$

where E_1 = experimental potential of the solution; E' = the constant potential of the cell; a_i = the activity (concentration) of the primary ion; K_{ij}^{pot} = potentiometric selectivity coefficient; a'_j is the known fixed activity of the interfering ion; z_i and z_j are integers relating to the charge in the primary (i) and interfering ions (j); s = the slope of the line resulting from a plot of E_1 (mV) versus a_i . $[s]$ varies with temperature in accordance with the relationship, $s = 2.303RT/z_iF$; T = temperature, K; R = gas constant; F = Faraday's constant. D represents the contribution to potential of all interfering ion species other than species j .

The ISE was calibrated using standard solutions where:

$$E_1 = E' + s(\text{Log}[a_i + K_i^{\text{pot}} z_i]), \quad (17)$$

and no interfering ions are present. Equation (15) demonstrates that it is theoretically possible for an interfering ion to reduce E_1 for a specific value of a_i , thereby reducing the interpreted ion concentration in the product water.

Given the high ion concentrations of Na^+ and Cl^- ions in the feed water, relative to other ions, it is considered unlikely that the observed decreases in EC or E_1 , between the feed water and the product water, could be attributed solely to the presence of interfering ions in the water.

7.3. Ion Removal Reaction Order

Most, but not all, ZVI ion removal reactions are first order [24–30]. The first-order rate constant is defined as:

$$k_{\text{obs}} = -\text{Ln}(C_{t=n}/C_{t=0})/t_r \text{ and } \text{Ln}(C_{t=n}) = -k_{\text{obs}} t_r + \text{Ln}(C_{t=0}) \quad (18)$$

where k_{obs} = observed rate constant; t_r = reaction time; $C_{t=0}$ = initial ion concentration; $C_{t=n}$ = ion concentration at time t_r . The first-order rate constant normally remains unchanged with increasing t_r . In this study, k_{obs} changed as a function of t_r (Table A3, Figure 16). This change in k_{obs} with t_r was statistically highly significant.

7.3.1. Interpretation of Statistical Significance

The coefficient of interpretation was used to determine the magnitude of the statistical significance. The coefficient of determination, R^2 , is the square of the Pearson correlation coefficient (PCC). This coefficient is used to give an indication of the strength of the statistical correlation between two variables, associated with a specific regression trend line [31,32]. By definition, R^2 falls within a range 1 to 0 and PCC falls between +1 and −1 [31,32]. The following interpretations are made [31,32]:

- PCC = 0.9 to 1.0 (R^2 = 0.81 to 1.00): Interpretation—very strong correlation
- PCC = 0.7 to 0.89 (R^2 = 0.49 to 0.79): Interpretation—strong correlation
- PCC = 0.4 to 0.69 (R^2 = 0.16 to 0.47): Interpretation—moderate correlation
- PCC = 0.1 to 0.39 (R^2 = 0.01 to 0.15): Interpretation—weak correlation
- PCC = 0.0 to 0.10 (R^2 = 0.00 to 0.01): Interpretation—negligible correlation

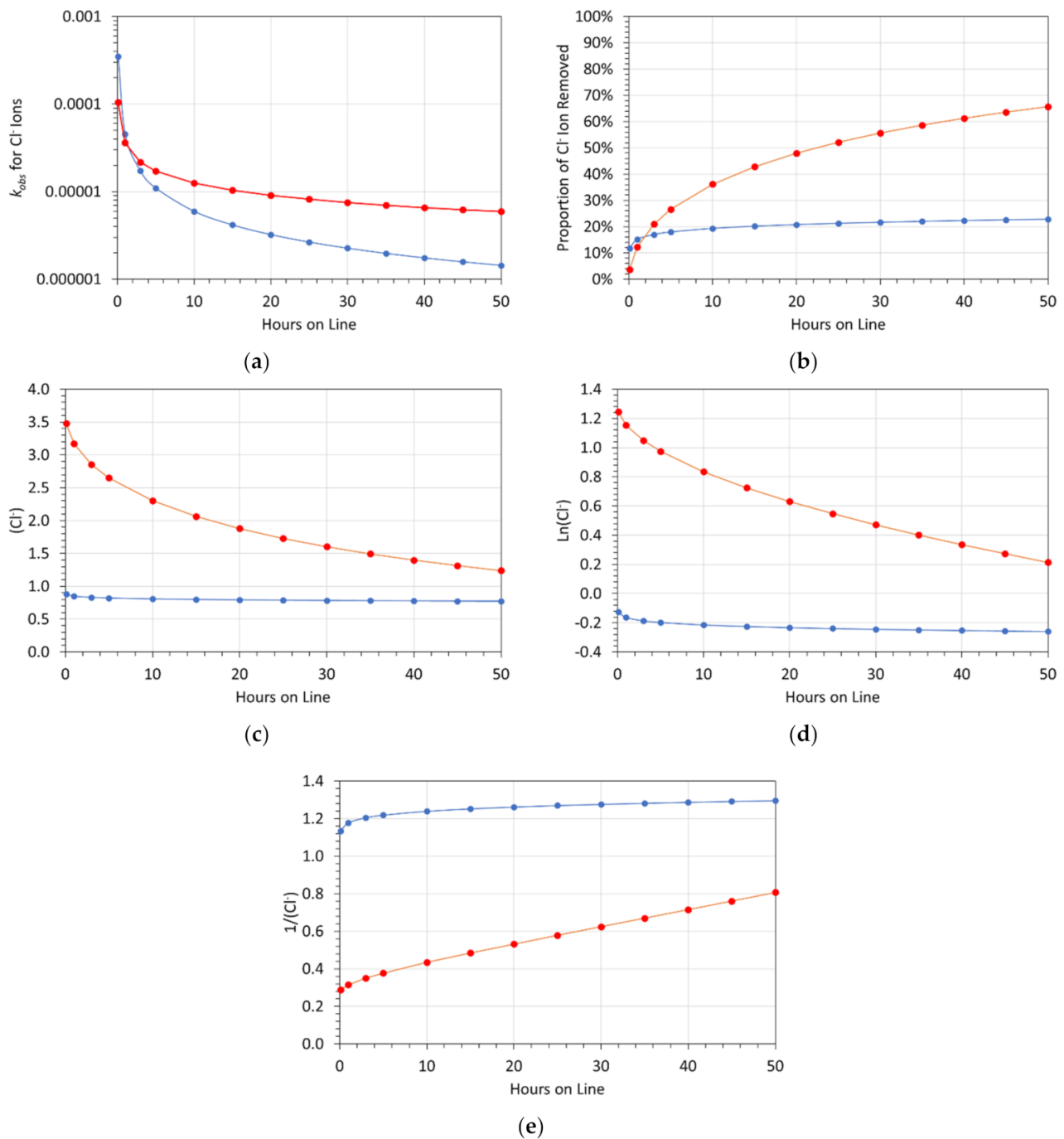


Figure 16. Example relationships. (a), k_{obs} vs. hours on line; (b) proportion of ion removed vs. hours on line; (c) zero-order reaction check. Cl^- ion concentration, g L^{-1} vs. hours on line; (d) first-order reaction check. $\text{Ln}(\text{Cl}^-)$ ion concentration, g L^{-1} vs. hours on line; (e) second-order reaction check. $1/\text{Cl}^-$ ion concentration, g L^{-1} vs. hours on line; data source: Table A3. Red line: Trial 18. $3.61 \text{ g Cl}^- \text{ L}^{-1}$; blue line: Trial 4. $1.0 \text{ g Cl}^- \text{ L}^{-1}$.

7.3.2. Relationship between k_{obs} and Hours on Line

Example relationships between hours on line and k_{obs} are provided in Figure 16a. These relationships demonstrate that k_{obs} decreases as the proportion of an ion removed increases. In these examples, after an initial 5 h operation, (i) the Cl^- ion removal can be interpreted as a zero-order, first-order or second-order reaction for the example (Figure 16), where Cl^- at $t = 0 = 1 \text{ g Cl}^- \text{ L}^{-1}$; (ii) the Cl^- ion removal can be interpreted as a second-order reaction for the example (Figure 16), where Cl^- at $t = 0 = 3.61 \text{ g Cl}^- \text{ L}^{-1}$.

This brief analysis implies that the ion removal reaction has two phases:

1. An initial fast reaction phase;
2. A subsequent slower reaction phase.

This may imply an initial high availability of reactant, followed by a slower reaction associated with the residual declining reactant volume.

7.4. Ion Removal

Each trial batch displayed a pattern of decreasing ion removal rate, with increasing reaction time (e.g., Table A3; Figure 16). Replacement of a water batch with a new water batch resulted in an initial increase in reaction rate, followed by the pattern of decreasing ion removal rate repeating. If k_{obs} is redefined as:

$$k_{obs} = k_{ins} [a[a_s]^b c[P_w]^d], \quad (19)$$

where k_{ins} = intrinsic rate constant for $a_s = 1$ and $P_w = 1$; a_s = surface area ($\text{m}^2 \text{g}^{-1}$), which is a surrogate for the number of active catalytic sites; P_w = weight of catalyst used; and $[a, b, c, d]$ are constants. In this study, P_w remained constant. Therefore, k_{obs} can be approximated as:

$$k_{obs} = k_{ins} [a[a_s]^b], \quad (20)$$

The observed power function declines in k_{obs} , with increasing time on line (Table A3) indicate that $[b]$ declines as a function of time from an initial value of 1.0. Linear declines result from $[a]$ declining as a function of time from an initial value of 1.0. Exponential and logarithmic declines result from a combination of $[a]$ and $[b]$ declining as a function of time from an initial value of 1.0.

Oxygenation results in the water pH increasing with time (Table A1) due to the increased presence of OH^- and $\text{OH}^\bullet$ ions. If $[a]$ and $[b]$ are Eh and pH sensitive or if their decline is due to site blocking by OH^- and $\text{OH}^\bullet$ ions, then it is reasonable to expect k_{obs} to decrease with increased time on line.

It is also reasonable to expect that replacement of the water in the reactor with a new fresh batch of water will result in desorption of OH^- and $\text{OH}^\bullet$ ions. This would be expected to increase one or more of $[a]$ and $[b]$.

The data indicate (Figure 17) that the (i) initial value of k_{obs} may increase with decreasing feed water ion concentration; (ii) the initial value of k_{obs} for a water batch can be higher or lower than the initial value of k_{obs} for the previous batch; (iii) the value of k_{obs} measured when freshwater is placed in the reactor can be two to nine magnitudes higher than the measured value of k_{obs} when the water from a batch is removed from the reactor.

7.5. Removed Product

The chemical composition of the removed NaCl product is unknown. The product is not present as a precipitate in the residual catalyst and is not observed as solid micron-sized particles in the product water. Extraction of the catalyst, following the processing of 50 batches (Figure 18), revealed the presence of small (0.7 to 3 microns) colloidal precipitates of an unknown composition in the associated extracted pore water (Figure 18c).

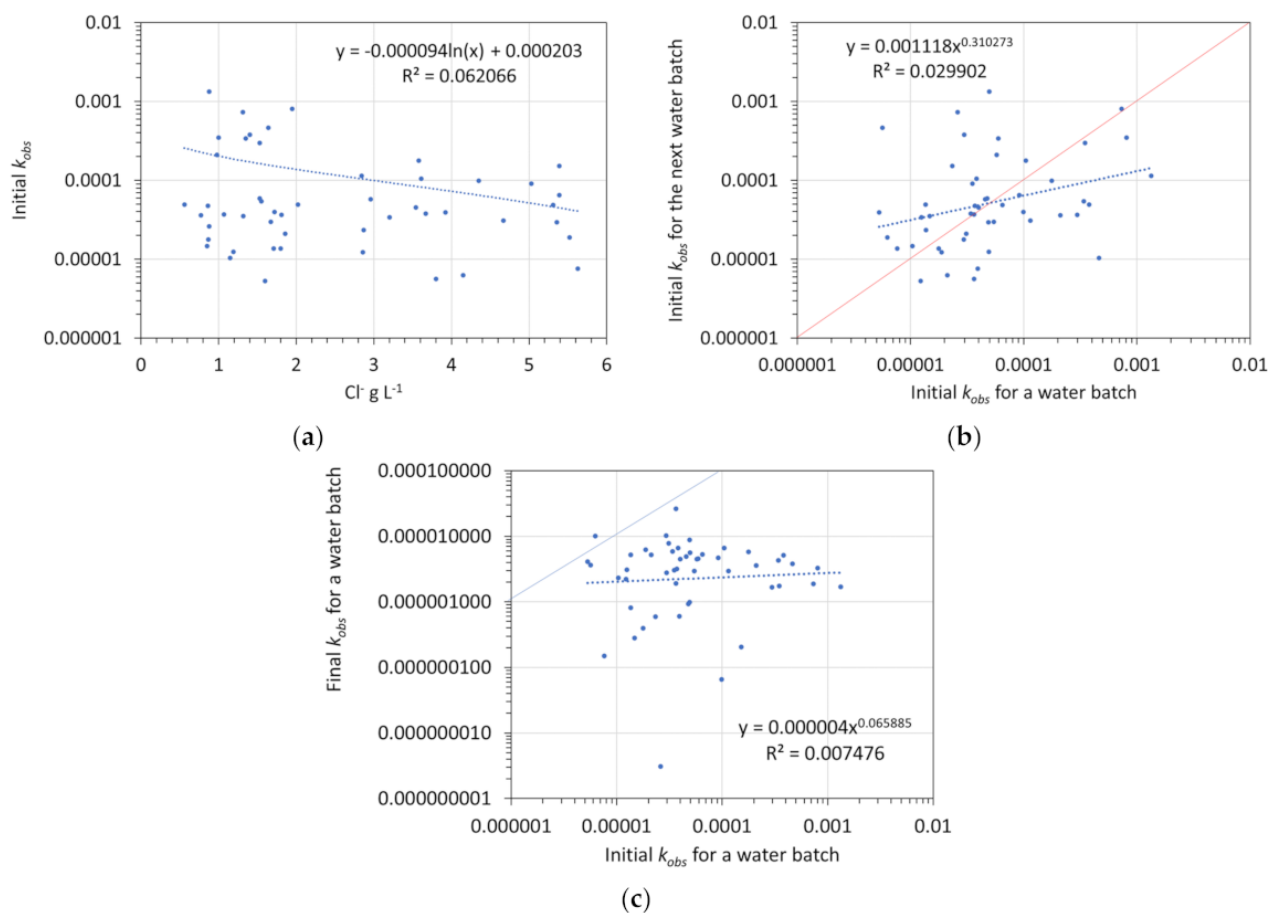


Figure 17. Variation in Cl^- rate constant. (a) Initial rate constant versus feed water Cl^- content; (b) initial rate constant for a batch versus initial rate constant for the next batch; (c) initial rate constant for a batch versus the final rate constant for a batch. Dotted blue line is a regression line. Solid blue line is a line of equal value.

The initial ZVI desalination model [15] assumed that the removed NaCl was incorporated in $\text{Fe}(\text{OH})_x$ (green rust) and FeOOH akageneite species. This would require the removed NaCl to be accumulated within the catalyst cartridge. This is not the case. Therefore, this model is not applicable. A successor model assumed that the NaCl was adsorbed by $\text{Fe}(\text{OH})_x$ and FeOOH species, before being redeposited as NaCl within dead-end pores encapsulated by $\text{Fe}(\text{OH})_x$ and FeOOH species [16]. This desalination model has been verified for pellets constructed from $m\text{-Fe}^0\text{:Fe(b)@n-C}^0$ polymers [33]. Ion removal using this process follows a zero-order reaction [33]. In this study, the catalyst bed was constructed with open pores (Figures 4 and 18) from uncemented particles, where $<5\%$ of the total porosity was contained in dead-end pores. The resultant ion removal had an initial fast removal stage followed by removal using a second-order reaction (Figure 16). Therefore, the desalination model applied to the pellets [33] is not applicable to this study.

In this study, the redox regime (Table A1, Figure A4) is in (Hydrogen Stability Zone 0), as defined in reference [34]. In this redox regime, the dominant Fe oxidation number is 3^+ [35]. Therefore, the catalytic polymer coating used (Figures 4 and 18) will be either $\text{SiO}_2\text{:Fe(a,b,c)@urea}$, $\text{SiO}_2\text{:Fe(a,b,c):urea}$, or $\text{SiO}_2\text{:Fe(a,b,c)}$. If the polymers had been operated and constructed in (Hydrogen Stability Zones 1 or 2 [34]), the constructed polymer would have been one of: $\text{SiO}_2\text{:n-Fe}^0\text{:urea}$, $\text{SiO}_2\text{:n-Fe}^0\text{:urea}$, $\text{SiO}_2\text{:n-Fe}^0\text{:Fe(a,b,c)@urea}$, $\text{SiO}_2\text{:n-Fe}^0\text{:Fe(a,b,c):urea}$, or $\text{SiO}_2\text{:n-Fe}^0\text{:Fe(a,b,c)}$. The symbol (:) indicates chemical bonding. The symbol (@) indicates physical bonding.

Entrained $n\text{-Fe}^0\text{:Fe(a,b,c)}$ polymers were used to remove Na^+ and Cl^- ions from water [11]. Ion removal using these polymers is characterized by a situation, where k_{obs} decreases with increasing t_r [11]. This is the observed position (Table A3, Figure 17).

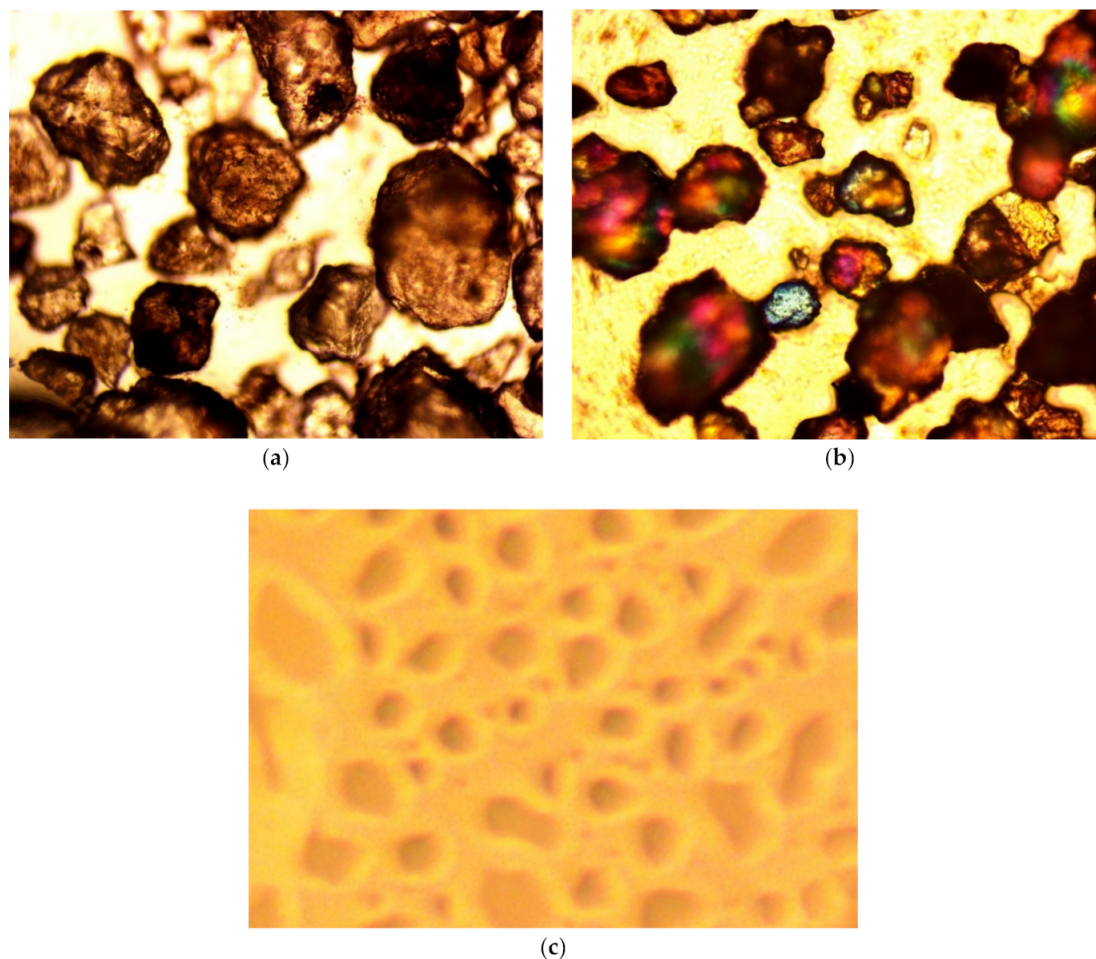
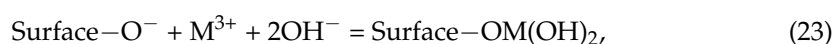
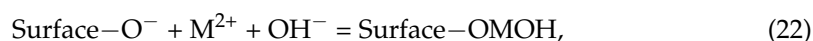
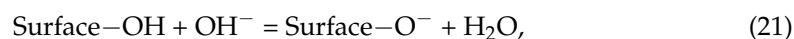


Figure 18. Extracted catalyst following the processing of 50 batches of water. (a) Catalyst: transmitted light, field of view = 1.3 mm; (b) catalyst: circular polarized light, field of view = 1.3 mm; (c) pore water precipitate: transmitted light, field of view = 0.03 mm.

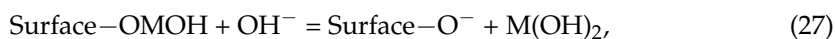
7.5.1. Interpreted Catalytic Model

The CPSAD operating model [10,33] used in this study uses pressure increases to adsorb reactants onto the catalytic site and pressure decreases to desorb products from the catalytic site [10,33]. The amorphous, hydrated, precipitated products in Figure 18c are consistent with adsorption and desorption of a cation ion (M) from the water (e.g., Fe^{3+} , Ca^{2+} , Mg^{2+}), where the catalyst surface has a basic reaction during pressure increases of the form:



and a basic reaction during pressure decreases of the form:



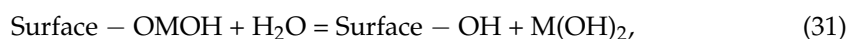
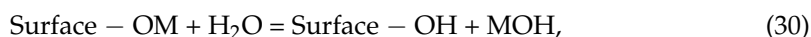


The desorbed $n\text{-M(a,b,c)}$ polymer $[\text{M(OH)}_x]_n$ or another metal polymer then aggregates within the water body and removes Na^+ and Cl^- ions from the water [11]. Under this model, k_{obs} would be expected to decline, as

- The availability of the metal (M) cation in the water decreased towards an equilibrium level.
- The growing $n\text{-M(a,b,c)}$ polymer became saturated with Na^+ and Cl^- ions.

Removal of product water containing the $n\text{-M(a,b,c)}$ polymer would result in desalination continuing over a long period of time, outside the reaction environment. This is the observed position (Table A2).

Replacement of the water, following partial desalination, will result in the reaction:



Changing the water batch results in regeneration of the catalyst. Under this model, the function of the catalyst is to catalyze the formation of entrained nano-metal polymers, which act as scavenging agents for the removal of Na^+ and Cl^- ions from the water.

7.5.2. Mechanism of Na^+ and Cl^- Ion Removal

In this study, the competing ions for Na^+ and Cl^- ions in the metal polymers were OH^- , SO_4^{2-} , HCO_3^- , and CO_3^{2-} ions. Examination of the product water identified the presence of entrained, amorphous, hydrated spheres or ellipsoids of metal polymer, with a maximum dimension in a range 0.01 to 0.15 mm (e.g., Figure 19). These polymers may have formed from the aggregation of the polymers ejected from the catalyst body (Figure 18c). Their basic structure is a metal polymer surrounding a fluid-filled cavity (Figure 19). This type of polymer structure is an active pollutant scavenger [11]. The fluid-filled cavity is effectively a mobile, dead-end pore, which grows by polymer particle aggregation and accretion [11]. The fluid contents of the pore are isolated from the water body and will not register on EC or ISE instruments analyzing the water body.



Figure 19. Extracted (from the product water) amorphous, fluid filled, hydrated ellipsoid of metal polymer: transmitted light, field of view = 0.13 mm.

An earlier study [33] established that $m\text{-Fe}^0:n\text{-Fe(b)}@n\text{-C}^0$ bounded dead-end pores can actively concentrate both Na^+ and Cl^- ions (and their products) within the dead-end pore. It is possible that the amorphous, hydrated spheres or ellipsoids of metal polymer (Figure 19) accumulated and concentrated the removed Na^+ and Cl^- ions recorded in this study.

This explanation would account for why, in some product water batches placed in storage for 2 years, there was an increase in Na^+ ion concentration after 2 years storage (Table A2).

7.6. Current Working Model

The current working model is:

- The $\text{SiO}_2@n\text{-Fe(a,b,c)}@n\text{-urea}$ polymer in a pressure–swing environment acts as a catalyst for the formation and release of $n\text{-metal}$ polymers, utilizing dissolved metal cations (e.g., Fe^{n+} ; Ca^{2+} , Mg^{2+} , Cu^{n+}) within the water to form hydrated metal hydroxide polymers;
- These metal polymers coalesce to form entrained, fluid-filled colloids;
- The fluid-filled colloids extract Na^+ and Cl^- ions from the water and deposit them within the fluid-filled cavities. The fluid-filled cavities may also extract OH^- , HCO_3^- , SO_4^- , NO_x^- , H^+ ions, and other anions/cations from the water [11]. Since the data (e.g., Table A3) indicate that the Na^+ and Cl^- ions are removed by different processes, it may be that some fluid cavities only contain (or are dominated by) Na^+ species, while others only contain (or are dominated by) Cl^- species.

If this working model is correct, then it is likely that the reactor could be repurposed to remediate most waters containing metal cations. The cations would be used to either form entrained, scavenging polymers within the water body or would be extracted and added to a polluted water body to affect remediation. An example process flow diagram showing how this concept could potentially be used to remediate water is provided in Figure 20.

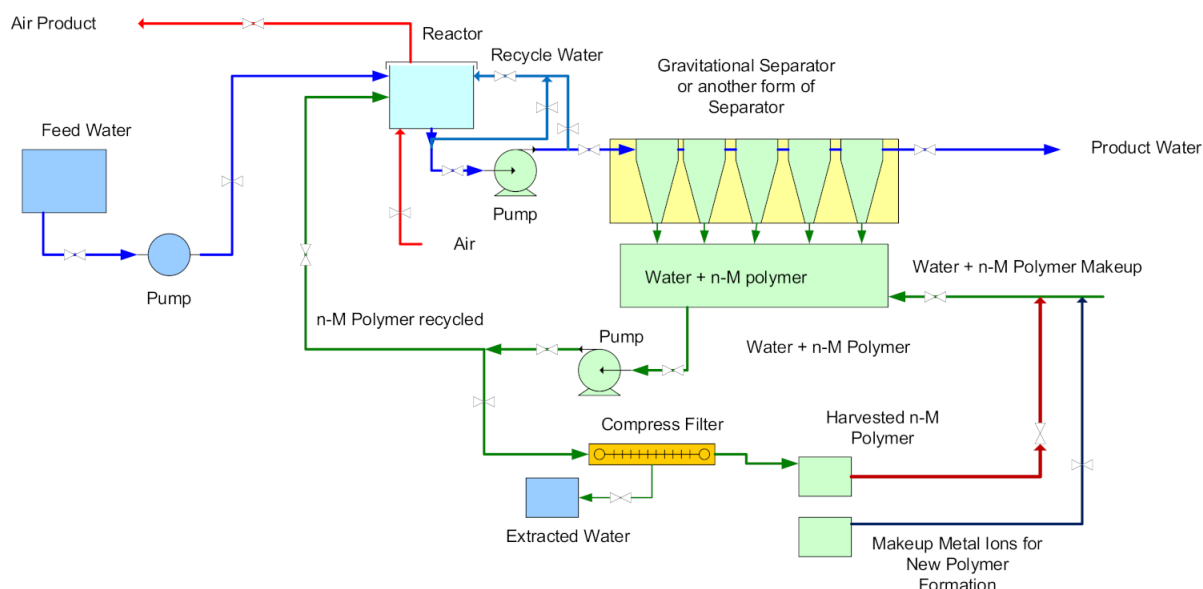


Figure 20. Possible reactor process flow where the reactor is used to remediate water.

8. Conclusions

This study established that a batch flow, bubble column, diffusion reactor train, incorporating recycle, can be operated as a catalytic pressure swing adsorption/desorption (separation) reactor (CPSAD) to partially desalinate water. The catalyst used was a $\text{SiO}_2@n\text{-Fe(a,b,c)}@n\text{-urea}$ and $\text{SiO}_2@n\text{-Fe(a,b,c)}$ polymer.

An individual catalyst charge was demonstrated to process >50 batches (43 m³) without loss of activity. The catalyst is structured such that replacement of one batch of processed water with a fresh batch of water automatically results in regeneration of the catalyst. The catalyst is used to produce entrained n-metal(a,b,c) polymers in the water. The metals used are derived from cations contained within the feed water. These entrained polymers aggregate and accumulate within the water body to form entrained polymers colloids, which encapsulate fluid-filled pores. These polymers act as scavengers, to remove Na⁺ and Cl[−] ions from the water. During reactor operation, the amount of desalination associated with each batch of water increases for a period of 3 to 30 h before the salinity stabilizes at a new lower level.

The trials identified that the process produces partially desalinated water, no reject brine, and that the water product contained some entrained nano/micron-sized colloidal flocculates. The process requires access to an energy source. The principal process operating cost is the cost and provision of compressed air, combined with costs associated with the addition and removal of water from the reactor. The expected process operating cost will vary with geographic location.

This study used an artificial saline water as a feedstock. The next stages in the development of this process will require operation using a natural saline water.

Funding: This research received no external funding.

Data Availability Statement: The data used in this study are placed in the tables and figures contained within the paper and in Appendix A.

Acknowledgments: The Editorial team and the three Reviewers are thanked for their constructive comments.

Conflicts of Interest: The author declares no conflict of interest.

Appendix A. Quantitative Data

Table A1. Basic parameters associated with each trial. F_w = feed water; P_{pw} = product water; T = temperature.

	F _w	P _{pw}	F _w	P _{pw}	F _w	P _{pw}	Air Flow Rate	Air Flow Duration	O ₂ Supplied	O ₂ Adsorbed
Trial	pH	pH	Eh, mV	Eh, mV	T, °C	T, °C	L/hr	hrs	L/L	g/L
1	5.85	6.26	460	397	16.9	16.5	65	8.95	0.14	0.04
2	6.30	7.19	420	437	15.7	14.7	180	45.22	9.49	1.86
3	6.28	7.17	441	422	15.3	15.5	180	45.78	2.01	0.65
4	6.30	7.37	532	501	15.0	15.6	60	56.93	0.83	0.38
5	6.56	8.75	438	385	16.6	15.0	60	61.67	0.90	0.41
6	5.98	6.28	464	395	12.2	12.5	60	17.65	0.26	nd
7	6.68	8.00	471	374	12.0	10.8	60	64.47	0.94	nd
8	6.57	7.50	456	285	7.9	10.1	60	36.30	0.53	nd
9	6.68	7.57	492	455	8.1	7.4	60	38.02	0.56	nd
10	6.26	6.90	449	334	8.7	7.5	60	44.00	0.64	nd
11	6.12	6.50	464	366	5.9	4.3	60	30.17	0.44	nd
12	6.09	6.22	440	355	6.5	2.7	60	38.13	0.56	nd
13	5.58	6.24	455	395	2.9	4.2	60	37.53	0.55	nd
14	5.54	6.05	465	430	6.3	1.9	60	22.40	0.33	nd
15	5.66	6.17	473	444	5.6	5.1	60	30.78	0.45	nd
16	5.90	7.01	515	444	4.6	6.3	60	33.43	0.49	nd
17	6.11	7.30	507	456	2.2	5.4	60	30.70	0.45	nd
18	6.40	7.25	499	437	4.1	5.7	60	30.78	0.45	nd
19	6.40	7.20	489	374	5.8	5.0	60	29.78	0.44	nd
20	5.61	6.08	454	355	4.3	2.9	60	29.88	0.44	0.12
21	5.73	6.32	437	357	3.8	5.9	60	34.22	0.50	0.11

Table A1. Cont.

	F _w	P _{pw}	F _w	P _{pw}	F _w	P _{pw}	Air Flow Rate	Air Flow Duration	O ₂ Supplied	O ₂ Adsorbed
Trial	pH	pH	Eh, mV	Eh, mV	T, °C	T, °C	L/hr	hrs	L/L	g/L
22	5.90	6.68	433	365	5.4	5.9	60	43.12	0.63	0.16
23	5.82	6.31	511	462	7.0	7.5	60	45.23	0.66	0.21
24	6.16	6.22	496	434	8.3	8.4	60	30.42	0.45	0.09
25	5.37	5.87	479	383	8.1	10.4	60	30.85	0.45	0.16
26	5.31	6.40	467	431	10.8	11.7	60	39.45	0.58	0.15
27	5.97	6.20	451	456	11.8	18.2	60	38.85	0.57	0.24
28	5.97	6.45	453	469	14.0	16.0	60	29.65	0.43	0.21
29	5.75	6.46	535	429	12.4	12.0	60	29.27	0.43	0.20
30	6.15	6.66	483	468	14.0	14.7	60	34.72	0.51	0.19
31	7.40	9.30	519	473	17.8	12.6	60	36.48	0.53	0.23
32	7.02	7.17	542	432	14.8	15.3	60	39.38	0.58	0.22
33	5.34	6.40	480	456	17.0	16.4	60	39.83	0.58	0.18
34	5.40	6.22	354	234	14.5	14.6	60	39.60	0.58	0.28
35	5.62	6.04	393	380	14.3	13.9	60	32.53	0.48	0.29
36	5.44	6.14	495	431	15.4	13.2	60	32.90	0.48	0.30
37	5.79	6.58	473	411	11.0	11.3	60	31.38	0.46	0.30
38	5.92	6.70	463	424	12.1	12.5	60	32.00	0.47	0.31
39	6.17	6.68	413	444	12.9	10.6	60	31.63	0.46	0.30
40	6.26	6.76	505	422	9.6	10.8	60	32.82	0.48	0.37
41	5.97	6.75	467	415	12.1	10.9	60	31.98	0.47	0.24
42	6.12	6.60	445	426	8.1	8.1	60	30.80	0.45	0.28
43	6.04	6.30	458	416	4.9	5.3	60	31.82	0.47	0.29
44	5.94	6.22	354	336	4.2	3.0	60	30.02	0.44	0.26
45	6.00	6.30	480	422	3.6	5.0	60	31.13	0.46	0.26
46	5.57	5.91	485	463	7.1	3.4	60	30.43	0.45	0.24
47	5.48	4.26	502	458	2.4	16.3	60	28.60	0.42	0.21
48	4.40	4.26	497	453	15.8	13.7	60	35.55	0.52	0.25
49	4.72	5.21	532	503	17.3	18.5	60	31.12	0.46	0.27
50	4.90	5.08	547	642	17.8	18.7	60	15.63	0.23	nd

Table A2. Salinity data and ion concentrations associated with each trial. F_w = feed water; P_{pw} = product water.

	F _w	P _{pw}	P _{pw} , after 2 Years Storage	F _w	P _{pw}	P _{pw} , after 2 Years Storage	F _w , EC	P _{pw} , EC	F _w	P _{pw}	P _{pw} , after 2 Years Storage
Trial	Cl [−] g/L	Cl [−] g/L	Cl [−] g/L	Na ⁺ g/L	Na ⁺ g/L	Na ⁺ g/L	mScm ^{−1}	mScm ^{−1}	NaCl, g/L	NaCl, g/L	NaCl, g/L
1	0.88	0.72	0.57	0.43	0.21	0.16	2.16	1.90	1.31	0.93	0.73
2	1.31	1.00	0.71	0.68	0.50	0.16	3.07	2.58	1.99	1.50	0.87
3	1.95	1.36	0.66	1.09	0.77	0.22	4.53	3.46	3.04	2.13	0.88
4	1.00	0.73	0.65	0.45	0.22	0.57	2.21	2.00	1.45	0.95	1.22
5	1.53	1.19	0.27	0.82	0.68	0.59	3.81	3.10	2.35	1.87	0.86
6	1.81	0.92	0.77	0.95	0.50	0.63	3.93	2.42	2.76	1.42	1.40
7	1.07	0.69		0.54	0.21		2.49	1.71	1.61	0.90	
8	0.86	0.53		0.45	0.17		2.07	1.23	1.31	0.70	
9	1.53	0.79	0.60	1.00	0.65	0.53	3.06	1.71	2.53	1.44	1.13
10	1.35	0.75	0.06	0.55	0.37	0.65	2.87	1.77	1.90	1.12	0.71
11	1.55	0.83		0.83	0.51		3.16	1.89	2.38	1.34	
12	1.67	1.25	0.91	0.94	0.65	0.62	2.54	1.92	2.61	1.90	1.53
13	1.40	0.73	0.22	0.79	0.40	0.85	2.02	1.19	2.19	1.13	1.07
14	0.56	0.35	0.47	0.44	0.24	0.35	0.88	0.63	1.00	0.59	0.82
15	1.19	0.94	0.55	0.63	0.50	0.63	2.03	1.58	1.82	1.44	1.18

Table A2. Cont.

	F _w	P _{pw}	P _{pw} , after 2 Years Storage	F _w	P _{pw}	P _{pw} , after 2 Years Storage	F _w , EC	P _{pw} , EC	F _w	P _{pw}	P _{pw} , after 2 Years Storage
Trial	Cl [−] g/L	Cl [−] g/L	Cl [−] g/L	Na ⁺ g/L	Na ⁺ g/L	Na ⁺ g/L	mScm ^{−1}	mScm ^{−1}	NaCl, g/L	NaCl, g/L	NaCl, g/L
16	3.20	1.35	0.75	1.22	0.70	0.31	4.88	2.72	4.42	2.05	1.06
17	3.67	1.75	0.60	1.24	0.58	0.62	5.30	2.34	4.91	2.33	1.22
18	3.61	1.25	0.65	1.32	0.58	0.69	5.31	2.20	4.93	1.83	1.34
19	3.58	1.85	0.03	1.32	0.66	0.80	5.73	2.21	4.90	2.51	0.83
20	4.35	2.19	0.81	1.49	0.66	0.80	6.62	2.24	5.84	2.85	1.61
21	1.72	0.60	0.52	0.82	0.51	0.54	3.42	1.41	2.54	1.11	1.06
22	3.54	0.91	0.53	2.05	0.79	0.44	6.28	2.24	5.59	1.70	0.97
23	2.96	2.36	0.61	1.71	0.70	0.59	4.95	2.03	4.67	3.06	1.20
24	0.98	0.64		0.43	0.22		1.49	1.00	1.41	0.86	
25	0.77	0.67		0.32	0.21		1.22	0.84	1.09	0.88	
26	3.80	2.47	0.99	2.62	1.21	0.97	9.11	4.38	6.42	3.68	1.96
27	1.64	0.68	0.33	0.71	0.45	0.49	2.62	1.50	2.35	1.13	0.82
28	1.15	0.79	0.33	0.52	0.36	0.49	2.02	1.41	1.67	1.15	0.82
29	0.85	0.69		0.36	0.32		1.49	1.04	1.21	1.01	
30	1.32	0.85		0.61	0.40		1.77	1.13	1.93	1.25	
31	5.03	1.78	0.64	2.22	0.90	0.72	7.70	3.24	7.25	2.68	1.36
32	5.39	2.19	0.54	2.72	0.83	0.61	9.46	3.61	8.11	3.02	1.15
33	5.31	1.44	0.69	2.15	0.65	0.62	8.18	2.89	7.46	2.09	1.31
34	5.36	1.68	0.53	2.15	0.72	0.71	8.18	3.13	7.51	2.40	1.24
35	0.87	0.73	0.27	0.42	0.26	0.45	1.77	1.19	1.29	0.99	0.72
36	1.71	0.91	0.34	0.58	0.47	0.30	2.56	1.87	2.29	1.38	0.64
37	2.02	0.93	0.88	0.58	0.35	0.46	2.02	1.50	2.60	1.28	1.34
38	0.88	0.67	0.56	0.35	0.29	0.51	1.64	1.24	1.23	0.96	1.07
39	2.84	1.63	0.22	1.69	0.83	0.42	7.02	3.12	4.53	2.46	0.64
40	4.67	2.07	0.42	1.83	1.20	0.58	7.01	3.49	6.50	3.27	1.00
41	1.86	0.67	0.08	1.47	1.16	0.25	1.68	1.31	3.33	1.83	0.33
42	4.15	1.80	0.11	2.72	1.45	0.12	6.62	3.48	6.87	3.25	0.23
43	5.52	2.71	0.28	3.45	2.13	0.43	7.41	5.06	8.97	4.84	0.71
44	2.86	2.12		2.36	1.63		5.75	3.55	5.22	3.75	
45	1.60	1.04	0.91	0.73	0.33	0.38	1.82	1.41	2.33	1.37	1.29
46	3.92	2.35	0.70	1.27	1.27	0.49	4.61	3.74	5.19	3.62	1.19
47	5.63	5.37	0.53	2.50	2.31	0.33	6.93	6.30	8.13	7.68	0.86
48	1.80	1.57	0.30	0.36	0.20	0.45	1.72	1.48	2.16	1.77	0.75
49	2.87	1.67		1.23	0.54		3.66	2.16	4.10	2.21	
50	5.39	1.32		0.29	0.18		1.80	1.31	5.68	1.50	

Table A3. Desalination rate constant decline analysis, measured values of k_{insf} , p , and R^2 associated with ion removal. The values measured from a regression plot of k_{obsf} vs. reaction time (a (hours)). $k_{obsf} = (-\ln(C_{t=n}/C_{t=0}))/t$. $C_{t=0}$ = ion concentration at $t = 0$. $C_{t=n}$ = ion concentration at $t = n$. ($t = n$) = time spent in the reaction environment, seconds = $3600a$. Decline curve type = power function; exponential (exp) function, natural logarithmic function; linear function. Power relationship: $k_{obsf} = k_{insf}(a)^p$; linear relationship: $k_{obsf} = k_{insf}(a) + p$; logarithmic relationship: $k_{obsf} = k_{insf} \times \ln(a \cdot p)$ exponential relationship: $k_{obsf} = k_{insf} \times e^{(a \cdot p)}$.

Cl [−] Ions					Na ⁺ Ions			
Trial	k_{inst}	p	R^2	Type	k_{inst}	p	R^2	Type
1	0.000000810	−1.508474430	98.77%	Power	0.00000108	−0.95101822	95.77%	Power
2	0.000074210	−0.995270020	97.30%	Power	−0.00000544	0.00002276	97.90%	Log
3	0.000097090	−0.919136460	98.28%	Power	0.00007177	−0.84561688	97.52%	Power
4	0.000045530	−0.882850490	94.92%	Power	0.00005379	−0.73529325	90.94%	Power

Table A3. Cont.

Cl [−] Ions					Na ⁺ Ions			
Trial	k_{inst}	p	R^2	Type	k_{inst}	p	R^2	Type
5	0.000040590	−0.864238440	95.29%	Power	0.00002852	−0.79388562	84.86%	Power
6	−0.000001570	0.000036600	96.03%	Linear	−0.00002051	0.00006921	98.76%	Log
7	−0.000005660	0.000024060	95.62%	Log	−0.00000799	0.00003494	91.96%	Log
8	−0.000007800	0.000029710	96.24%	Log	−0.00001161	0.00004936	98.32%	Log
9	−0.000009150	0.000038320	96.60%	Log	0.00020484	−1.24428285	95.32%	Power
10	0.000063540	−0.729027840	96.83%	Power	0.00003571	−0.77617141	77.44%	Power
11	−0.000008610	0.000034700	94.78%	Log	−0.00000587	0.00002590	80.95%	Log
12	−0.000004500	0.000019390	95.55%	Log	−0.00000256	0.00001246	92.25%	Log
13	0.000072520	−0.718988630	98.03%	Power	−0.00000872	0.00003541	97.58%	Log
14	−0.000008060	0.000030720	96.30%	Log	−0.00001436	0.00005180	97.55%	Log
15	−0.000001560	0.000008840	84.35%	Log	−0.00000182	0.00000921	71.07%	Log
16	−0.000004680	0.000023140	91.65%	Log	0.00004299	−0.66268792	76.81%	Power
17	−0.000005250	0.000026020	78.44%	Log	0.00000442	0.00002082	81.83%	Log
18	0.000036130	−0.461442230	90.19%	Power	0.00008015	−0.72064622	95.24%	Power
19	0.000047630	−0.570702040	80.65%	Power	0.00006918	−0.67556193	91.71%	Power
20	−0.000016540	0.000061080	98.44%	Log	0.98437059	0.00002882	90.45%	Linear
21	−0.000005910	0.000026320	44.15%	Log	−0.00000038	0.00001731	89.05%	Linear
22	−0.000006790	0.000029980	75.19%	Log	−0.00001174	0.00004927	98.22%	Log
23	−0.000008870	0.000037240	90.96%	Log	−0.00000856	0.00003673	94.73%	Log
24	0.000044180	−0.678686120	76.48%	Power	0.00002140	−0.04321600	85.40%	Exp
25	−0.000005740	0.000023100	74.60%	Log	−0.00000358	0.00001564	91.45%	Log
26	0.000005670	−0.011208300	40.98%	Exp	0.00001068	−0.01966159	85.11%	Exp
27	0.000073350	−0.800614600	90.64%	Power	−0.00000328	0.00001549	84.38%	Log
28	0.000010380	−0.037586380	85.18%	Exp	0.00005004	−0.82143232	89.53%	Power
29	−0.000002410	0.000009170	74.19%	Log	−0.00000168	0.00000527	58.43%	Log
30	−0.000005370	0.000022850	93.01%	Log	−0.00000574	0.00002400	89.76%	Log
31	−0.000014470	0.000058060	92.46%	Log	−0.00000902	0.00003835	97.75%	Log
32	−0.000009910	0.000041890	86.77%	Log	−0.00000816	0.00003800	94.00%	Log
33	−0.000006690	0.000033530	94.62%	Log	−0.00000671	0.00003356	91.82%	Log
34	−0.000003230	0.000022090	66.75%	Log	−0.00000767	0.00003584	95.11%	Log
35	−0.000002890	0.000011060	71.92%	Log	0.00002031	−0.45352578	76.38%	Power
36	−0.000001400	0.000010400	28.35%	Log	−0.00000166	0.00000878	37.38%	Log
37	−0.000007310	0.000032590	90.22%	Log	−0.00000524	0.00002219	64.41%	Log
38	0.000102540	−1.113570140	97.57%	Power	−0.00000247	0.00001213	52.54%	Log
39	−0.000019610	0.000069390	75.14%	Log	−0.00000634	0.00002824	94.29%	Log
40	0.000018310	−0.229992450	46.14%	Power	−0.00000015	0.00000964	8.67%	Linear
41	−0.000000400	0.000021190	93.82%	Linear	−0.00000006	0.00000636	7.50%	Linear
42	0.000002720	0.000000020	58.75%	Log	0.00001162	−0.01262812	34.21%	Exp
43	−0.000002110	0.000013990	55.08%	Log	−0.00000243	0.00001126	49.15%	Log
44	−0.000001680	0.000008420	67.42%	Log	0.00009117	−0.91433379	86.07%	Power
45	0.000005280	−0.006283530	10.39%	Exp	0.00001331	−0.01573847	15.46%	Exp
46	−0.000006450	0.000024400	80.66%	Log	−0.00000492	0.00001875	48.57%	Log
47	−0.000001250	0.000004760	76.29%	Log	−0.00000290	0.00001146	67.36%	Log
48	−0.000002140	0.000008710	68.31%	Log	−0.00000191	0.00001422	64.55%	Log
49	−0.000000570	0.000023390	73.67%	Linear	−0.00000030	0.00001534	78.01%	Linear
50	−0.000025310	0.000093570	95.73%	Log	−0.00002396	0.00008871	97.22%	Log

Table A4. Indicative relationship between crop type, irrigation water salinity, and crop yield relative to crop yield when irrigated with freshwater.

Crop	Constants			Irrigation Water Salinity, g L ⁻¹						
	<i>a</i>	<i>b</i>	<i>c</i>	1	2	3	4	5	7	9
Almond, Plum	0.7284	0.1337	0.3	18.7%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Apricot	0.9052	0.1748	0.3	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Avocado, Blackberry, Boysenberry	0.8898	0.1687	0.3	1.2%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Barley	0.1000	0.4000	0.3	100.0%	100.0%	100.0%	88.0%	75.0%	49.0%	23.0%
Beans	0.726	0.0855	0.3	14.2%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Beets	0.3632	0.1828	0.3	71.1%	23.8%	0.0%	0.0%	0.0%	0.0%	0.0%
Broadbean	0.3840	0.0761	0.3	57.7%	7.8%	0.0%	0.0%	0.0%	0.0%	0.0%
Broccoli	0.3740	0.1321	0.3	64.6%	16.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Cabbage	0.3912	0.0890	0.3	58.0%	7.2%	0.0%	0.0%	0.0%	0.0%	0.0%
Cantaloupe	0.2904	0.0806	0.3	70.3%	32.6%	0.0%	0.0%	0.0%	0.0%	0.0%
Carrot	0.5704	0.0731	0.3	33.2%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Cotton	0.1042	0.4046	0.3	100.0%	100.0%	99.8%	86.3%	72.7%	45.6%	18.5%
Corn	0.4808	0.1023	0.3	47.7%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Cowpea	0.5548	0.0897	0.3	36.8%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Cucumber	0.5344	0.1691	0.3	47.4%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Date Palm	0.1428	0.0707	0.3	88.5%	69.9%	51.4%	32.8%	14.3%	0.0%	0.0%
Fig, Olive, Pomegranate	0.3532	0.1187	0.3	66.0%	20.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Flax	0.4808	0.1023	0.3	47.7%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Grape	0.3804	0.0699	0.3	57.5%	8.1%	0.0%	0.0%	0.0%	0.0%	0.0%
Grapefruit, Orange, Lemon, Apple, Pear, Walnut	0.6452	0.1457	0.3	30.7%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Groundnut	1.2076	0.4853	0.3	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Lettuce	0.5192	0.0851	0.3	41.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Onion	0.6352	0.0944	0.3	26.9%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Peach	0.8244	0.1716	0.3	10.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Pepper	0.5704	0.1088	0.3	36.7%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Potato	0.4808	0.1023	0.3	47.7%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Radish	0.5140	0.0759	0.3	40.8%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Raspberry	0.8856	0.1073	0.3	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Rice	0.4696	0.1743	0.3	56.4%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Safflower	0.4344	0.2874	0.3	72.3%	15.8%	0.0%	0.0%	0.0%	0.0%	0.0%
Sesbania	0.2816	0.0812	0.3	71.5%	34.9%	0.0%	0.0%	0.0%	0.0%	0.0%
Soybean	0.7984	0.4977	0.3	46.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Sorghum	0.2820	0.1342	0.3	76.8%	40.1%	3.4%	0.0%	0.0%	0.0%	0.0%
Spinach	0.3076	0.0779	0.3	67.8%	27.8%	0.0%	0.0%	0.0%	0.0%	0.0%
Strawberry	1.3370	0.1693	0.3	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Sugar Beet	0.1180	0.4046	0.3	100.0%	100.0%	94.4%	79.1%	63.8%	33.1%	2.4%
Sweet Corn	0.4808	0.1023	0.3	47.7%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Sweet Potato	0.4448	0.0842	0.3	50.6%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Tomato	0.3992	0.1254	0.3	60.6%	8.7%	0.0%	0.0%	0.0%	0.0%	0.0%
Wheat	0.1428	0.4286	0.3	100.0%	100.0%	87.2%	68.6%	50.0%	12.9%	0.0%
Alfalfa	0.2968	0.0753	0.3	68.9%	30.4%	0.0%	0.0%	0.0%	0.0%	0.0%
Barley (Hay)	0.0696	0.2143	0.3	100.0%	100.0%	94.3%	85.2%	76.2%	58.1%	40.0%
Bermuda Grass	0.2568	0.2219	0.3	88.8%	55.4%	22.0%	0.0%	0.0%	0.0%	0.0%
Clover, berseem	0.7680	0.2201	0.3	22.2%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Clover, alsike, ladino, red, strawberry	0.4696	0.0863	0.3	47.6%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Corn (forage)	0.2384	0.0803	0.3	77.0%	46.0%	15.1%	0.0%	0.0%	0.0%	0.0%
Crested Wheat Grass	0.1600	0.0703	0.3	86.2%	65.4%	44.6%	23.8%	3.0%	0.0%	0.0%
Harding Grass	0.2988	0.1698	0.3	78.1%	39.3%	0.4%	0.0%	0.0%	0.0%	0.0%
Lovegrass, Meadow Foxtail	0.3332	0.0834	0.3	65.0%	21.7%	0.0%	0.0%	0.0%	0.0%	0.0%
Orchard Grass	0.2968	0.0753	0.3	68.9%	30.4%	0.0%	0.0%	0.0%	0.0%	0.0%

Table A4. Cont.

Crop	Constants			Irrigation Water Salinity, g L ⁻¹						
	<i>a</i>	<i>b</i>	<i>c</i>	1	2	3	4	5	7	9
Perennial Rye Grass	0.2984	0.2074	0.3	81.9%	43.2%	4.4%	0.0%	0.0%	0.0%	0.0%
Sudan Grass	0.1724	0.0602	0.3	83.6%	61.2%	38.8%	16.4%	0.0%	0.0%	0.0%
Tall Fescue	0.2096	0.1011	0.3	82.9%	55.6%	28.4%	1.1%	0.0%	0.0%	0.0%
Tall Wheat Grass	0.2748	0.2580	0.3	90.1%	54.4%	18.6%	0.0%	0.0%	0.0%	0.0%
Trefoil, big	0.7680	0.2201	0.3	22.2%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Trefoil, Birdsfoot narrow leaf	0.4000	0.2500	0.3	73.0%	21.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Vetch	0.4440	0.1679	0.3	59.1%	1.3%	0.0%	0.0%	0.0%	0.0%	0.0%
Wheat Grass	0.1664	0.1548	0.3	93.8%	72.2%	50.6%	29.0%	7.3%	0.0%	0.0%
Wild Rye, beardless	0.2384	0.0803	0.3	77.0%	46.0%	15.1%	0.0%	0.0%	0.0%	0.0%

Table A5. Expected crop yield, following partial desalination of irrigation water, when compared to irrigation with freshwater.

Crop	Constants			Salinity of Water Entering the Partial Desalination Reactor, g L ⁻¹						
	<i>a</i>	<i>b</i>	(1 + <i>c</i>)(1 − <i>e</i>)	1	2	3	4	5	7	9
Almond, Plum	0.72840	0.13370	0.78	56.6%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Apricot	0.90520	0.17480	0.78	46.9%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Avocado, Blackberry, Boysenberry	0.88980	0.16870	0.78	47.5%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Barley	0.10000	0.40000	0.78	100.0%	100.0%	100.0%	100.0%	100.0%	85.4%	69.8%
Beans	0.72600	0.08550	0.78	51.9%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Beets	0.36320	0.18280	0.78	90.0%	61.6%	33.3%	5.0%	0.0%	0.0%	0.0%
Broadbean	0.38400	0.07610	0.78	77.7%	47.7%	17.8%	0.0%	0.0%	0.0%	0.0%
Broccoli	0.37400	0.13210	0.78	84.0%	54.9%	25.7%	0.0%	0.0%	0.0%	0.0%
Cabbage	0.39120	0.08900	0.78	78.4%	47.9%	17.4%	0.0%	0.0%	0.0%	0.0%
Cantaloupe	0.29040	0.08060	0.78	85.4%	62.8%	40.1%	17.5%	0.0%	0.0%	0.0%
Carrot	0.57040	0.07310	0.78	62.8%	18.3%	0.0%	0.0%	0.0%	0.0%	0.0%
Cotton	0.10420	0.40460	0.78	100.0%	100.0%	100.0%	100.0%	99.8%	83.6%	67.3%
Corn	0.48080	0.10230	0.78	72.7%	35.2%	0.0%	0.0%	0.0%	0.0%	0.0%
Cowpea	0.55480	0.08970	0.78	65.7%	22.4%	0.0%	0.0%	0.0%	0.0%	0.0%
Cucumber	0.53440	0.16910	0.78	75.2%	33.5%	0.0%	0.0%	0.0%	0.0%	0.0%
Date Palm	0.14280	0.07070	0.78	95.9%	84.8%	73.7%	62.5%	51.4%	29.1%	6.8%
Fig, Olive, Pomegranate	0.35320	0.11870	0.78	84.3%	56.8%	29.2%	1.7%	0.0%	0.0%	0.0%
Flax	0.48080	0.10230	0.78	72.7%	35.2%	0.0%	0.0%	0.0%	0.0%	0.0%
Grape	0.38040	0.06990	0.78	77.3%	47.6%	18.0%	0.0%	0.0%	0.0%	0.0%
Grapefruit, Orange, Lemon, Apple, Pear, Walnut	0.64520	0.14570	0.78	64.2%	13.9%	0.0%	0.0%	0.0%	0.0%	0.0%
Groundnut	1.2076	0.4853	0.78	54.3%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Lettuce	0.5192	0.0851	0.78	68.0%	27.5%	0.0%	0.0%	0.0%	0.0%	0.0%
Onion	0.6352	0.0944	0.78	59.9%	10.3%	0.0%	0.0%	0.0%	0.0%	0.0%
Peach	0.8244	0.1716	0.78	52.9%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Pepper	0.5704	0.1088	0.78	66.4%	21.9%	0.0%	0.0%	0.0%	0.0%	0.0%
Potato	0.4808	0.1023	0.78	72.7%	35.2%	0.0%	0.0%	0.0%	0.0%	0.0%
Radish	0.5140	0.0759	0.78	67.5%	27.4%	0.0%	0.0%	0.0%	0.0%	0.0%
Raspberry	0.8856	0.1073	0.78	41.7%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Rice	0.4696	0.1743	0.78	80.8%	44.2%	7.5%	0.0%	0.0%	0.0%	0.0%
Safflower	0.4344	0.2874	0.78	94.9%	61.0%	27.1%	0.0%	0.0%	0.0%	0.0%
Sesbania	0.2816	0.0812	0.78	86.2%	64.2%	42.2%	20.3%	0.0%	0.0%	0.0%
Soybean	0.7984	0.4977	0.78	87.5%	25.2%	0.0%	0.0%	0.0%	0.0%	0.0%
Sorghum	0.2820	0.1342	0.78	91.4%	69.4%	47.4%	25.4%	3.4%	0.0%	0.0%
Spinach	0.3076	0.0779	0.78	83.8%	59.8%	35.8%	11.8%	0.0%	0.0%	0.0%
Strawberry	1.3370	0.1693	0.78	12.6%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Sugar Beet	0.1180	0.4046	0.78	100.0%	100.0%	100.0%	100.0%	94.4%	76.0%	57.6%

Table A5. Cont.

Crop	Constants			Salinity of Water Entering the Partial Desalination Reactor, g L ⁻¹						
	<i>a</i>	<i>b</i>	(1 + <i>c</i>)(1 − <i>e</i>)	1	2	3	4	5	7	9
Sweet Corn	0.4808	0.1023	0.78	72.7%	35.2%	0.0%	0.0%	0.0%	0.0%	0.0%
Sweet Potato	0.4448	0.0842	0.78	73.7%	39.0%	4.3%	0.0%	0.0%	0.0%	0.0%
Tomato	0.3992	0.1254	0.78	81.4%	50.3%	19.1%	0.0%	0.0%	0.0%	0.0%
Wheat	0.1428	0.4286	0.78	100.0%	100.0%	100.0%	98.3%	87.2%	64.9%	42.6%
Alfalfa	0.2968	0.0753	0.78	84.4%	61.2%	38.1%	14.9%	0.0%	0.0%	0.0%
Barley (Hay)	0.0696	0.2143	0.78	100.0%	100.0%	100.0%	99.7%	94.3%	83.4%	72.6%
Bermuda Grass	0.2568	0.2219	0.78	100.0%	82.1%	62.1%	42.1%	22.0%	0.0%	0.0%
Clover, berseem	0.7680	0.2201	0.78	62.1%	2.2%	0.0%	0.0%	0.0%	0.0%	0.0%
Clover, alsike, ladino, red, strawberry	0.4696	0.0863	0.78	72.0%	35.4%	0.0%	0.0%	0.0%	0.0%	0.0%
Corn (forage)	0.2384	0.0803	0.78	89.4%	70.8%	52.2%	33.6%	15.1%	0.0%	0.0%
Crested Wheat Grass	0.1600	0.0703	0.78	94.6%	82.1%	69.6%	57.1%	44.6%	19.7%	0.0%
Harding Grass	0.2988	0.1698	0.78	93.7%	70.4%	47.1%	23.8%	0.4%	0.0%	0.0%
Lovegrass, Meadow Foxtail	0.3332	0.0834	0.78	82.4%	56.4%	30.4%	4.4%	0.0%	0.0%	0.0%
Orchard Grass	0.2968	0.0753	0.78	84.4%	61.2%	38.1%	14.9%	0.0%	0.0%	0.0%
Perennial Rye Grass	0.2984	0.2074	0.78	97.5%	74.2%	50.9%	27.6%	4.4%	0.0%	0.0%
Sudan Grass	0.1724	0.0602	0.78	92.6%	79.1%	65.7%	52.2%	38.8%	11.9%	0.0%
Tall Fescue	0.2096	0.1011	0.78	93.8%	77.4%	61.1%	44.7%	28.4%	0.0%	0.0%
Tall Wheat Grass	0.2748	0.2580	0.78	100.0%	82.9%	61.5%	40.1%	18.6%	0.0%	0.0%
Trefoil, big	0.7680	0.2201	0.78	62.1%	2.2%	0.0%	0.0%	0.0%	0.0%	0.0%
Trefoil, Birdsfoot narrow leaf	0.4000	0.2500	0.78	93.8%	62.6%	31.4%	0.2%	0.0%	0.0%	0.0%
Vetch	0.4440	0.1679	0.78	82.2%	47.5%	12.9%	0.0%	0.0%	0.0%	0.0%
Wheat Grass	0.1664	0.1548	0.78	100.0%	89.5%	76.5%	63.6%	50.6%	24.6%	0.0%
Wild Rye, beardless	0.2384	0.0803	0.78	89.4%	70.8%	52.2%	33.6%	15.1%	0.0%	0.0%

Table A6. Proportion of expected crop yield with freshwater irrigation (Table A4), added by irrigating with partially desalinated water. Calculated as Results in Table A5—Results in Table A4.

Crop	Constants			Salinity of Water Entering the Partial Desalination Reactor, g L ⁻¹						
	<i>a</i>	<i>b</i>	(1 + <i>c</i>)(1 − <i>e</i>)	1	2	3	4	5	7	9
Almond, Plum	0.72840	0.13370	0.78	37.9%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Apricot	0.90520	0.17480	0.78	46.9%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Avocado, Blackberry, Boysenberry	0.88980	0.16870	0.78	46.3%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Barley	0.10000	0.40000	0.78	0.0%	0.0%	0.0%	12.0%	25.0%	36.4%	46.8%
Beans	0.72600	0.08550	0.78	37.8%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Beets	0.36320	0.18280	0.78	18.9%	37.8%	33.3%	5.0%	0.0%	0.0%	0.0%
Broadbean	0.38400	0.07610	0.78	20.0%	39.9%	17.8%	0.0%	0.0%	0.0%	0.0%
Broccoli	0.37400	0.13210	0.78	19.4%	38.9%	25.7%	0.0%	0.0%	0.0%	0.0%
Cabbage	0.39120	0.08900	0.78	20.3%	40.7%	17.4%	0.0%	0.0%	0.0%	0.0%
Cantaloupe	0.29040	0.08060	0.78	15.1%	30.2%	40.1%	17.5%	0.0%	0.0%	0.0%
Carrot	0.57040	0.07310	0.78	29.7%	18.3%	0.0%	0.0%	0.0%	0.0%	0.0%
Cotton	0.10420	0.40460	0.78	0.0%	0.0%	0.2%	13.7%	27.1%	37.9%	48.8%
Corn	0.48080	0.10230	0.78	25.0%	35.2%	0.0%	0.0%	0.0%	0.0%	0.0%
Cowpea	0.55480	0.08970	0.78	28.8%	22.4%	0.0%	0.0%	0.0%	0.0%	0.0%
Cucumber	0.53440	0.16910	0.78	27.8%	33.5%	0.0%	0.0%	0.0%	0.0%	0.0%
Date Palm	0.14280	0.07070	0.78	7.4%	14.9%	22.3%	29.7%	37.1%	29.1%	6.8%
Fig, Olive, Pomegranate	0.35320	0.11870	0.78	18.4%	36.7%	29.2%	1.7%	0.0%	0.0%	0.0%
Flax	0.48080	0.10230	0.78	25.0%	35.2%	0.0%	0.0%	0.0%	0.0%	0.0%
Grape	0.38040	0.06990	0.78	19.8%	39.6%	18.0%	0.0%	0.0%	0.0%	0.0%

Table A6. Cont.

9	Constants			Salinity of Water Entering the Partial Desalination Reactor, g L ⁻¹						
	<i>a</i>	<i>b</i>	(1 + <i>c</i>)(1 − <i>e</i>)	1	2	3	4	5	7	9
Grapefruit, Orange, Lemon, Apple, Pear, Walnut	0.64520	0.14570	0.78	33.6%	13.9%	0.0%	0.0%	0.0%	0.0%	0.0%
Groundnut	1.2076	0.4853	0.78	54.3%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Lettuce	0.5192	0.0851	0.78	27.0%	27.5%	0.0%	0.0%	0.0%	0.0%	0.0%
Onion	0.6352	0.0944	0.78	33.0%	10.3%	0.0%	0.0%	0.0%	0.0%	0.0%
Peach	0.8244	0.1716	0.78	42.9%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Pepper	0.5704	0.1088	0.78	29.7%	21.9%	0.0%	0.0%	0.0%	0.0%	0.0%
Potato	0.4808	0.1023	0.78	25.0%	35.2%	0.0%	0.0%	0.0%	0.0%	0.0%
Radish	0.5140	0.0759	0.78	26.7%	27.4%	0.0%	0.0%	0.0%	0.0%	0.0%
Raspberry	0.8856	0.1073	0.78	41.7%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Rice	0.4696	0.1743	0.78	24.4%	44.2%	7.5%	0.0%	0.0%	0.0%	0.0%
Safflower	0.4344	0.2874	0.78	22.6%	45.2%	27.1%	0.0%	0.0%	0.0%	0.0%
Sesbania	0.2816	0.0812	0.78	14.6%	29.3%	42.2%	20.3%	0.0%	0.0%	0.0%
Soybean	0.7984	0.4977	0.78	41.5%	25.2%	0.0%	0.0%	0.0%	0.0%	0.0%
Sorghum	0.2820	0.1342	0.78	14.7%	29.3%	44.0%	25.4%	3.4%	0.0%	0.0%
Spinach	0.3076	0.0779	0.78	16.0%	32.0%	35.8%	11.8%	0.0%	0.0%	0.0%
Strawberry	1.3370	0.1693	0.78	12.6%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Sugar Beet	0.1180	0.4046	0.78	0.0%	0.0%	5.6%	20.9%	30.7%	43.0%	55.2%
Sweet Corn	0.4808	0.1023	0.78	25.0%	35.2%	0.0%	0.0%	0.0%	0.0%	0.0%
Sweet Potato	0.4448	0.0842	0.78	23.1%	39.0%	4.3%	0.0%	0.0%	0.0%	0.0%
Tomato	0.3992	0.1254	0.78	20.8%	41.5%	19.1%	0.0%	0.0%	0.0%	0.0%
Wheat	0.1428	0.4286	0.78	0.0%	0.0%	12.8%	29.7%	37.1%	52.0%	42.6%
Alfalfa	0.2968	0.0753	0.78	15.4%	30.9%	38.1%	14.9%	0.0%	0.0%	0.0%
Barley (Hay)	0.0696	0.2143	0.78	0.0%	0.0%	5.7%	14.5%	18.1%	25.3%	32.6%
Bermuda Grass	0.2568	0.2219	0.78	11.2%	26.7%	40.1%	42.1%	22.0%	0.0%	0.0%
Clover, berseem	0.7680	0.2201	0.78	39.9%	2.2%	0.0%	0.0%	0.0%	0.0%	0.0%
Clover, alsike, ladino, red, strawberry	0.4696	0.0863	0.78	24.4%	35.4%	0.0%	0.0%	0.0%	0.0%	0.0%
Corn (forage)	0.2384	0.0803	0.78	12.4%	24.8%	37.2%	33.6%	15.1%	0.0%	0.0%
Crested Wheat Grass	0.1600	0.0703	0.78	8.3%	16.6%	25.0%	33.3%	41.6%	19.7%	0.0%
Harding Grass	0.2988	0.1698	0.78	15.5%	31.1%	46.6%	23.8%	0.4%	0.0%	0.0%
Lovegrass, Meadow Foxtail	0.3332	0.0834	0.78	17.3%	34.7%	30.4%	4.4%	0.0%	0.0%	0.0%
Orchard Grass	0.2968	0.0753	0.78	15.4%	30.9%	38.1%	14.9%	0.0%	0.0%	0.0%
Perennial Rye Grass	0.2984	0.2074	0.78	15.5%	31.0%	46.6%	27.6%	4.4%	0.0%	0.0%
Sudan Grass	0.1724	0.0602	0.78	9.0%	17.9%	26.9%	35.9%	38.8%	11.9%	0.0%
Tall Fescue	0.2096	0.1011	0.78	10.9%	21.8%	32.7%	43.6%	28.4%	0.0%	0.0%
Tall Wheat Grass	0.2748	0.2580	0.78	9.9%	28.6%	42.9%	40.1%	18.6%	0.0%	0.0%
Trefoil, big	0.7680	0.2201	0.78	39.9%	2.2%	0.0%	0.0%	0.0%	0.0%	0.0%
Trefoil, Birdsfoot narrow leaf	0.4000	0.2500	0.78	20.8%	41.6%	31.4%	0.2%	0.0%	0.0%	0.0%
Vetch	0.4440	0.1679	0.78	23.1%	46.2%	12.9%	0.0%	0.0%	0.0%	0.0%
Wheat Grass	0.1664	0.1548	0.78	6.2%	17.3%	26.0%	34.6%	43.3%	24.6%	0.0%
Wild Rye, beardless	0.2384	0.0803	0.78	12.4%	24.8%	37.2%	33.6%	15.1%	0.0%	0.0%

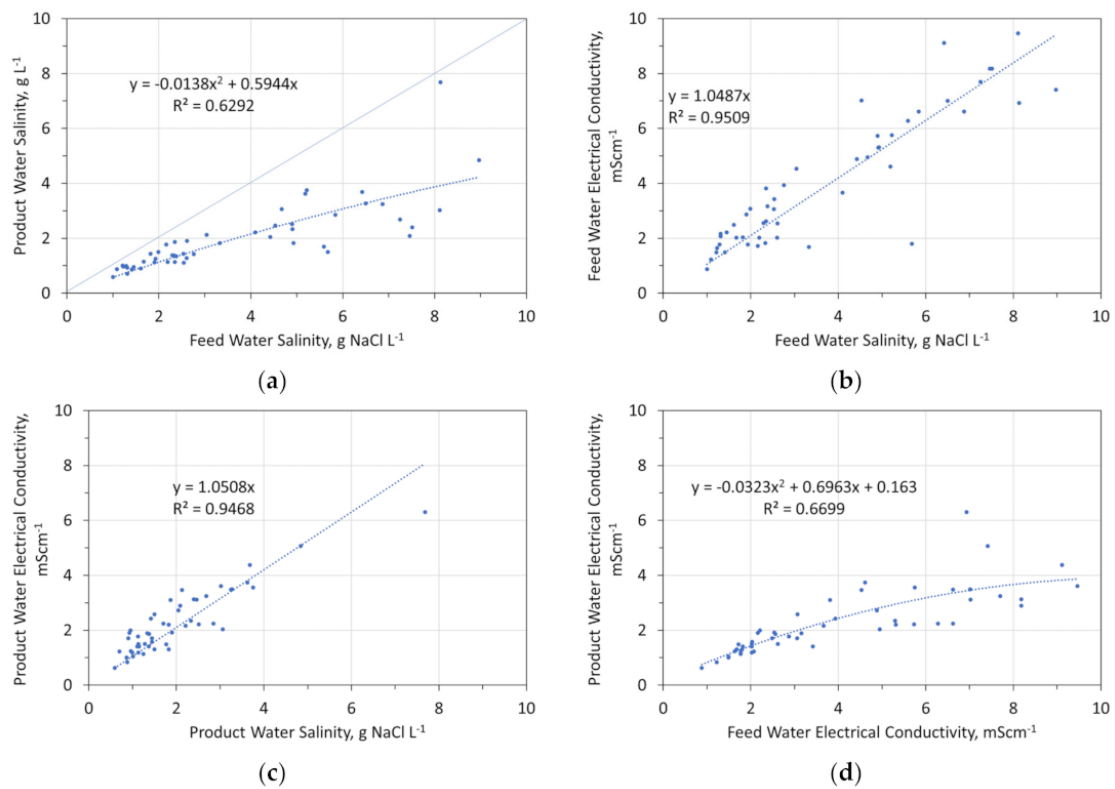


Figure A1. Feed water and product water salinity measurements. (a), Feed water salinity versus Product water salinity; (b), Feed water salinity versus Feed Water electrical conductivity; (c), Product water salinity versus Product water electrical conductivity; (d), Feed water electrical conductivity versus Product water electrical conductivity.

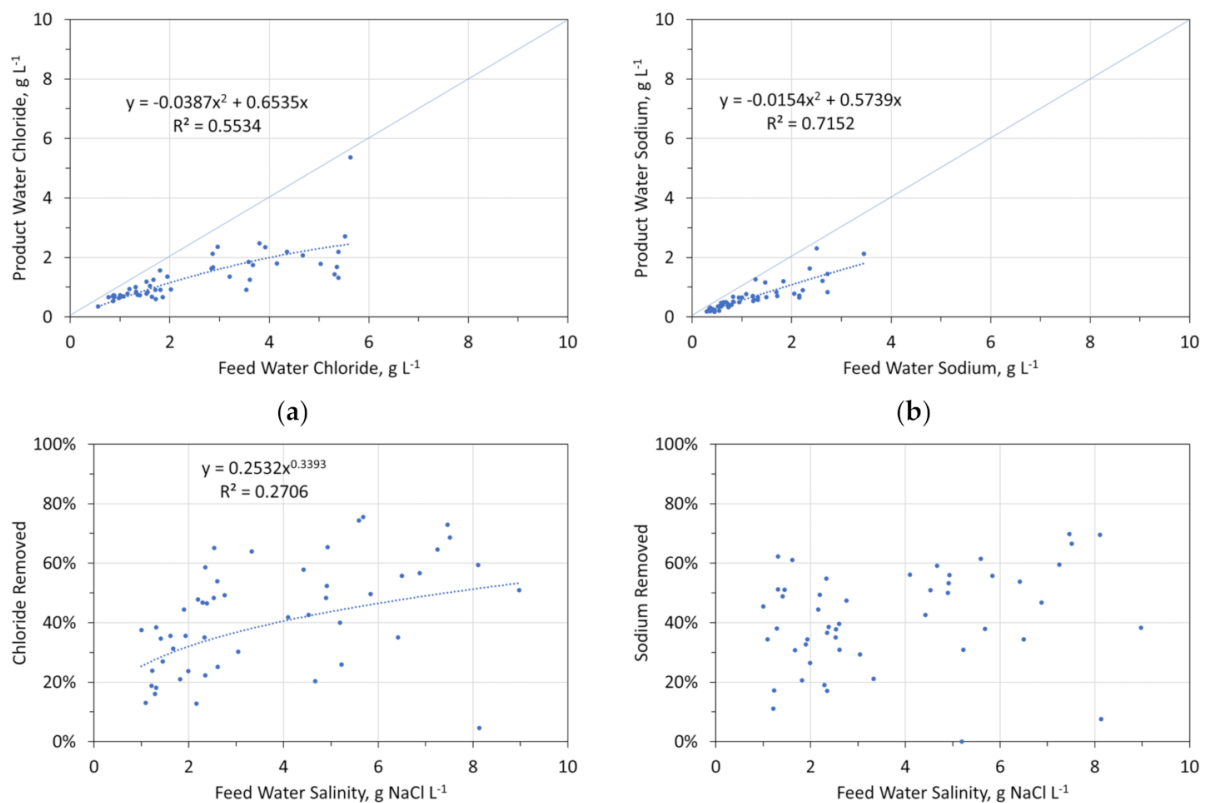


Figure A2. Cont.

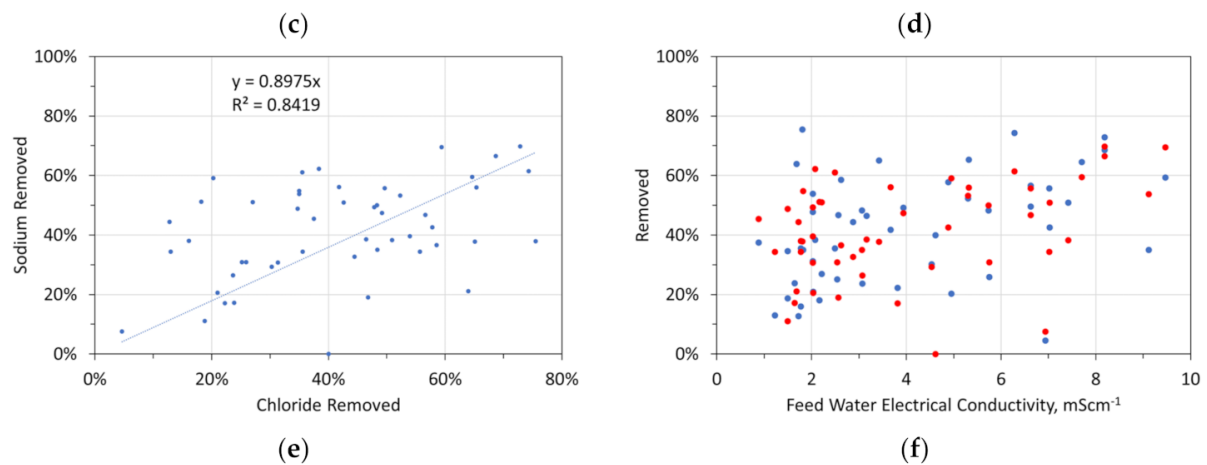


Figure A2. Ion removal. (a), Feed water chloride ion concentration versus product water chloride ion concentration; (b), Feed water sodium ion concentration versus product water sodium ion concentration; (c), Feed water salinity versus proportion of chloride ions in the feed water removed; (d), Feed water salinity versus proportion of sodium ions in the feed water removed; (e), Proportion of chloride ions in the feed water removed versus proportion of sodium ions in the feed water removed; (f), Feed water electrical conductivity versus the proportion of ions removed from the product water; Blue dots = chloride ions; red dots = sodium ions.

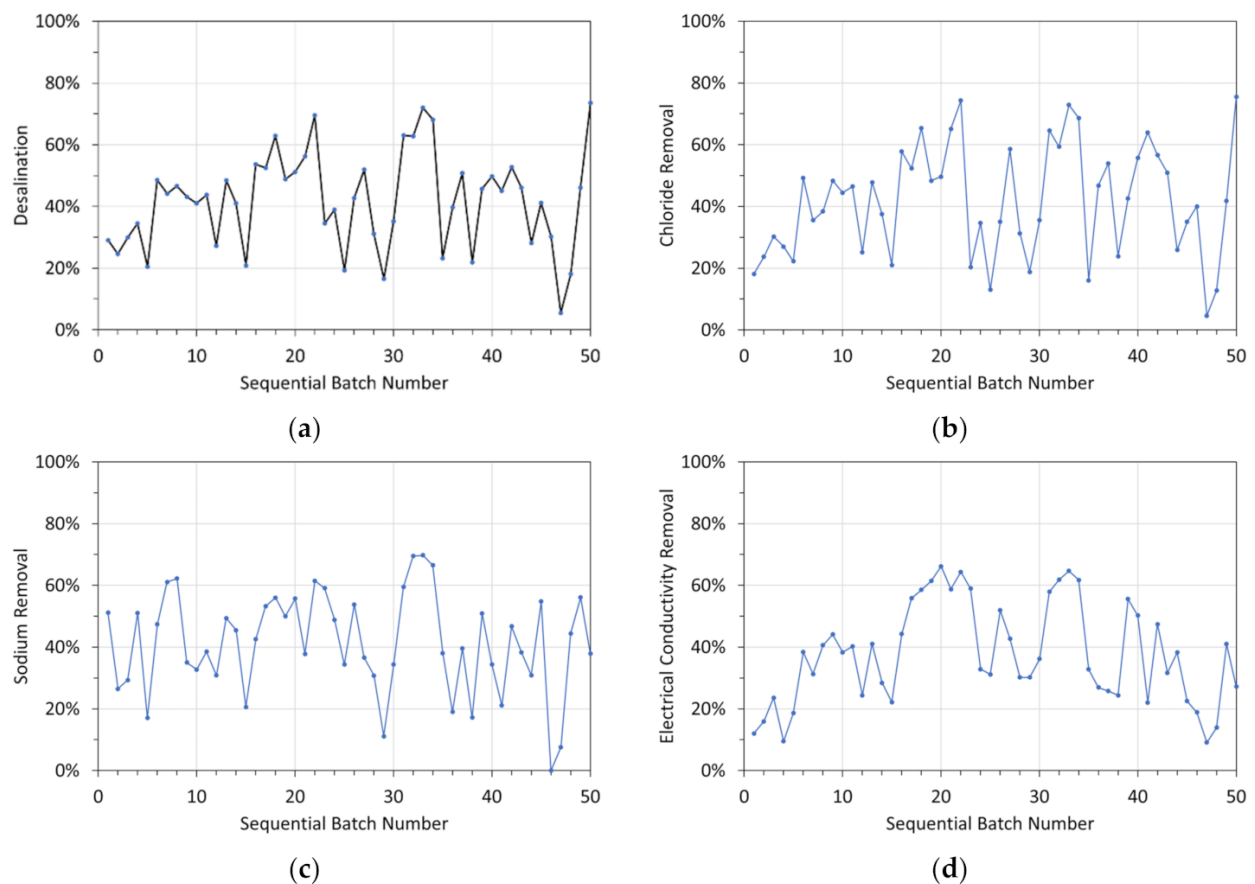


Figure A3. Desalination as a function of sequential batch number. (a), Sequential batch number versus desalination; (b), Sequential batch number versus chloride removed; (c), Sequential batch number versus sodium removed; (d), Sequential batch number versus electrical conductivity removed.

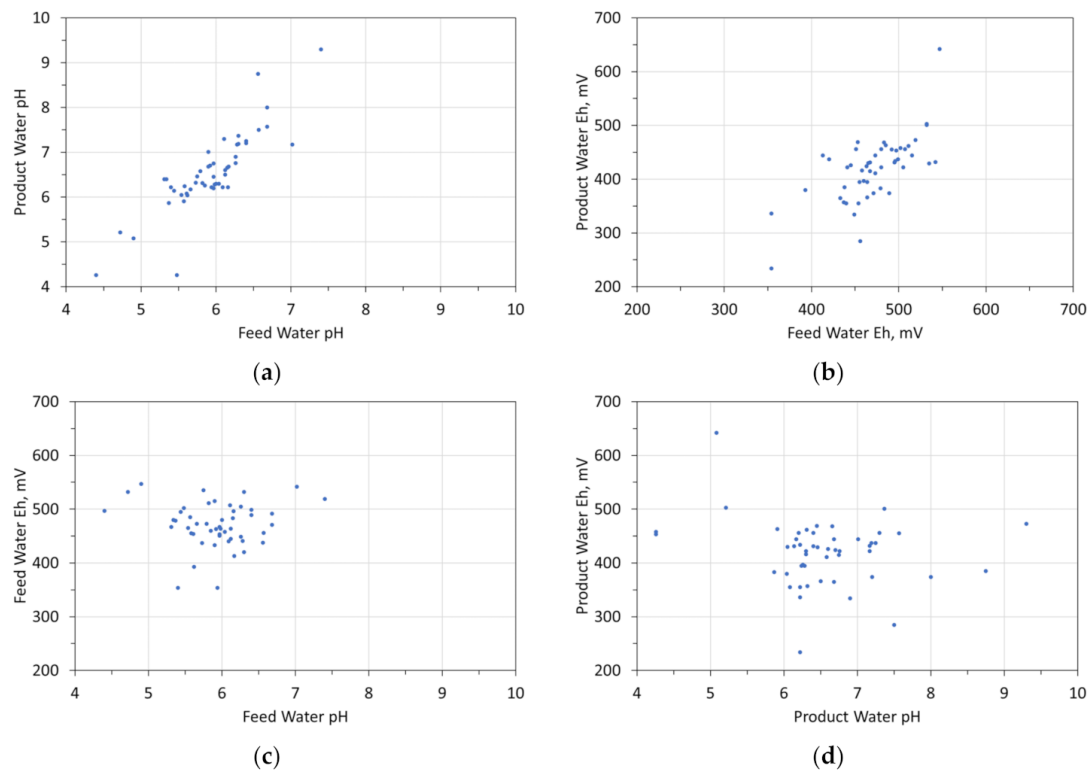


Figure A4. Redox parameters. (a), Feed water pH versus product water pH; (b), Feed water Eh versus product water Eh; (c), Feed water pH versus feed water Eh; (d), Product water pH versus product water Eh.

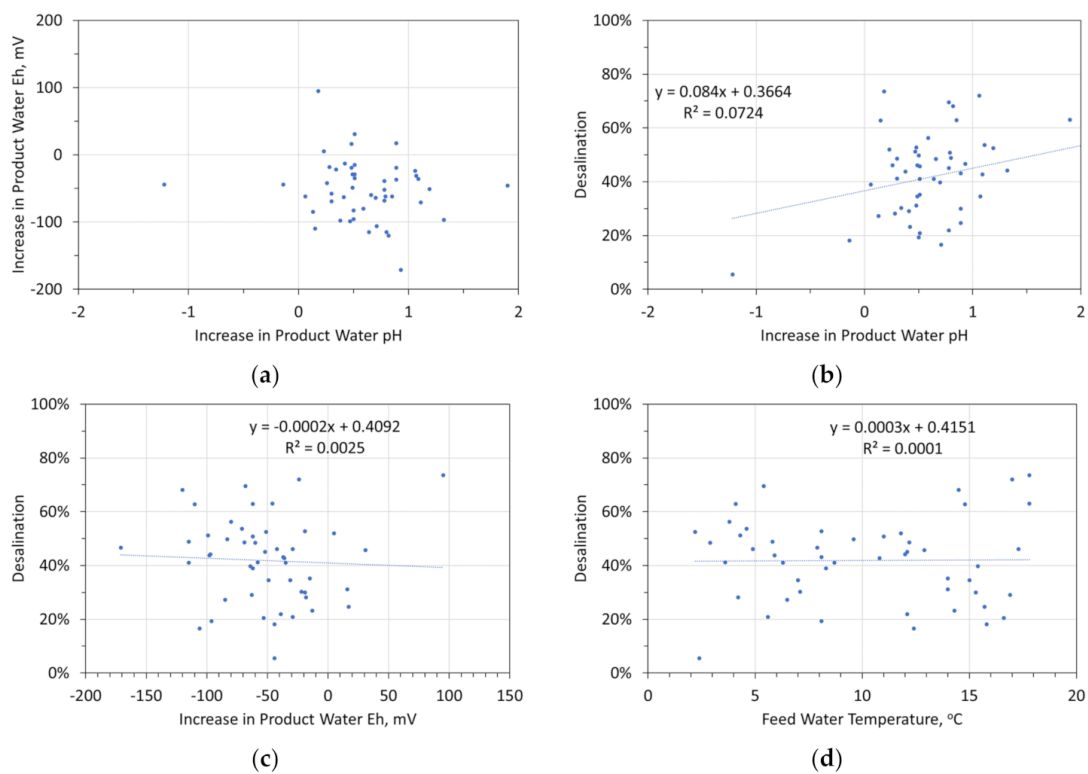


Figure A5. Change in redox parameters and their relationship to desalination. (a), increase in Product water pH versus Increase in product water Eh; (b), Increase in product water pH versus Desalination; (c), Increase in product water Eh versus desalination; (d), Temperature versus desalination.

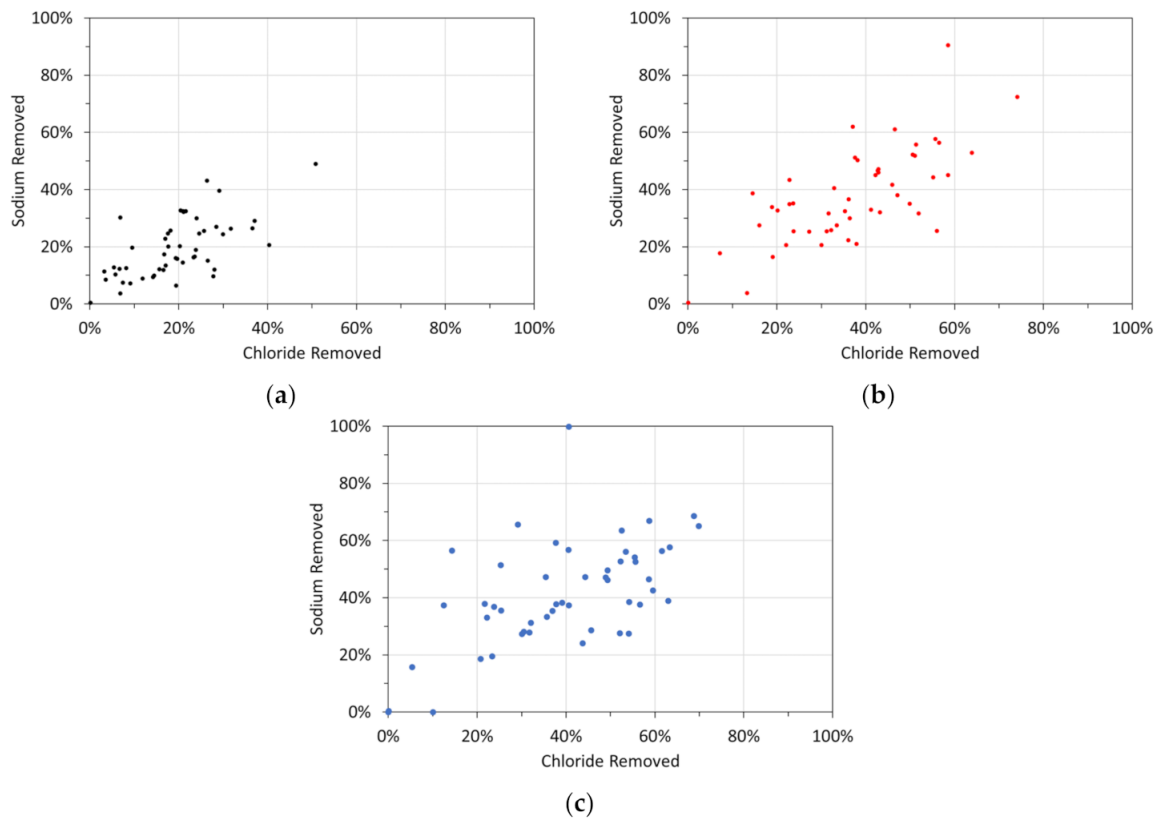


Figure A6. Relationship between ion removal and time spent in the reaction environment: (a) 3 h; (b) 15 h; (c) 30 h; the 3 h to 30 h results are determined from the data in Appendix A Table A3.

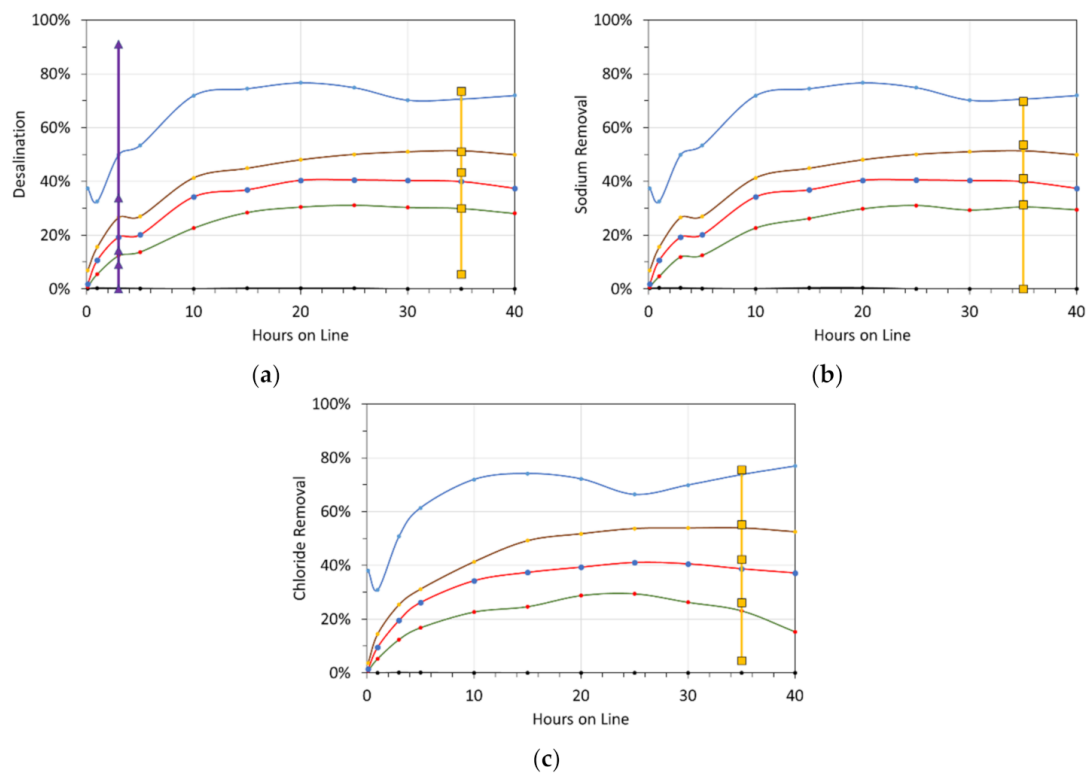


Figure A7. Probability distribution for ion removal versus hours on line. (a), Desalinations vs. hours on line; (b), Sodium removal versus hours on line; (c), Chloride removal versus hours on line. Black

line = minimum ion removal; green line is 25% probability of a lower removal; red line is 50% probability of a lower ion removal; brown line is a 75% probability of a lower ion removal; blue line is a 98% probability of a lower ion removal. Vertical orange line is this study. Vertical purple line is a separate reactor type [10], which terminated operation after 3 h.

References

- Wang, X. Managing Land Carrying Capacity: Key to Achieving Sustainable Production Systems for Food Security. *Land* **2022**, *11*, 484. [\[CrossRef\]](#)
- Rosa, L. Adapting agriculture to climate change via sustainable irrigation: Biophysical potentials and feedbacks. *Environ. Res. Lett.* **2022**, *17*, 063008. [\[CrossRef\]](#)
- Negacz, K.; Malek, Z.; Vos, A.; Vellinga, P. Saline soils worldwide: Identifying the most promising areas for saline agriculture. *J. Arid Environ.* **2022**, *203*, 104775. [\[CrossRef\]](#)
- Machado, R.M.A.; Serralheiro, R.P. Soil Salinity: Effect on Vegetable Crop Growth. Management Practices to Prevent and Mitigate Soil Salinization. *Horticulturae* **2017**, *3*, 30. [\[CrossRef\]](#)
- Ayers, R.S.; Westcot, D.W. *Water Quality for Agriculture*; FAO Irrigation and Drainage Paper; Food and Agriculture Organization of the United Nations: Rome, Italy, 1985; Volume 29.
- Wei, C.; Li, F.; Yang, P.; Ren, S.; Wang, S.; Wang, Y.; Xu, Z.; Xu, Y.; Wei, R.; Zhang, Y. Effects of Irrigation Water Salinity on Soil Properties, N₂O Emission and Yield of Spring Maize under Mulched Drip Irrigation. *Water* **2019**, *11*, 1548. [\[CrossRef\]](#)
- Amer, R. Spatial Relationship between Irrigation Water Salinity, Waterlogging, and Cropland Degradation in the Arid and Semi-Arid Environments. *Remote Sens.* **2021**, *13*, 1047. [\[CrossRef\]](#)
- Slater, Y.; Reznik, A.; Finkelshtain, I.; Kan, I. Blending Irrigation Water Sources with Different Salinities and the Economic Damage of Salinity: The Case of Israel. *Water* **2022**, *14*, 917. [\[CrossRef\]](#)
- Silber, A.; Israeli, Y.; Elingold, I.; Levi, M.; Levkovitch, I.; Russo, D.; Assouline, S. Irrigation with desalinated water: A step toward increasing water saving and crop yields. *Water Resour. Res.* **2015**, *51*, 450–464. [\[CrossRef\]](#)
- Antia, D.D.J. Provision of Desalinated Irrigation Water by the Desalination of Groundwater Abstracted from a Saline Aquifer. *Hydrology* **2022**, *9*, 128. [\[CrossRef\]](#)
- Antia, D.D.J. Water Treatment and Desalination Using the Eco-materials n-Fe⁰ (ZVI), n-Fe₃O₄, n-Fe_xO_yH_z[mH₂O], and n-Fe_x[Cation]_nO_yH_z[Anion]_m [rH₂O]. In *Handbook of Nanomaterials and Nanocomposites for Energy and Environmental Applications*, 1st ed.; Kharisova, O.V., Torres-Martínez, L.M., Kharisov, B.I., Eds.; Springer: Berlin/Heidelberg, Germany, 2021; pp. 3159–3242.
- Terreni, J.; Trottmann, M.; Franken, T.; Heel, A.; Borgschulte, A. Sorption-Enhanced Methanol Synthesis. *Energy Technol.* **2019**, *7*, 1801093. [\[CrossRef\]](#)
- Alpay, E.; Chatsiriwech, D.; Kershenbaum, L.S.; Hull, C.P.; Kirkby, N.F. Combined reaction and separation in pressure swing processes. *Chem. Eng. Sci.* **1994**, *49*, 5845–5864. [\[CrossRef\]](#)
- Alpay, E.; Kenney, C.N.; Scott, D.M. Simulation of rapid pressure swing adsorption and reaction processes. *Chem. Eng. Sci.* **1993**, *48*, 3173–3186. [\[CrossRef\]](#)
- Antia, D.D.J. Desalination of Water Using ZVI (Fe⁰). *Water* **2015**, *7*, 3671–3831. [\[CrossRef\]](#)
- Antia, D.D.J. ZVI (Fe⁰) desalination: Catalytic partial desalination of saline aquifers. *Appl. Water Sci.* **2018**, *8*, 71. [\[CrossRef\]](#)
- Lai, B.; Chen, Z.; Zhou, Y.; Yang, P.; Wang, J.; Chen, Z. Removal of high concentration p-nitrophenol in aqueous solution by zero valent iron with ultrasonic irradiation (US-ZVI). *J. Hazard. Mater.* **2013**, *250*, 220–228. [\[CrossRef\]](#) [\[PubMed\]](#)
- Schwarz, H.A. Some Applications of Time-Dependent Rate Constant Theory to Radiation Chemistry. *J. Chem. Phys.* **1971**, *55*, 3650–3657. [\[CrossRef\]](#)
- Nosrati, K.; Movahedirad, S.; Amin, M.; SobatiAli, S.; Sarbanha, A. Experimental study on the pressure wave attenuation across gas-solid fluidized bed by single bubble injection. *Powder Technol.* **2017**, *305*, 620–624. [\[CrossRef\]](#)
- Huang, F.; Takahashi, M.; Guo, L. Pressure wave propagation in air-water bubbly and slug flow. *Prog. Nucl. Energy* **2005**, *47*, 648–655. [\[CrossRef\]](#)
- Lide, D.R. *CRC Handbook of Chemistry and Physics*, 89th ed.; CRC Press: Boca Raton, FL, USA, 2008; ISBN 13:978-1-4200-6679-1.
- Dimeski, G.; Badrick, T.; St John, A. Ion selective electrodes (ISEs) and interferences—A review. *Clin. Chim. Acta* **2010**, *411*, 309–317. [\[CrossRef\]](#)
- Deyhimi, F. A method for the determination of potentiometric selectivity coefficients of ion selective electrodes in the presence of several interfering ions. *Talanta* **1999**, *50*, 1129–1134. [\[CrossRef\]](#)
- Liu, T.; Wang, Z.L.; Sun, Y. Manipulating the morphology of nanoscale zero-valent iron on pumice for removal of heavy metals from wastewater. *Chem. Eng. J.* **2015**, *263*, 55–61. [\[CrossRef\]](#)
- Shu, Y.; Ji, B.; Cui, B.; Shi, Y.; Wang, J.; Hu, M.; Luo, S.; Guo, D. Almond Shell-Derived, Biochar-Supported, Nano-Zero-Valent Iron Composite for Aqueous Hexavalent Chromium Removal: Performance and Mechanisms. *Nanomaterials* **2020**, *10*, 198. [\[CrossRef\]](#)
- Hao, D.; Chen, Y.; Zhang, Y.; You, N. Nanocomposites of zero-valent iron@biochar derived from agricultural wastes for adsorptive removal of tetracyclines. *Chemosphere* **2021**, *284*, 131342. [\[CrossRef\]](#) [\[PubMed\]](#)
- Zhang, Q.; Wang, Y.; Wang, Z.; Zhang, Z.; Wang, X.; Yang, Z. Active biochar support nano zero-valent iron for efficient removal of U (VI) from sewage water. *J. Alloys Compd.* **2021**, *852*, 156993. [\[CrossRef\]](#)

-
28. Lin, J.; Sun, M.; Liu, X.; Chen, Z. Functional kaolin supported nanoscale zero-valent iron as a Fenton-like catalyst for the degradation of Direct Black G. *Chemosphere* **2017**, *184*, 664–672. [[CrossRef](#)] [[PubMed](#)]
 29. Cheng, I.F.; Muftikian, R.; Fernando, Q.; Korte, N. Reduction of nitrate to ammonia by zero-valent iron. *Chemosphere* **1997**, *35*, 2689–2695. [[CrossRef](#)]
 30. Park, M.H.; Jeong, S.; Lee, G.; Park, H.; Kim, J.Y. Removal of aqueous-phase Pb (II), Cd (II), As (III), and As (V) by nanoscale zero-valent iron supported on exhausted coffee grounds. *Waste Manag.* **2019**, *92*, 49–58. [[CrossRef](#)]
 31. Schober, P.; Boer, C.; Schwarte, L.A. Correlation Coefficients: Appropriate Use and Interpretation. *Anesth. Analg.* **2018**, *126*, 1763–1768. [[CrossRef](#)]
 32. Taylor, R. Interpretation of the Correlation Coefficient: A Basic Review. *J. Diagn. Med. Sonogr.* **1990**, *6*, 35–39. [[CrossRef](#)]
 33. Antia, D.D.J. Purification of Saline Water Using Desalination Pellets. *Water* **2022**, *14*, 2639. [[CrossRef](#)]
 34. Antia, D.D.J. Remediation of Saline Wastewater Producing a Fuel Gas Containing Alkanes and Hydrogen Using Zero Valent Iron (Fe^0). *Water* **2022**, *14*, 1926. [[CrossRef](#)]
 35. Pourbaix, M. *Atlas of Electrochemical Equilibria in Aqueous Solutions*; NACE International: Houston, TX, USA, 1974; p. 644.