

Metals Recovery from Seawater Desalination Brines: Technologies, Opportunities and Challenges

Amit Kumar^{1,2#*}, Gayathri Naidu^{3#}, Hiroki Fukuda⁴, Fengmin Du¹, Saravanamuth Vigneswaran³, Enrico Drioli⁵, John H. Lienhard V¹

¹Department of Mechanical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Ave., Cambridge MA 02139-4307 USA.

²Department of Chemical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Ave., Cambridge MA 02139-4307 USA.

³Centre for Technology in Water and Wastewater, School of Civil and Environmental Engineering, University of Technology Sydney, P.O. Box 123, Broadway, Ultimo, NSW 2007, Australia.

⁴Department of Materials Engineering, University of British Columbia, 309-6350 Stores Road, Vancouver, British Columbia, V6T 1Z4, Canada.

⁵Institute on Membrane Technology (ITM-CNR), c/o University of Calabria, 87036 Rende, Italy.

#These authors contributed equally.

Corresponding Authors email:

amitkum@mit.edu (Amit Kumar)

lienhard@mit.edu (John H. Lienhard V)

Abstract

The urgent need for environmental sustainability has increasingly prompted policy makers to emphasize resource recovery from desalination brine streams. Recent research on resource recovery from waste stream has shown rising momentum with near term viability for several new technologies. In this article, we focus on new opportunities for metal resource recovery from seawater desalination brine, while outlining associated sustainability challenges and opportunities. The potential of metals recovery is discussed.

Keywords

Resource recovery, Metal recovery, Seawater, Desalination brine, Lithium, Adsorption, Electrochemical method, Circular economy

Introduction

Seawater desalination, a major source of water production, utilizes seawater to produce freshwater. Desalinated water is expected to play a key role in narrowing the water demand-supply gap by extending water supplies beyond what is available from the hydrological cycle. Based on global data, there are approximately 15,906 operational desalination plants producing around 95 million m³/day of desalinated water ¹. Of the desalination technologies, reverse osmosis (RO) is by far the dominant process, accounting for 84% of the total number of operational desalination plants. The recovery rate of seawater RO (SWRO) can span from 30% by up to 55% (for a two-pass system). Typical SWRO plants operate at recovery ratios of about 45% ². As a result of this, the process generates large volumes of concentrated brine. Globally, seawater desalination plants are estimated to generate 124.5 million m³/day brine, which are treated as waste and often disposed into the coastal ocean ³⁻⁶.

Concentrated seawater brine contains various resources (ions and salts) that can be recovered, potentially leading to economic benefits and reduced waste disposal. Almost every element in the periodic table can be found in seawater and likewise in desalination brines, including valuable elements such as lithium (Li), uranium (U), rubidium (Rb), and strontium (Sr), among others (Figure 1). These elements are present in seawater brine at low concentrations (0.19 to 0.30 mg/L) along with other dominant ions, such as potassium (K), calcium (Ca), and magnesium (Mg) at higher concentrations. Recovery of these valuable elements is challenging: firstly, their selective separation from other dominant ions is difficult; and secondly, they are not easy to precipitate and crystallize using a single recovery operation. In this perspective article, we focus on recovery of metals from seawater brine (noting that useful non-metal elements, such as bromine (Br) and boron (B), are also present), and we discuss associated sustainability challenges and opportunities.

Presently, land-based mining of resources faces sustainability challenges given that high grade mineral ore deposits are declining. Mining processes can be very energy and water intensive; and mining wastes may create lasting environmental damage. Although the concentrations of valuable elements in brines such as seawater are very low in comparison to land-based mineral ores, the amounts available in the oceans are huge. The mass ratio of ocean abundance to land reserves ³ for Li, Sr, U, and Rb is 10³ to 10⁶. Globally, the total amount of Li in seawater is estimated to be around 230 Gt ⁷. Further, extraction of Li from concentrated brine is estimated to cost 30% to 50% less than that from mined ores ⁸. If metals are economically recovered from the brine concentrate, not only can the water production cost be reduced by the revenue from the minerals recovered, but also the environmental problems associated with brine disposal can be reduced. It is safe to say that extraction of elements from brine would support a more sustainable economy.

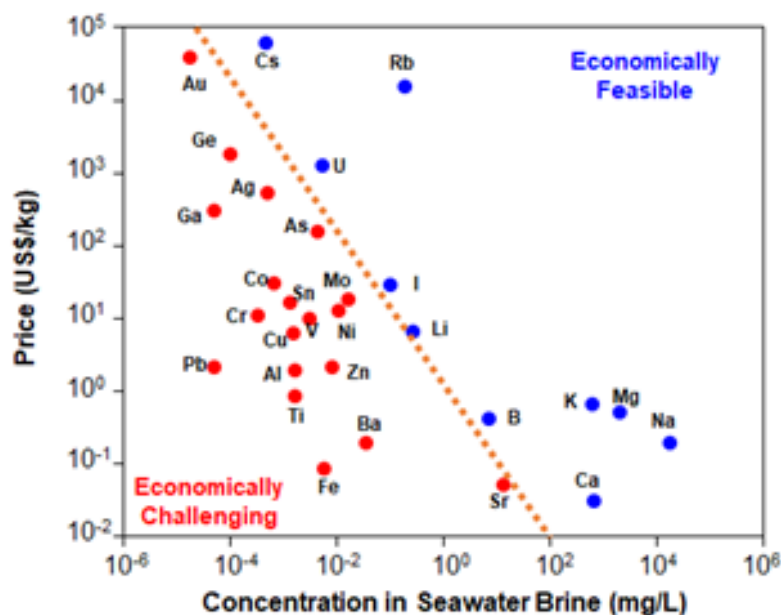


Figure 1. Element concentration and price ³ (element concentration in seawater brine is estimated based on average 40% recovery rate of desalination plant). Market prices of elements are based on 2018 USGS metal commodities summaries ⁹, Sodaya et al. ¹⁰, and Kramer ¹¹. Economic feasibility of extracting an element from seawater brine is considered based on the element market price, concentration in brine as well as the extraction cost ¹². For simplicity, extraction cost ratio is assumed to be 1 for all elements. Economic feasibility means that the product of (market price of element \times element concentration in brine) is greater than the extraction cost. The elements on the right-hand side of the dotted line are potentially economical to be extracted from seawater brine based on the concentration and market price ratio greater than one. The economics is expected to be more favorable with increasing distance to the right from the dotted line and further away from the horizontal axis towards the top. Figure 1 is reproduced from authors' previous work.³ The authors acknowledge permission to re-use from Royal Society of Chemistry.

Economic Implications of Resource Recovery from Seawater and Energy Industry

Research in resource recovery has shown potential for producing valuable elements from waste brines. We focus on seawater brine, as it contributes the largest volume of waste brine in comparison to all others ^{1,5}. In contrast to the mining industry, which usually requires a large water input for production, the extraction of valuable resources from seawater brine can result in greater profitability for water desalination and oil and gas operations ^{3,13,14}. However, whether these technologies can be implemented for large-scale use is dependent the net value of recovered resources, which is a function of the market price of recovered elements, the concentration in the brine, and the extraction cost of any particular element ¹². Since consistent and updated data on global volume and rejection capacity of SWRO brine is widely available ^{1,4,5,15}, we utilize that data as a model input to evaluate the economic potential of extracting resources from SWRO brine. Figure 1 presents a rough estimate of the economic feasibility of recovering various elements from the brine based on their market prices and available concentrations in the brine. It should also be

noted that, from a practical point of view, the cost of direct brine disposal strongly affects the economic feasibility ¹².

In addition to factors related to costs and revenues, the market consumption/demand of certain elements available from the waste brine must also be considered while determining the economic potential of resource recovery. For instance, although Rb stands out due to its high market price, its application demand is rather low (based on the world production and consumption factor). Contrarily, resources such as Li have high market demand and therefore are more viable for extraction.

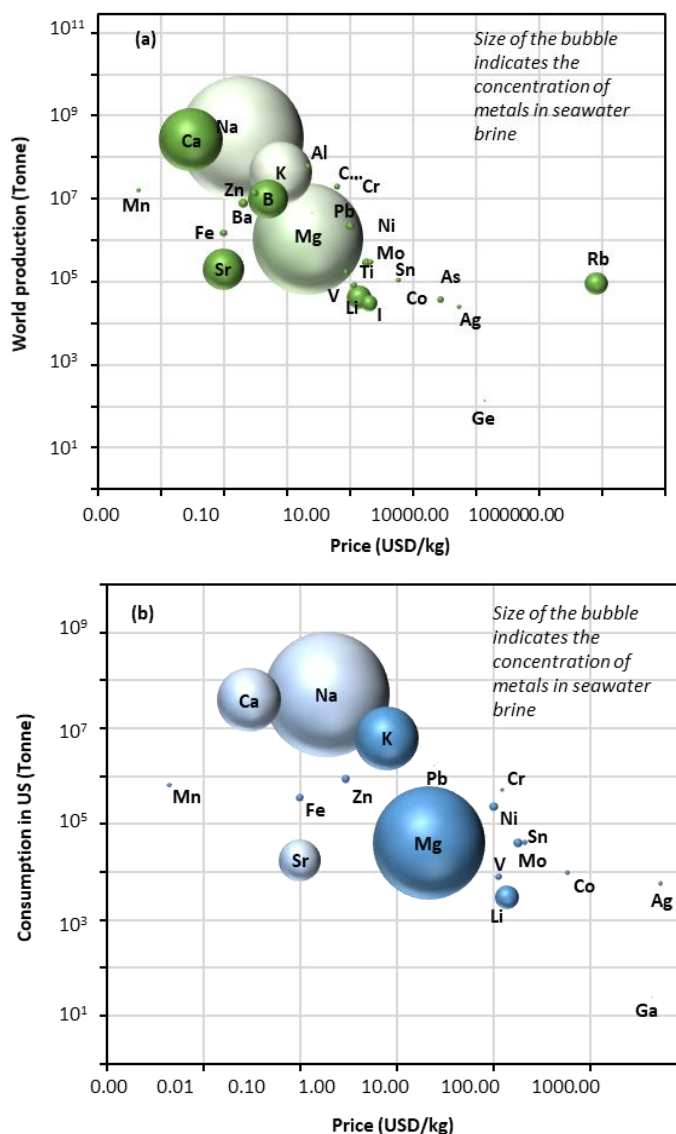


Figure 2. Element consumption, price, and concentration. Element extraction feasibility ranking based on element economic value (price in USD) as a function of: **(a)** production /world demand; and **(b)** consumption in US. Varied bubble size represents element concentration in seawater brine (logarithmic scale). Values are based on 2018 USGS metal commodities summaries (2018) ⁹.

Sustainable Resource Recovery

The sustainability of element recovery from brines must be considered based on the concentration of the elements (Figure 2). For instance, sodium chloride, magnesium hydroxide, and potash are economically and technically viable for production from seawater brine, given that these elements are present in high concentrations and do possess economic demand/consumption (as shown in Figure 2)¹². Hence, in practice, Na, Mg, Ca, and K have been extracted from seawater, predominantly as hydroxide/carbonate salts. Extraction of Na^+ , Ca^{2+} , Mg^{2+} and K^+ from desalination plants in Saudi Arabia is estimated to have a potential revenue of US\$ 18 billion/yr¹⁶. The sale of sodium chloride has the potential to decrease the cost of produced water treatment by 1.31-1.37 \$/m³¹⁷, and salt production for human consumption or chlor-alkali purposes from seawater desalination brines can be implemented profitably in several regions of the world¹⁸. K is extracted from seawater as a byproduct of solar salting¹². Mg is extracted commercially from seawater as magnesium hydroxide and oxides, predominantly by precipitating with lime and dolomite^{3,19}. In 2017, approximately 70% of US Mg supply in the form of magnesium oxide came from seawater and natural brines⁹. In contrast, extraction of Ca from seawater and its related brine has not been widely developed due to its low economic value. One desalination facility, in Southern California in the US, reportedly produces calcium carbonate on a commercial basis²⁰.

Ongoing research has focused on the recovery of Cs^+ , Rb^+ , Li^+ , Sr^{2+} and U(VI) from seawater and its brine. With regard to potential extraction methods, we emphasize adsorption and electrochemical separation methods (Table 1) due to: their capacity for selective resource recovery in complex mixtures such as seawater brine; their low energy requirement; and their flexibility of chemical modification and operation, including potential use in an integrated system with membrane processes^{21–23}. The integration of adsorbent and membrane processes^{21,22} is highly favorable for simultaneous water and resource recovery.

Li is a valuable resource for energy storage, as it possesses beneficial characteristics such as high storage density. The demand for Li is projected to increase from 237,000 metric tons of lithium carbonate equivalent (LCE) in 2018 to 4.4–7.5 million metric tons of LCE by 2100,²⁴ owing to its increasing usage in rechargeable lithium ion batteries⁷. In addition to lithium ion batteries, Li has uses in various other industries, such as glass and ceramics, greases, and metallurgical applications^{25,26}. Figure 3 shows a typical Li production process from brines. The second step in the process, concentration, is the most important part and new technologies are still being studied by many researchers²⁷. Figure 3 shows a typical lithium production process from brines. The second step in the process, concentration, is the most important part and new technologies are still being studied by many researchers. For Li extraction from seawater, research has focused on finding the best adsorbents with high Li uptake, chemical stability and selectivity^{28–29}; developing novel electrochemical methods such as electrodialysis³⁰ and electrolysis with specific electrodes³¹; as well as coupling the Li extraction with membrane and ion-exchange processes^{29,30}.

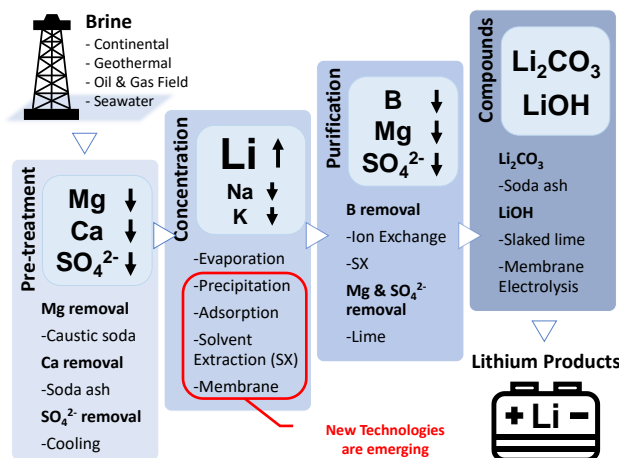


Figure 3. Li production process from brine sources. In the pre-treatment, divalent ions are removed from brine as precipitates. Li is concentrated in the next step by rejecting other monovalent ions such as Na⁺ and K⁺ ions. Some impurities such as B in the Li-concentrated solution are removed³², and lithium carbonate or lithium hydroxide is produced as a pure Li compound.

However, these explorations have yet to achieve industrial commercialization, as some of the approaches did reach benchmarking stages. This indicates that the Li extraction process still requires further research and optimization to attain practical feasibility. Interestingly, for Li recovery from oil and gas produced wastewater¹⁴, a few successful cases were achieved by two Canadian companies, MGX Minerals Inc.³³ and Standard Lithium Ltd.³⁴. Specifically, for seawater, one of the main challenges of using an Li-ion adsorbent to selectively extract Li⁺ is the severe competition from other major ions present at high concentrations. In fact, Li selectivity over other monovalent cations such as Na⁺ and K⁺ still needs to be improved. A key strategy to improve selectivity is to make the adsorbent have the proper-sized structure with holes which can capture Li⁺ only. Successful adsorbents such as lithium manganese oxide³⁵ have a structure that only accepts Li⁺ and rejects Na⁺ and K⁺, while monovalent cation exchange resins with simple anion functional groups lack this selectivity³⁶. Further, Li-ion sieve adsorbents have a microcrystalline or fine-grained powdery nature, which limits the capacity to regenerate and reuse the adsorbent. It also makes it challenging to practically apply the powder form of the adsorbent in conventional fixed-bed columns as it may lead to clogging, large pressure loss, and slow filtration rates. To overcome these difficulties, the combination of adsorbents and electrochemistry is increasingly attracting attention. Lawagon et al.³¹ used electrical power to drive Li⁺ into the structure of adsorbents and also to make the regeneration of the adsorbent easier.

An integrated MD-adsorbent system^{22,23} benefits both processes by providing long contact time for encapsulated adsorbents to selectively extract elements, enabling the usage of powdered adsorbents (higher adsorption capacity as a result of higher surface area) and raising the element concentration by MD. Likewise, embedding adsorbent with metal organic frameworks such as Cr-MIL, UiO-66 and ZIF-8 containing selective functional groups onto polymer membranes will produce selective ion exchange membranes that can be incorporated to an electrochemical process. In this scenario, embedding metal organic framework nanomaterials into the membrane can favourably manipulate the membrane nanochannels to match the specific pore size of an ion such as Li. This in turn, will enable rapid and selective transportation of Li ions while rejection/sieving

out competing ions at relatively low energy requirement, especially when the process is coupled with renewable energy³⁷.

U is another example of element whose extraction from seawater or its brine would be economically feasible (based on Figure 1). Either batch or column adsorption processes have been proposed, with a large variety of adsorbents being applied^{38,39-40}. This also applies to the extraction of Rb/Cs/Sr⁴¹⁻⁴², which are among the most feasible elements. Nonetheless, it should be noted that the four elements have relatively low market consumption/demand (Figure 2), limiting the practicality of large-scale extraction operations despite the relatively high unit values.

Additionally, in comparison with typical mining and recycling, we need more pilot-scale and full-scale data on mining from seawater brines. The data must be in a form useful to companies and governments that make site specific decisions on resource production.

Finally, the techno-economic analysis is necessary to implement these technologies in practical cases. For instance, selective Li recovery from seawater mining with a conventional chemical precipitation approach involves multiple steps that may be chemically intensive and time consuming⁴³. Meanwhile membrane electrochemical driven systems such as electrodialysis (ED) and membrane capacitive deionization (MCDI) are promising as rapid and low-chemical recovery processes for Li recovery^{37,44}. To date no detailed techno-economic assessment of electrochemical processes has been carried out. ED is a similar process to CDI in its electrochemical driving force but distinct in its ion removal for selective resource recovery. A relatively low voltage is required for MCDI (< 1.8 V). However, in a stack mode, the key distinguishing feature of ED is its ability to incorporate many membrane pairs between a single set of electrodes while MCDI, employs a pair of electrodes in each cell of the stack, resulting a bulky and costly system. Even so, energy recovery and optimization of operating conditions of pilot-scale MCDI systems have reported the possibility of attaining a stand-alone operation powered by renewable (solar) energy⁴⁴. Additionally, MCDI requires a significantly thinner membrane, which is envisioned to accelerate the transfer of ions across an ion exchange membrane/electrode interface, a potentially favourable feature for selective Li transfer/recovery. The varying views on the performance efficiency of electrochemical processes are attributed to the lack of comparative study, especially in large scale-systems (product rate of over $1 \text{ m}^3/\text{day}$). Moreover, to date, no work has reported on the comparative performance in terms of specific energy consumption for Li selective efficiency.

Table 1. Recovery of elements from seawater and brine using adsorption or electrochemical methods

Elements	Source type	Method	Ref.
Na, Cl	Seawater RO brine	Electrodialysis /evaporation/crystallisation	45
	Seawater	Electrodialysis (17-25 pairs of unit cells) after sand filtration/evaporation	46
	Synthetic RO brine	Electrodialysis (5 pairs of unit cells) /evaporation/crystallisation in vacuum evaporator	47

Mg	Seawater	Adsorption on carboxylic cation exchange resin. Desorption of Mg by eluting with Na ₂ CO ₃ , NaHCO ₃ . MgCO ₃ crystals in eluate	48
K	Synthetic seawater	Solution flow through a jacket pipe containing a K- ionic sieve membrane reactor made-up of K- selective synthetic zeolite. K was selectively adsorbed in the presence of Na, Ca, Mg.	49,50
	Seawater	Batch adsorption by a modified synthetic zeolite W. Selective rapid K adsorption. Very high K/Na selectivity	51
Br	Seawater RO brine	Electrodialysis concentrate was treated with chlorine gas to produce bromine gas.	52
Li	Seawater	Batch adsorption data compared with literature values on several other adsorbents	28
	Seawater	Adsorption on λ -MnO ₂ /desorption separation/vacuum evaporation and precipitation as carbonate	35
	Seawater and seawater RO brine	Adsorption on mixed matrix nanofiber membrane/Mn oxide adsorber in batch, and continuous flow-through membrane permeate system. Regenerated using 0.5 M HCl.	29
	Seawater	A combination of electrodialysis and ionic liquid membrane to enable selective Li ions to permeate through the membrane from anode to cathode side	30
	Synthetic seawater	Electrochemical selective recovery using Li _{1-x} Ni _{1/3} Co _{1/3} Mn _{1/3} O ₂ /Ag electrodes	31
Rb, Cs	Seawater RO brine	Batch adsorption using potassium cobalt hexacyanoferrate ion exchange adsorbent	41
	Seawater RO brine	Column adsorption on Cs treat (potassium cobalt hexacyanoferrate)	38
	Synthetic seawater brine	Column adsorption and desorption with KCl using organic polymer encapsulated potassium copper hexacyanoferrate, followed by recovery by adsorption on resorcinol formaldehyde ion exchange resin and desorption using HCl	22
Sr	Synthetic seawater	Batch and inflow adsorption on macroporous LTA (synthetic zeolite) monolith. Rapid adsorption with very high adsorption capacity.	53
	Synthetic seawater	Batch adsorption on titanate nanotubes upon Ca removal as Ca(OH) ₂ . Sr desorbed by HCl addition	54
	Synthetic seawater	Batch adsorption on alginate microsphere. Sr desorption by CaCl ₂	42
U	Seawater RO brine	Column adsorption on amidoxime-functionalised Purolite S910 resin	38
	Seawater	Column adsorption in series and parallel on amidoxime-based polymeric adsorbent. After	39

		adsorption for 8 weeks the adsorbent digested with aqua regia to measure adsorbed U. Maximum adsorption capacity 3.3 mg U/g adsorbent	
	Synthetic seawater	Batch adsorption on polyacrylonitrile/polygorskite composite chemically modified with amidoxime groups. U desorbed by HCl. Regenerated adsorbent fully for 5 cycles. Maximum adsorption at pH 5. Ionic strength had little effect	55
	Seawater	Batch adsorption on porous polymer with amidoxime pendant group. Optimum adsorption at pH 6. Adsorbent regenerated fully during 3 cycles. Regenerated adsorbent with Na ₂ CO ₃	56
	Seawater	Batch adsorption on high affinity ligands (diphosphonic acid, phosphonic acid, hydroxypyridinone) installed on high surface area nanostructured materials. Adsorbent fully regenerated in 4 cycles using Na ₂ CO ₃	57
	Seawater	Batch (laboratory) and column (56 days, field) adsorption on high surface area polyethylene fibre adsorbent grafted with amidoxime groups	58
	Seawater	Adsorption on electrospun nanofibrous amidoxime-based adsorbent. Desorption with 0.5 M HCl.	59
	Synthetic seawater	Adsorbent with Zr metal-organic framework containing orthogonal phosphorylurea groups had adsorption capacity saturation at pH 2.5 of 188 mg U/g in batch adsorption study	40
B	Seawater	Adsorption on a B selective resin CRB05 containing N-methyl glucamine functional group and desorption using HCl or H ₂ SO ₄	60
	Seawater	Adsorption on a chitosan/ferric hydroxide composite adsorbent. Continuous column experiment with 5 cycles of adsorption/desorption (using 0.01 M NaOH) removed 10.7 mmol B/mol Fe(OH) ₃	61

To support wider commercialization and industrialization of brine resource recovery processes, the authors believe that future research should be directed towards the following objectives:

- Further improvement of adsorbents, for instance grafting adsorbents with metal organic frameworks containing specific functional groups to enhance selectivity and rapid uptake towards the desired ion, preferably Li⁺, also other economically favourable metals, such as Mg²⁺, Rb⁺, Cs⁺ and U.
- Development of novel electrochemical methods for capture a desired metal, such as has been done for Li³¹.

- Engineering of adsorbent configurations to maximize adsorption efficiency (as close to equilibrium as possible during the constrained contact time) from seawater and to facilitate the regeneration process.
- Integration of adsorbent and membrane processes, for instance using membrane distillation (MD) with absorbents in the feed tank, eliminating an additional fixed-bed column process for resource recovery while simultaneously recovering water for reuse.
- Scaling-up of existing processes in the literature such as in the Sea4Value project in Europe⁶². This also includes the application of novel materials (e.g., adsorbents) on a larger scale while solving some related issues such as the difficulty in applying raw powders from the laboratory within industrial reactors.
- Detailed techno-economic assessment of potential recovery process (especially for Li and Mg, which have the highest economic potentials), with consideration of extraction costs and generated revenues, particularly in comparison to the present decoupled business-cases for existing brine disposal techniques and land-mining to extract these resources.

Summary and Future Outlook

Currently, the industry faces increasing pressure to embody principles of sustainability as a result of more stringent environmental regulations, depletion of natural resources, and increasing demand driven by population growth and rising living standards. This trend has resulted in a paradigm shift towards resource recovery from waste streams. Seawater and its desalination brine have recently been attracting academic and industrial attention for their abundant resources. Although various technologies have been studied for resource recovery from seawater brine, challenges remain in both science and application, the primary one being the complex composition of the solutions and the extremely low concentrations of most of these valuable resources. These knowledge gaps should be bridged to make the best use of resources in seawater brines.

To narrow the gaps, adsorption is superior to other techniques in view of its comparatively low cost, wide range of applications, simplicity of design, ease of operation, and most importantly, its capacity for selective resource recovery. In fact, current research has led to novel configurations of adsorption systems, more selective and productive adsorbents, and electrochemical means to mediate the adsorption and release of elements. The combination of electrochemical and adsorption methods can be both economical and environmentally friendly.

Nevertheless, we lack a detailed economic assessment with which to establish the feasibility of these new technologies for valuable resource recovery from seawater brine. A comparison to extracting resources from land mining, for example, would justify the economic profitability of the recovery process. From a practical point of view, a focus on scaling up these novel technologies and evaluating their performance under practical conditions is of vital importance, in cases such as embedding recovery in a working desalination plant. Despite the present challenges, we posit that resource recovery from seawater has strong potential to become a highly sustainable, innovative and profitable industry.

Notes

The authors declare no competing financial interest.

Biographies

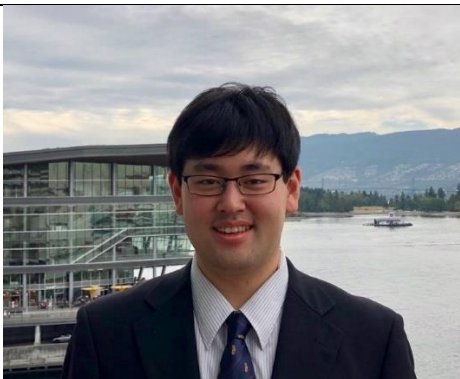


Amit Kumar has industrial and academic experience in sustainable systems and manufacturing. Currently he is working on sustainable manufacturing and integrated systems for Amgen Inc. He also holds a Research affiliate position at MIT. He completed his PhD with a focus on process engineering and design of integrated systems at Ghent University in Belgium. He completed his postdoctoral studies in the Chemical Engineering Department at Massachusetts Institute of technology (MIT). He was an adjunct researcher at Harvard University during his postdoc. After his postdoc, he worked as a research scientist in the Mechanical Engineering and Chemical Engineering department at MIT. His research interests include sustainable systems and manufacturing. He has published more than 40 peer reviewed journal articles among *PNAS*, *Nature Reviews Chemistry*, *Nature Catalysis*, and *Science*. He has received 25 major awards including the international doctoral dissertation award (AWMA), and NAMS, IWA Biofilm Technologies, and Marie Curie Awards. He served as the Director of Strategy and Impact for the MIT Energy Club.



Gayathri Naidu is a Senior Lecturer and ARC DECRA Fellow with the School of Civil and Environmental Engineering and Centre for Technology in Water and Wastewater at University of Technology Sydney (UTS), Australia. She obtained her bachelor's and master's degrees in Engineering from University of Malaya Kuala Lumpur and Imperial College London, respectively; and her PhD in Environmental Engineering from UTS Australia. Gayathri's core research is dedicated to exploring the three Rs in seawater and wastewater –

that is remediation, reuse and recovery. She synthesises nanomaterials and membranes, as well as model, design and implements hybrid solar membrane brine treatment processes to drive the global water industry towards sustainable water reuse and recovering valuable resources – lithium, rubidium and rare earth elements.



Hiroki Fukuda is a chemical engineer in the field of environmental engineering. He completed B.Eng. in Resources and Environmental Engineering at Waseda University in Tokyo (2017) and M.A.Sc. in Materials Engineering at University of British Columbia (UBC) in Vancouver (2019). His research interest is in separation technologies for environmental, energy and resource problems. He has worked on boron removal from wastewater, lithium extraction from brine and so on. He is now focusing on resource harvesting from wastewater using membrane technology. He has received Ernest Peters Master's Award by Canadian Institute of Mining, Metallurgy and Petroleum (CIM) and Civil Engineering Excellence Award by UBC. He is currently a PhD student in Civil Engineering at UBC and a VP-finance of UBC BCWWA (BC Water & Waste Association) student chapter.



Fengmin Du holds B.Sc. and M.Sc. in Chemical Engineering at Technical University of Munich. He was a visiting graduate student at MIT where he conducted research on recovery of caustic soda from high salinity reverse osmosis brine by membrane chlor-alkali electrolysis. and is currently a Ph.D. student at Department of Chemistry and Applied Bioscience (D-CHAB), ETH Zurich. In cooperation with BMW Group, his current research focuses on the degradation mechanisms in automotive polymer electrolyte membrane fuel cells (PEMFCs).



Saravanamuthu Vigneswaran is currently a Distinguished Professor of Environmental Engineering and was the Founding Director of Centre of Technology in Water and Wastewater (2009-2018) at the University of Technology, Sydney (UTS), Australia. He obtained his Doctor of Engineering and Dr.Sc. from the University of Montpellier and University of Toulouse, respectively. He is a Distinguished Fellow of the International Water Association. During the last 25 years, he has made significant contributions to the understanding of membrane systems in water reuse, resource recovery and desalination, and sustainable water systems in developing countries. He has several national and international projects in these areas. He has obtained over 15 Australian Research Council grants and worked as investigator and work package leader in four EU projects. He has served as UTS coordinator of several consortiums: Australian National Centre of Excellence for Desalination, Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRC CARE). He has published over 350 journal papers, books, and book chapters.

He holds several international and national awards, including Google Impact Challenge Technology against Poverty Prize (2017), IWA Global Project Innovation and Development Awards in Research (2012,2019), and Kamal Fernando Mentor Award (2018).



Enrico Drioli is an Emeritus Professor at the School of Engineering of the University of Calabria, and he is a Founding Director of the Institute on Membrane Technology, CNR, Italy. Since 2018, he has been a Guest Professor of the School of Marine Science and Technology of Harbin Institute of Technology, Weihai, PRC. Since 2012, he has been a Distinguished Adjunct Professor at CEDT King Abdulaziz University, Jeddah Saudi Arabia; since 2010, he has been a WCU Distinguish Visiting Professor at Hanyang University, Seoul Korea. His research activities focus on membrane science and engineering, membranes in artificial organs, integrated membrane processes, membrane preparation and transport phenomena in membranes, membrane distillation and membrane contactors, and catalytic membrane and catalytic membrane reactors. He is involved in many international societies, scientific committees, editorial boards, and international advisory boards.



John H. Lienhard V is the Abdul Latif Jameel Professor of Water and Mechanical Engineering at MIT. During more than 30 years on the MIT faculty, Lienhard's research and educational efforts have focused on heat and mass transfer, water purification and desalination, and thermodynamics. Lienhard's research on water purification includes humidification-dehumidification desalination, membrane distillation desalination, forward and reverse osmosis, nanofiltration, electrodialysis, solar-driven desalination, solvent extraction, bubble columns, scale formation and membrane fouling, salinity gradient power, management of high salinity brines, and thermodynamic and energy efficiency analysis of desalination cycles. Lienhard has also done research on high heat flux engineering, liquid jet impingement cooling, and convection. Lienhard has directly supervised more than 85 graduate theses, and he is the author of three textbooks and more than 300 peer-reviewed publications. He has been issued 37 US patents, most of which have been commercialized through start-up companies. Lienhard has also received many awards for his research and teaching. As director of the Abdul Latif Jameel Water and Food Systems Lab, he coordinates MIT's research in food security and water supply for a growing population on a warming planet.

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TOC/Abstract Graphic



Synopsis

Seawater brines contain economically feasible metals and they can be sustainable metal resources for our society.