



Novel findings in desalination

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HIGHLIGHTS

- Variable salinity partial desalination with alginate demonstrated.
- 16.8% and 20.6% reduction in Na⁺ and Cl⁻ ions using ionotropic gelation.
- Density phase gel separation improved desalination over filtration.
- Gelling agent found to be recyclable.

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ABSTRACT

Ionotropic gelation and density phase separation of high affinity salt ions and alginate gels have been investigated for the functional application of salt water desalination. Partial desalination has been demonstrated using ion chromatography, electron microscopy and electron dispersive X-ray spectroscopy. Despite being only a partial process, these findings show a less complex energy expenditure process compared with conventional desalination by the utilisation of alginate as a complete replacement for filter technology and pumping. This research has identified how this desalination process functions at a range of salinities between full strength seawater and freshwater and is simultaneously able to recycle alginate as a potential replacement sustainable chemical vector to filtration technology.

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1. Introduction

The salinity of the sea ranges between 33 ppt and 38 ppt. The major contributing ionic composition of seawater has been measured as 19.353 g/kg (Cl), 10.781 g/kg (Na), 1.284 g/kg (Mg), 2.712 g/kg (S), 0.4176 g/kg (Ca), 0.399 g/kg (K), [19]. The oceans contain over 97% of global water, another 2% is locked away as ice with 1% estimated to be distributed between the atmospheric and hydrospheric cycles. Agriculture, industry and a rising global population are placing great pressure on the availability and distribution of water in some regions of the world. For example Los Angeles in California is the second biggest city in the USA, which imports the vast quantity of water it consumes. Freshwater from the Sacramento-San Joaquin Delta supplies 25 million people and has supported 450 miles of intensive agriculture in the central valley. Continued sustainability of such water provision and utilisation depends on a manmade network of flood engineering systems and irrigation infrastructure such as dams which have transformed and controlled water supplies. With weather patterns and climate change affecting conventional storage systems and distribution of freshwater

supplies, desalination offers both an ionic conversion process and supply solution to a significant technical challenge. Many arid nations such as Saudi Arabia depend on the energetic intensive approach of conventional desalination processes for their water provision.

The two common commercial desalination technologies used in arid climates are Reverse Osmosis (RO) and multi-stage flash distillation (MSF). Both technologies are energy intensive. MSF uses 4 kW h/m³, RO uses 6–8 kW h/m³ without energy recovery and 4–5 4 kW h/m³ with energy recovery [12]. Enhanced process efficiency combining ultra-filtration with two-pass reverse osmosis at 47% efficiency can achieve 3 kW/m³ [17]. Energy expenditure for RO is directly proportional to the salt concentration of the saline water being desalinated. The pressure required is about 70 bar for seawater desalination and from between 44.8 bar for 18 ppt to 82.7 bar for 45 ppt salinities, respectively [4]. The energetic expenditure and associated economic cost of desalination has resulted in its use being restricted to countries with access to energy, capital expenditure or financial investment. Desalination technologies use energy in the form of electricity, pressure or heat to separate seawater into freshwater and brine. Distillation technologies at elevated temperatures are susceptible to salt corrosion and require specialist materials to avoid limescale and salt deposition. Reverse Osmosis functions at ambient temperatures and elevated pressures (3–8 MPa) using specialist filters with a pore size of 0.0001–0.0006 μm that

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are able to filter monovalent, divalent ions, virus particles and bacteria. Reverse osmosis is the final stage of desalination which is preceded by micro, ultra and nanofiltration membrane technology.

Fouling of reverse osmosis membranes occurs by dissolved organic matter present in seawater as by-products of living organisms including bacteria, macroalgae and microalgae. Long chain carbohydrate polysaccharides gels or alginates are known to severely foul the specialist membranes used in reverse osmosis desalination plants [13]. This fouling limits the life of RO membranes to about 2 years, requiring stock replenishment and increased overhead costs over and above the energetic process of RO desalination. Prior research has investigated membrane technology, the functional chemical molecular groups on the surface of the membrane in close interaction with saltwater as it intercepts the membrane and the affinity for fouling alginates [23]. However, to date there has been no investigation of the ionic interaction of saltwater and alginates before and after filtration using a microfiltration membrane with a pore size in the region of between 0.5 and 5 μm . An increased pore sized membrane is advantageous in desalination technology due to a longer membrane lifecycle, lower or even gravity fed seawater pressure displacement, lower energy use and reduced capital and operational expenditure. The development of a low-energy desalination process could have profound implications for societal progress including the provision of freshwater to low-income communities. With detrimental implications for reduced sustainable supply of both fossil fuels and water in many regions of the world, this research advocates an alternative approach in desalination technology functioning via modifications to the pre-treated water at ambient temperatures and pressures rather than the membrane.

Alginates are a worldwide commercial commodity extracted from brown macroalgae. Alginate is the most abundant polysaccharide of brown seaweeds constituting 40% composition of cell walls [5]. Brown algae are classified as Phaeophyceae under phylum Chrysophyta. It is estimated that there are between 1500 and 2000 species of brown macroalgae [9]. World production of brown algae was 6,784,179 wet metric tons in 2010, mainly from four species in East Asian seas *Laminaria japonica*, *Undaria pinnatifida*, *Sargassum fusiforme* and *Phaeophyceae* [11]. In natural environments, alginates exist as calcium, potassium and sodium salts of alginic acid present in the cell wall of brown seaweeds [8]. Alginates are a biochemical group of linear unbranched polysaccharides derived from marine macroalgae which contain β -D-mannuronic acid and α -L-guluronic acid residues. The composition, sequence and molecular weight determine the physical and rheological properties of alginates. Over 100 species of macroalgae are presently used in food, medicine, fertiliser or for phycocolloids and chemicals. Seaweeds are mainly used in the human food industry where they are processed for texturing agents and stabilisers such as propylene glycol alginate (PGA). They also have usage in paper processing and textile industries. There exists variation in the quality of alginates from different seaweeds based on the ratio of guluronic to mannuronic acids. Chilean seaweeds have unique alginate hydrocolloid properties from *Lessonia* species for food and pharmaceutical applications. In the last decade there have been changes in procurement of alginates in the global market place as *Laminaria* and *Lessonia* species with high guluronic acid content produce the strongest gels for commercial applications [3]. Abundance of macroalgae species in temperate coastal regions is an attractive source of biomass for novel applications including energy sources from fermentation or anaerobic digestion. Allocation of such marine natural resources are of particular interest for local energy generation where terrestrial biofuel is unable to expand further due to high percentages of net primary productivity already being appropriated for human use, such as the North Atlantic coast of North America and Europe and the western seaboard of South America Hughes et al. [10]. The novel application of alginates for use in desalination would complement current developing interest and market application potential of biofuel and food technologies.

Table 3.1

Major ions (mg/L).

Major	Seawater			Major ions (mg/L)		
	Na ⁺	Cl ⁻	Ca ²⁺	Na ⁺	Cl ⁻	Ca ²⁺
SW/FW	7767	15,828	329	22	0	37
SAG/FAG	6916	20,162	270	96	0	12
SBG/FBG	6269	14,417	528	66	420	305
SF/FF	6466	12,568	557	72	1405	305
Mass (g) filtered material	8,418			2,249		

2. Material & methods

2.1. Full salinity and freshwater desalination comparison

A multifilament mesh polypropylene 1 μm rated 25 litre capacity filter bag approximately 18 by 80 cm when flat packed (Lenntech BV) was used as the experimental microfilter. 18.2 M Ω de-ionised water was used for freshwater (Merck Millipore) and 33 g/L aquarium salt (Instant Ocean®) was added to de-ionised water to make artificial seawater. Ion chromatography (ICS900 Dionex Thermo Fisher Scientific) analysed anions and cations for both seawater and freshwater at various stages of the desalination process. Energy Dispersive X-ray Electron microscopy (Oxford instruments/AZtecEnergy analysis software) was used to detect and quantify filtered material from both freshwater and seawater samples and secondary recycled alginate.

1% (w/v) refined sodium alginate powder derived from brown macroalgae with a medium viscosity composed of polyuronic, glucuronic and mannuronic acid residues (Sigma-Aldrich®) was dissolved into de-ionised water in a 2 litre erlenmeyer flask and stirred with a magnetic stirrer for 12 h until completely dissolved. 4 L of artificial seawater and 4 L of de-ionised water were prepared and stored in equal volumes in duplicate 3 \times 2 litre erlenmeyer flasks. 10% (v/v) of a 1% (w/v) sodium alginate solution was mixed thoroughly into flasks containing both seawater and freshwater. During continued mixing 10% (v/v) of a 1% CaCl₂ (w/v) solution (Sigma-Aldrich®) was blended into the solution inducing a mild gelation in both of the seawater and freshwater. Solutions were poured into the filter bags. A sample of the filtrate was retained for analysis, the remainder was disposed. Filtered material was extracted from filter bags and dried at 60 °C for 48 h to avoid heat degradation and analysed by electron microscopy and gravimetrically. 5 g of the dry filtered seawater material and 2 g of the dry filtered freshwater material was re-suspended in 500 mL of 1% sodium carbonate (Sigma-Aldrich®) and incubated at 50 °C for 2 h with regular stirring. The resulting solution was re-used for repeat filtration.

50 mL water samples were extracted from seawater and freshwater (SW/FW). Further 50 mL water samples were extracted at the following stages: after addition of sodium alginate solution (SAG/FAG), after addition of CaCl₂ solution (SBG/FBG) and from the final filtrate (SF/FF). A negative control analysed samples of artificial seawater with no additives before filtration (SB) and after filtration (SFNG). Water samples at each stage of processing were analysed for major anions and cations using ion chromatography. 100 μL samples were diluted with 4.9 mL de-ionised water and each analysed via ion chromatography for major ions

Table 3.2

Minor ions (mg/L).

MINOR	Seawater			Freshwater		
	SO ₄ ²⁻	K ⁺	Mg ²⁺	SO ₄ ²⁻	K ⁺	Mg ²⁺
SW/FW	1607.0	360.6	965.9	0.0	0.2	24.2
SAG/FAG	2001.6	300.1	865.9	0.0	0.7	6.4
SBG/FBG	1365.5	256.4	760.8	0.0	0.6	1.2
SF/FF	1271.8	264.3	799.1	0.0	1.6	1.1
Mass (g) filtered material	8,418			2,249		

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